TALLINNA TEHNIKAÜLIKOOL
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Department of Materials and Environmental Technology

WET ROUTE CARBONATION OF INDUSTRIAL WASTES FOR CEMENT INDUSTRY DECARBONIZATION

TÖÖSTUSJÄÄTMETE POOLKUIV KARBONISEERIMINE CO_2 EMISSIOONIDE VÄHENDAMISEKS TSEMENDITÖÖSTUSES

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AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.
No academic degree has been applied for based on this material. All works, major viewpoints and data of the other authors used in this thesis have been referenced.

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Contents

List of abbriviations

GHG - Greenhouse gas

CCS - Carbon Capture and Storage

EU - European union

VKG - Vire keemia Grupp

KKT - Kiviõli Keemiatööstus

PF - Pulverized firing

CFB - Circulating fluidized-bed

SET - Plan-Strategic Energy Technology Plan

CCU - Carbon capture and utilization

Ca-looping - calcium looping

DCP - Direct carbonation process

FA - Coal fly ash

EAF - Electric arc furnace

CKD - Cement kiln dust

NSF - Blast furnace slag

CDW - Concrete demolition waste

BPD - Cement bypass dusts

EEJ - Eesti Elektrijaam

BEJ - Balti Elektrijaam

Espa - Electrostatic precipitators ash

CM - Concrete mixer

XRD - X-ray powder diffraction

XRF - X-ray fluorescence

BOS - Burnt oil shale

BET - Brunauer-Emmet-Teller method

TC - Total carbon

Introduction

Carbon dioxide enters the atmosphere through burning fossil fuels (coal, natural gas, oil and oil shale), solid waste, trees and other biological materials, and also as a result of certain chemical reactions include cement production. CO_2 itself. is not bad problem,bun the problem is that we have produced such a big amount of CO_2 due to human actions, that the amount of CO_2 in the atmosphere is growing too fast and going to a dangerous level. In order to significantly reduce the impact on the environment, it is necessary to act according to sustainable development.For proper use of resources and reduce human foot print all possible carbone capture and utilization technologies are used .For searching for possible new solutions for reducing greenhouse gases, a good example is the general work of many instances. The carbonation process through aquouse carbonation as the CO_2 capture and cement production with clinker process wich is one of the most important building materials worldwide. CO_2 is an unavoidable by-product of the process and in order to significantly reduce the climate impact of cement production, carbon capture is unavoidable. Material suitable for absorbing carbon dioxide that in the same time is suitable for the production of cement is the one of the objective of this work. Accordingly the process includes the possibility of using this material in the future, the study of the process in the laboratory with different parameters is the main task described in this work.

1. Literature review

1.1. Global climate change

It is postulated that the current warming of the global climate is the result of an increase in anthropogenic greenhouse gas (GHG) emissions, particularly CO_2, since pre-industrial times. The increase in atmospheric CO_2 over the last two and a half centuries has been attributed to two major anthropogenic forcing fluxes: (i) emissions from fossil fuel combustion and industrial processes and (ii) land use change. The planet's average surface temperature has risen about 0.9 °C since the late 19th century, a change driven largely by increased carbon emissions into the atmosphere. The Paris Agreement helped mobilize the global community behind the goal of limiting the increase in global average temperatures to less than 2°C degree above pre-industrial levels comparison with 1.8°C degree in 2018. Most of the warming occurred in the past 35 years, with the five warmest years on record taking place since 2010. Global fossil CO_2 emissions have increased every decade from an average of 3.1± 0.2 Gt /yr in the 1960s to an average of 9.4± 0.5 Gt/yr during 2008–2017 The growth rate in these emissions decreased between the 1960s and the 1990s, from 4.5 % /yr in the 1960s (1960–1969) to 2.8 % /yr in the 1970s (1970–1979), 1.9 % /yr in the 1980s (1980–1989), and 1.0 % /yr in the 1990s (1990–1999). After this period, the growth rate began increasing again in the 2000s at an average growth rate of 3.2 % /yr, decreasing to 1.5 % /yr for the last decade (2008–2017). Global average atmospheric CO_2 has increased from 280 ppm in the 1750 s to 410 ppm in 2019 (NASA). Since the use and supply of global energy is projected to continue to grow, especially as developing countries pursue industrialization, fossil fuels are expected to maintain their dominance in the global energy mix to 2030 and beyond. If follow 1,5 °C degree scenarios CO_2 emissions are likely to be 40 Gt in 2020 and 20 Gt CO_2 in 2040. If no proactive mitigative action is taken, the CO_2 emissions are 60 Gt in 2020 and more than 80Gt in 2040. The latest data indicate that world CO_2 emissions were 37,1 Gt in 2017 [1].

1.1.1. CO_2 emissions from different sectors

The power and cement sectors are the two main industries contributing to global CO_2 emission. The cement industry alone has contributed about 7% of global CO_2 emission [2] and that in terms of is 2,6 Gt CO_2 emission per year. About 60% of the CO_2 emissions in a cement plant comes from the calcination of the limestone that is used as raw material, whereas the remaining 40% comes from the combustion of fossil fuels that supply the heat for clinker production and for limestone calcination.[1] Among the different methods proposed for reducing CO_2 emissions in the cement industry there are the use of fossil fuels with low carbon content (e.g. natural gas), the use of carbon neutral fuels (e.g. biomass), the thermal efficiency improvement, the reduction of the clinker/cement ratio by using a larger fraction of additives in the final cement. Therefore, to achieve significant cuts in CO_2 emissions in a cement production process, it is necessary to implement Carbon Capture and Storage (CCS) techniques [2].

Such a quantity of CO_2 emissions already strongly influences the state of the environment and this is only going exponentially worse. Thus, EU decided to create a strategic plan that would allow in a rigid form to eliminate or at least control different areas.

1.1.2. Estonian oil shale-based energy sector

In 2017, Eesti Energia used its existing oil shale stock in production and mined 11.2 million tonnes of oil shale, which is 74% of the company’s annual rate. Most of it was used to produce heat, power and shale oil. As the first and only company to do so, VKG used the oil shale allowances carried forward from previous years. In 2017, the company extracted 3.2 million tonnes of oil shale, which was 117% of the annual allowance. VKG produced oil products, chemicals, various chemical products and heat and power. KKT, which produces shale oil products, mined 1.2 million tonnes of oil shale, which is 59% of the annual allowance. The company with the lowest mining volume is Kunda Nordic Tsement, which used oil shale mainly as a fuel in the cement production process. In 2017, the company mined 74,000 tonnes of oil shale [3].

Being dependent on low-grade fossil fuel as a primary energy source has serious consecuences as Estonia ranks as the first across the EU in CO_2 emission per kWh, because Estonian oil shale is characterized by especially high specific carbon emissions (29.1 tC/TJ)[4].Also, energy generation results in close to 20 million tonnes of by-products each year. In 2017, the oil shale industry generated around 6.26 million tonnes of mine waste and 9.23 million tonnes of ash [3].

The Narva power plants consist of the Eesti, Balti and Auvere power plants. Their combined maximum annual production capacity is 12 TWh. As Estonia consumes about 8 TWh of electricity per year, the Eesti Energia power plants play an important role in supplying the country with electricity. Narva power plants use two different oil shale combustion technologies: pulverized firing (PF) and circulating fluidized-bed (CFB) technology [5].

In 2017, the circular economy was the central topic in the oil shale industry. Its potential in the oil shale sector was discussed thoroughly at a conference organized by the Tallinn University of Technology's Virumaa College Oil Shale Competence Centre and VKG's annual environmental seminar [6]. Sector experts discussed the developments in existing directions in the circular economy: use of fly ash in construction and agriculture, the polymer industry and production of concrete and treating phenolic water. The possibility of using by-products of the oil shale industry in completely new fields was also considered.

1.1.3. EU Horizon 2020

Horizon 2020 has the political backing of Europe's leaders and the Members of the European Parliament. They agreed that investment in research and innovation is essential for Europe's future and so put it at the heart of the Europe 2020 strategy for smart, sustainable and inclusive growth.

Horizon 2020 is helping to achieve this by coupling research to innovation and focusing on three key areas: excellent science, industrial leadership and societal challenges. The goal is to ensure Europe produces world-class science and technology that drives economic growth.

By 2020, the EU aims to reduce its greenhouse gas emissions by at least 20%, increase the share of renewable energy to at least 20% of consumption, and achieve energy savings of 20% or more. All EU countries must also achieve a 10% share of renewable energy in their transport sector. Through the attainment of these targets, the EU can help combat climate change and air pollution, decrease its dependence on foreign fossil fuels, and keep energy affordable for consumers and businesses. The European Strategic Energy Technology Plan (SET Plan) aims to accelerate the development and deployment of low-carbon technologies. It needs to improve new technologies and bring down costs by coordinating national research efforts and helping to finance projects. The SET Plan promotes research and innovation efforts across Europe by supporting the most impactful technologies in the EU's transformation to a low-carbon energy system. It promotes cooperation amongst EU countries, companies, research institutions, and the EU itself. Implementing the Strategic Energy Technology Plan – the EU's strategy to accelerate the development and deployment of low carbon technologies such as solar power, smart grids, and carbon capture and storage [7]

1.2. Carbon capture in cement sector

Carbon capture and storage (CCS) is the process of capturing and storing carbon dioxide (CO_2) before it is released into the atmosphere. The technology can capture CO_2 released by burning fossil fuels in electricity generation and industrial processes such as cement production. The second two methods are transporting the carbon dioxide, and securely storing the carbon dioxide emissions, underground in depleted oil and gas fields or deep saline aquifer formations will not be reviewed in this thesis.

CO_2 can be captured using different methods, the main ones are: (i) post-combustion, (ii) pre-combustion and (iii) oxyfuel. Post-combustion technology removes CO_2 from the flue gases that result from burning fossil fuels. Pre-combustion methods – carried out before burning the fossil fuel – involve converting the fuel into a mixture of hydrogen and CO_2. Oxyfuel technology produces CO_2 and steam by burning fossil fuels with almost pure oxygen.

More recently, a related alternative – carbon capture and utilization (CCU) – has started to attract attention worldwide because it can turn waste CO_2 emissions into valuable products such as chemicals and fuels or materials, while at the same time contributing to climate change mitigation. One of the advantages of CCU over CCS is that utilization of CO_2 is normally a profitable activity as products can be sold [8].

1.2.1. Carbon capture by - Ca-looping

Carbon capture technologies such as amine scrubbing [9], ammonia scrubbing [10], oxy-combustion (IEA, 2008, ECRA, 2009)[11], anti-sublimation[12], indirect calcination [13], chemical and calcium looping [14] have received great interest to capture CO_2 from cement industry.

Chemical-looping is based on the reversible reaction of CO_2 on specific metal oxides at high temperature. CaO-based sorbents have attracted the most attention owing to their high absorption capacity, wide availability, and low cost. The post-combustion calcium looping (Ca-looping) process, first proposed by [15], uses a state-of-the-art circulating fluidized bed (CFB) system and offers relatively small energy penalty. The Ca-looping process has been proposed as a proper way to reduce CO_2 emissions from power plants [16]. The lime carbonation/calcination cycle is based on the separation of CO_2 from combustion gases by the use of lime as an effective CO_2 sorbent to form $CaCO_3$. The separation of CO_2 is carried out at high temperature using CaO as regenerable sorbent. The reverse, calcination reaction produces a gas stream rich in CO_2 and reagentes the sorbent -CaO- for subsequent carbonation cycles [17]. One of the greatest challenges related to this method is the deterioration of the CO_2 capture capacity when these materials are used over countless cycles of carbonation and calcination reactions [18]

1.2.2. Clinker process

Raw meal used for clinker production consists mainly of $CaCO_3$, coming from limestone or marl, and oxides of Si, Fe and Al, which are typically introduced through additional raw materials in order to achieve the targeted composition. The raw meal is ground in the raw mill, where it is also dried via direct contact with hot gas coming from the preheating tower. The dried raw meal from the raw mill, is heated up in a five-stage suspension (or cyclone) preheater.

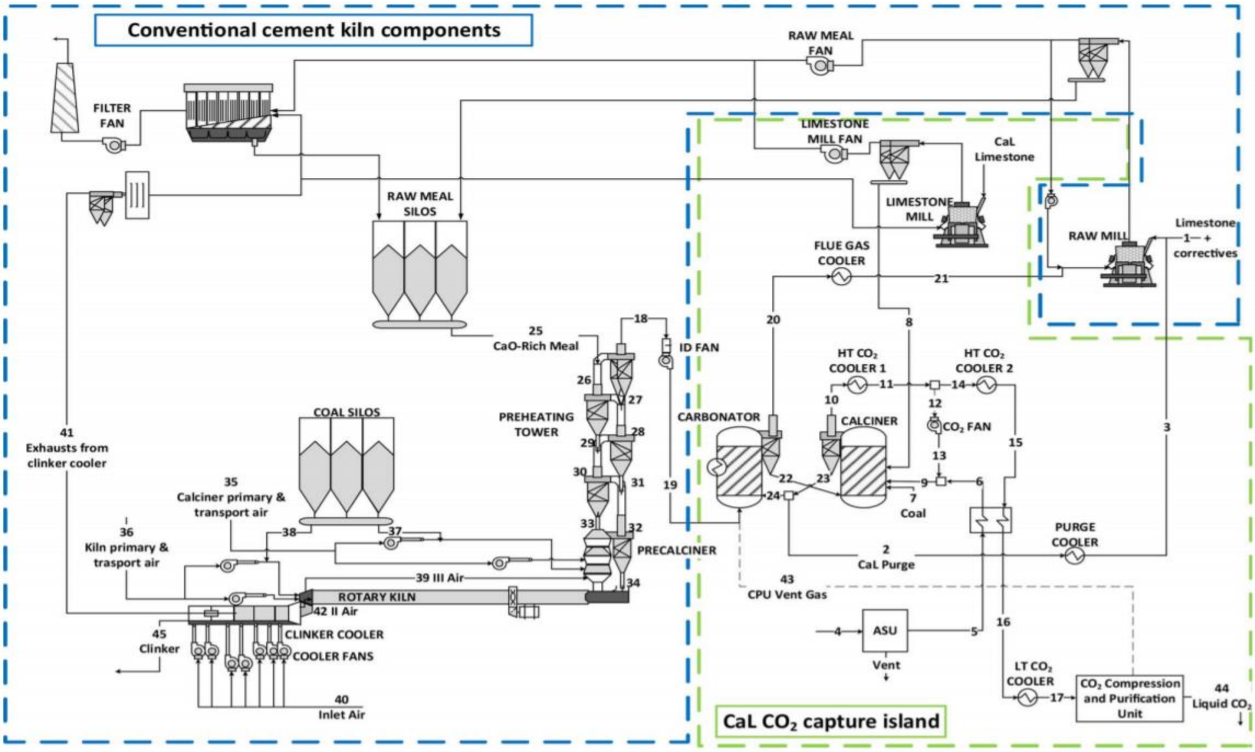


Figure 1.1 Clinker process configuration. [19]

The raw material is fed to the top of the pre-heating tower and it is preheated sequentially from the first to the fifth stage (counted starting from the top of the tower) against the hot exhaust gas flowing from the bottom to the top. Each suspension preheater stage is composed of a duct, where solid particles are entrained upwards and heated up by the gas, and a cyclone which separates the solids and distributes them to the following stage towards the bottom of the tower. Additional cyclones and dust filters are needed downstream of the raw mill to separate the entrained solids before sending the exhaust gas to the stack. The preheated solids at the exit of the fourth suspension preheater stage are fed to the pre-calciner, where most of the $CaCO_3$ contained in the raw meal is calcined into CaO and CO_2.Energy needed for this endothermic reaction is provided by the combustion of coal using low temperature primary transport air and high temperature tertiary air from the clinker cooler at 1050 °C. Flue gas leaving the rotary kiln at 1078 °C also flows through the pre-calciner. Calcination degree (defined as the ratio between the moles of CaO and the total moles of Ca at calciner exit) of around 94% is reached in the pre-calciner, which operates with an outlet temperature of 862 °C. Pre-calcined raw meal and calciner off-gas enter the last cyclone of the preheating tower where solids are separated and fed to the rotary kiln , whereas flue gas flows upwards and enters the duct of the fourth cyclone, located above.

The rotary kiln represents the core of the clinker production process. In this reactor, the completion of the $CaCO_3$ calcination and the formation of the main clinker constituents occur. The kiln is a long refractory lined tube, slightly inclined towards the clinker discharge end, that rotates at 1.3–3.5 revolutions per minute. As a result of the combination of kiln rotation and inclination, the solid-liquid material moves towards the hot end of the reactor, where coal combustion occurs. The combustion air in the rotary kiln comes from the clinker cooler (so called secondary air, about 90%), from the primary air and from the transport air that is directly fed to the kiln burner with the coal. After the combustion zone, the flue gas moves towards the pre-calciner, in counter-current with the solids. As the solid phase moves towards the rotary kiln burner, the different clinker phases are formed thanks to the high temperature. Temperature of about 1450 °C is reached by the hot clinker at the end of the kiln, before being discharged to a grate cooler.

In the clinker cooler, clinker is rapidly cooled down to minimize the formation of undesired coarse crystals that would lead to erratic cement setting, at the same time preventing the dissociation of alite ($3CaO{\cdot}SiO_2$), the most important clinker constituents which provides the required properties to clinker, in belite ($2CaO{\cdot}SiO_2$) and free lime (CaO). Clinker is transported over a reciprocating grate, through which the cooling air flows in cross flow arrangement. Ambient air is used as cooling medium in the clinker cooler. Most of this air is heated up to a very high temperature and then used as secondary and tertiary combustion air in the rotary kiln and the pre-calciner, respectively. An almost equivalent stream of air at lower temperature (∼300 °C) is generated in the final part of the clinker cooler, which is ultimately emitted to the atmosphere after filtration. Clinker exiting the cooler is ultimately ground and mixed with gypsum (bi-hydrate calcium sulphates) and/or other materials like pozzolana, limestone, fly ash and slag to make cement [19].

1.3. Mineral carbonation technology

Mineral carbonation technology (MCT) is a process whereby CO_2 is chemically reacted with calcium- and/or magnesium-containing minerals to form stable carbonate materials which do not incur any long-term liability or monitoring commitments.Mineral carbonation (MC) is an accelerated form of weathering of naturally occurring silicate rocks and has been proposed as an alternative approach for CO_2 sequestration [20].

When CO_2 reacts with metal oxides the corresponding carbonate is formed, and heat is released according to the following chemical reaction:

$$MO + CO_2 \rightarrow MCO_3 + heat \qquad (1.0)$$

The reaction is exothermic, and amount of heat depends on the specific metal and on the material containing the metal oxide [21].

Mineral carbon sequestration can be accomplished either in situ (underground in geologic formations) or ex situ (above ground in a chemical processing plant). The sequestration of CO_2 in carbonates can be achieved through various process routes:

(1) **Direct carbonation (DC)** is the simplest approach, where a Ca/Mg rich solid is carbonated in a single process step. DC can be further divided into gas–solid carbonation and direct aqueous mineral carbonation. The direct aqueous mineral carbonation-route with the aid of pre-treatments (DCP) is considered as the state of the art and is typically selected to compare other technologies.

(2) **Indirect carbonation (IC)** consists of first extracting from the feedstock the reactive Mg/Ca oxide or hydroxide in one step and then, in a subsequent step, reacting the leached cations with CO_2 to form the desired carbonate.Indirect carbonation routes include hydrochloric (HCl) acid extraction, the molten salt process, other acid extraction, bioleaching, ammonia extraction and caustic extraction followed by carbonation reactions. These technologies can be applied to both natural minerals and alkaline waste residues and will be briefly reviewed prior to a detailed discussion on the types of wastes that can be utilized for mineral carbon sequestration [22].

Mineral carbon sequestration has a number of advantages over other carbon storage techniques. Not only is mineral carbon sequestration a permanent method of CO_2 disposal but the products are environmentally benign and could potentially be sold for profit. In addition, mineral carbon sequestration can be used in areas where other storage techniques, such as geologic carbon sequestration, are either not available or not feasible.

1.3.1. Gas–solid carbonation

The direct gas-solid or dry carbonation process consists of converting silicate or metal oxides directly to carbonates using gaseous of supercritical CO_2. The gas solid carbonation is the simplest approach to mineralization, as described below [23]

$$Ca, Mg - silicate(s) + CO_2(g) \rightarrow (Ca, Mg)CO_3(s) + SiO_2(s) \quad (1.1)$$

The process chemistry of gas-solid carbonation also can be expressed, in terms of various reacting minerals as followed:

$$CaO(s) + CO_2(g) \rightarrow CaCO_{3(s)}, \Delta H = -179 \text{ kJ/mol } CO_2 \quad (1.2)$$

$$CaSiO_{3(s)} + 2CO_{2(g)} \rightarrow CaCO_{3(s)} + SiO_{2(aq)}, \quad \Delta H = 90 \text{ kJ/mol } CO_2 \quad (1.3)$$

$$Ca_2SiO_{4(s)} + 2CO_{2(g)} \rightarrow 2CaCO_{3(s)} + SiO_{2(s)}, \quad \Delta H = -44 \text{ kJ/mol } CO_2 \quad (1.4)$$

$$Mg_2SiO_{4(s)} + 2CO_{2(g)} \rightarrow 2MgCO_{3(s)} + SiO_{2(s)}, \quad \Delta H = -44.5 \text{ kJ/mol } CO_2 \quad (1.5)$$

The challenges of the gas-solid or dry process include: (I) the slow reaction kinetics at ambient pressure and temperature; (ii) the significant energy requirements. In order to accelerate the process several pretreatment options for feedstock such asgrinding and thermal activation to increase the reaction surface area can be considered.

In addition, the dry carbonation process is very energy intensive that offsets the environmental benefits. Moreover, the low capture efficiency makes it currently unviable on the industrial scale.

1.3.2. Aqueous carbonation

Since dry carbonation exhibits a slow reaction rate with low carbonation conversion, more efforts in the literature have focused on the performance of aqueous (wet) carbonation. The addition of water can significantly increase the reaction kinetics due to the mobilization of ions in the reaction of carbonic acid with alkaline metals. The carbonation of alkaline solid wastes is carried out with the direct contact of flue gases from stack, in the presence of water. The wastewater (or circulated process water) can be used also to avoid the consumption of freshwater.

The process chemistry of aqueous carbonation depends on the composition of initial material, as in addition to Ca/Mg oxides also Ca/Mg-siliates and their hydrated compounds may react with CO_2.

The main steps include slaking of lime and dissolution of $Ca(OH)_2$ to form Ca^{2+} and OH^- ions to the solution:

Then contemporary dissolution of gaseous CO_2 into a liquid phase, converting carbonic acid to carbonate and /or bicarbonate ions:

$$CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)} \rightarrow\ H_2CO_{3(aq)} + HCO_{3(aq)}^{-} + CO_{3(aq)}^{2-} \tag{1.6}$$

Final step includes consequent nucleation and precipitation of carbonates. It is noted that the balance between these processes is dependent on the kinetics and solubility of the feedstock present and possible product.

$$(Ca, Mg)_{(aq)}^{2+} + CO_{3(aq)}^{2-} \rightarrow (Ca, Mg)CO_{3(s)} \tag{1.7}$$

The challenge in CO_2 fixation by carbonation of alkaline wastes is to accelerate the reaction and exploit the heat of reaction to minimize energy and material loss [23].

Slurry phase

Slurry is a semi-liquid mixture, typically of fine particles of manure, cement, or coal suspended in water insoluble substance. Slurry phase system involves processing of contaminated material in reactors to increase the rate of carbonation. The is a three-phase system with particulate matter and water, typically 10 to 30% w/s ratio, and air. The optimum carbonation conditions for the fly ash in the reactor set-up were reached at an intermediate level of moisture with 0.2–0.3 w/s ratios. There is optimum water content during mineral carbonation, since too much or too little water is not favorable for the kinetics and chemistry of the reaction. Too much water limits the reaction due to the blockage of pores in the solid, as it interferes with the diffusion of CO_2 gas into the liquid film around the solid fly ash particles, where the dissolution of gas and leaching of Ca^{2+} ions take place [24]. On the other hand, low water contents does not create the moist environment required for aqueous carbonation to take place, including the negative effect on the leaching out of calcium. Even without water, direct gas–solid carbonation can take place, but at extremely slow rates compared to aqueous carbonation [25].

1.3.3. Overview of suitable alkaline wastes for mineral carbonation

Common industrial alkaline byproducts include coal fly ash (FA), electric arc furnace (EAF) dust and steel-making slag especially oil shale ash, waste concrete and cement kiln dust (CKD), municipal waste incinerator (MSWI) ash, asbestos mine tailings and bauxite residue. In addition to the potential CO_2 mitigation associated with the mineral carbonation, this process adds significant environmental benefit in the handling of industrial byproducts that may otherwise be considered as waste (or hazardous waste) materials [26]. This approach has a number of advantages: (i) these materials are often associated with CO_2 point source emissions; (ii) they tend to be chemically less stable than geologically derived minerals and thus require a lower degree of pre-treatment and less energy intensive operating conditions to enhance carbonation yields, (iii) waste materials could supply a readily available source of calcium or magnesium mineral matter (preferably in the form of CaO or $Ca(OH)_2$) without the need for mining; they are typically fine-grained with high reactive surface areas, (iv) hazardous waste can be reclassified through pH-neutralization and mineral transformation and finally (v) the end product of the sequestration step may be amendable for re-use in products such as road base or other construction material as well as pure and precipitated Ca or Mg-carbonates [27].

Steel slag is a byproduct of iron and steel manufacturing and includes the impurities separated from iron during ore smelting. Slag is comprised of a heterogeneous mixture of crystalline components, including iron oxides, calcium and magnesium hydroxides, oxides, and silicates, and quartz. Slag content varies depending on the ore and the smelting process. Steel slag is an ideal feedstock for mineral carbonation due to its high alkalinity and, more specifically, high Ca content [26]. The annual production of steel slags is about 21 million tons in Europe and the composition and properties of different slag types varys depending on the type of processing [28]: **blast furnace slag (NSF)** - either air-cooled (ABS) or granulated (GBS); **basic oxygen furnace slag** (BOS); **electric arc furnace slag (EAC)**, or stainless/high alloy steel production slag (EAFS); **secondary metallurgical slag**, e.g. ladle furnace slag (SECS); **other slags**, e.g. de-sulphurisation slag. **Blast furnace slag (NSF)** is derived from iron production by melting the residues and coke ashes after grinding and separation of iron from ore and consist predominantly calcium silicates [29].

Oil shale ashes formed in boilers operating at different combustion technologies differ significantly by their chemical and phase composition as well as by physical structure and surface properties. In the context of CO_2 sequestration and ash stabilization, the availability of lime for hydration and carbonation reactions are of key importance. Carbonation of oil shale ash has previously been investigated in the context of its relatively high content of free lime (up to 30% depending on combustion technology). In addition to free lime, ashes also contain up to 30% of Ca-Mg-silicates ($CaSiO_3$, Ca_2SiO_4, $Ca_3Mg(SiO_4)_2$) as potential CO_2 binders [30].

Concrete demolition waste (CDW) is a by-product generated during the construction and demolition waste recycling process. Waste cement is calcium-rich (portlandite and CSH) with an average particle size of <100 µm. The weight fraction of waste cement is about 17% of waste concrete and total extraction content of calcium from waste cement achieves up to 30% in weight. Therefore, by comparison with recycled aggrecates, waste cement could perform better as a sequestration material of CO_2. Crushed concrete aggregates and waste cement derived from construction and demolition waste represent a potentially large source of alkalinity (e.g. portlandite) for the formation of thermodynamically stable carbonate minerals [31].

Cement kiln dust (CKD) is an alkali-rich dust produced during cement manufacturing. CKD is a fine by-product of Portland cement and lime high-temperature rotary kiln production. Typical CKD contains 38–48% CaO and 1.5–2.1% MgO, but a significant amount of CKD is already carbonated. **Cement bypass dusts (BPD)**, removed after kiln firing, have much lower carbonate content, and therefore much higher potential to capture CO_2[32].

1.4. Main objectives

The increase in CO_2 concentration in atmosphere is mostly caused by anthropogenic factors such as fossil fuels basesed energy sector and cement industry. Current study seeks to find possibilities for CCS in cement industry by the use of mineral carbonation.

This work can be divided into three stages:

1. Practical part, in which experiments were carried out using different wastes and by varying operating conditions;
2. Analytical part, in which composition and physical parameters of the initial and carbonated samples were determined;
3. Modelling, in which the model built on lime solubility and carbonation kinetics, and the process was simulated and the modelling results were compared with experimental data in order to validate the model.

The main objectives in this study was:

1. In this study was to identify the most promising materials for CO_2 capture based on oil shale ash bypass dust, blastfurnace slag and concrete demolition waste samples using wet (semi-dry) process route;
2. to study the effect of diferent process parameters on CO_2 capture;
3. to build a kinetic model.

2. Industrial wastes

2.1. List of samples

The main objects of the study were oil shale ashes from different different oil and power plants, bypass dust, blastfurnace slag and concrete demolition wastes.

2.1.1. Oil shale ash samples

In this work we use 8 different oil shale ash samples (Table 2.1.) provided by AS Eesti Energia: circulating fluidazed bed ashes BEJ Espa and BEJ Total from Balti power plant, EEJ Espa and EEJ Total from Eesti power plant, Auvere Espa and Auvere total from Auvere power plant, Enefit280 from Enefit280 oil producing units and pulverized firing ash DeSOx from an SO_2 removal system (Novel Integrated Desulphurization, Alstom Power).

BEJ Espa, EEJ Espa and Auvere Espa were collected from electrostatic precipitators and BEJ Total, EEJ Total and Enefit280 burnt oil shale samples from total ash silo.

Table 2.1. Oil shale ash samples

Marking	Process	Type
EEJ Espa	Circulating fluidized bed	Electrostatic precipitators
EEJ Total	Circulating fluidized bed	Total ash silo
BEJ Espa	Circulating fluidized bed	Electrostatic precipitators
BEJ Total	Circulating fluidized bed	Total ash silo
DeSOx	Pulverized firing	Novel Integrated Desulphurization
Auvere Espa	Circulating fluidized bed	Electrostatic precipitators
Auvere Total	Circulating fluidized bed	Total ash silo
Enefit 280	Circulating fluidized bed	Total ash silo

2.1.2. Concrete demolition waste samples

In this work we use 4 different concrete demolition waste (CDW) samples (Table 2.2). Two different suppliers of concrete demolition wastes made their material available for testing: I.L.C. s.r.l (Rondissone, TO) and Isoltrasporti (Isola Sant'Antonio, AL).

Table 2.2 CDW samples

Marking	**Type**	**Company**
CDW 1	Fine fraction from demolition waste	Italy I.L.C. s.r.l
CDW 2	Fine fraction of recycled demolition waste submitted to washing process	Italy I.L.C. s.r.l
CDW 3	Fine fraction from demolition waste	Italy Isoltrasporti
CDW 4	Fine fraction of recycled demolition waste submitted to washing process	Italy Isoltrasporti

Different types of materials were delivered: fine fraction of recycled demolition waste (CDW1 and CDW3), fine fraction from demolition waste selectively derived from concrete (CDW2) and fine fraction of recycled demolition waste submitted to washing process (CDW4).

2.1.3. ByPass dust and blastfurnace slag

The samples of blast furnace (NSF) slag sample derived from iron production by melting the residues and coke ashes after grinding and separation of iron from ore (from Bremen, Germany) and cement by-pass dust (BPD) from Robilante (Italy) were included to this study (Table 2.3).

Table 2.3 Bypass dust and Blastfurnace slag samples

Name	**Tape**	**Place**
BPD	Cement kiln dust	Italy
NSF	Blast furnace slag	Germany

2.2. Analysis methods

2.2.1. Moisture content

The moisture content was determined by EVS 668:2018 standard [33]. Empty container is weighing on an analytical balance, after which approximately 5-6 grams of the sample are weighed. An open container is placed in a thermostat for three hours at a temperature of 105°C, and then for 30 minutes in a dessicator. The container is weighed and the moisture content in the sample is determined by the formula:

$$W[\%] = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100 \tag{2.1}$$

2.2.2. Total carbon content (TC)

The total carbon analyzing via TC analyzer ELTRA CS 580 Carbon sulphur determinator. The measuring method is based on the principle of sample combustion and the analysis of the gases given off, through infrared absorption.

The sample is placed in a combustion boat and pushed into the furnace (1100°C) where the carbonates decompose. The results are displayed in C%, which then calculate the mineral CO_2 content in the sample by using following formula:

$$CO_2 = \frac{44 \times C\%}{12} \tag{2.2}$$

or as calcium carbonate ($CaCO_3$)

$$CaCO_3 = \frac{CO_2 \times 100}{44} \tag{2.3}$$

2.2.3. Free CaO content

The free lime content was determined via ethylene glycol method [34]. Sample ~ 0.5 g was mixed with 50 ml of ethilenglycol, and placed in thermostat at temperature of 60°C for 30 min. During that time the suspension was shaked 3 times. Then the suspension was filtered via vacuum filter and titrated with HCl 0,1 n using methilred indicator until red color. Free lime content is calculated by the formula:

$$CaO = \frac{V_{HCl} \times 0.1N \times 28.04 \times 100}{1000 \times m_{ash}} \tag{2.4}$$

expressed as calcium hydroxide ($Ca(OH)_2$):

$$Ca(OH)_2 = \frac{CaO \times 74}{56} \tag{2.5}$$

2.2.4. CO_2 from gas phase

The CO_2 from gas phase was detected via two methods. First, portable TESTO (Figure 3.17) was used, but it proved to be ineffective in case of high CO_2 concentrations (70% CO_2). Then the experimental setup was equipped with more suitable Doutec infrared analyzer.

The gas intake tube was connected to the gas outlet from the reactor which allowed continuous CO_2 detection throughout the experiment. Measurements were taken first in every 30 seconds and then in every five minutes depending on the process progress.

2.3. Experimental setup and operating parameters

Firstly, the experiments were carried out in a semi-batch Eirich EL1 type intensive mixer with maximal volume of material 1 L (Figure 1.2). The experiments wee carried out in wet route conditions [35] using liquid to solid ratio of 0.2-0.3 w/w (Table 2.4). The solid sample was placed into mixer, then the water was added through the hole on top of mixer. The mixer was started at fixed rotation speed (300-3000 rpm), the inlet gas flow and CO_2 concentration was kept constant (50-400 L/h; 20-70% CO_2 in air) and the outlet gas flow was measured by Doutec infrared analyzer. the samples taked during experiment were dried in thermostat for 3 h at 105 °C and analyzed for total carbon and free lime content as the main indicators for the carbonation process.

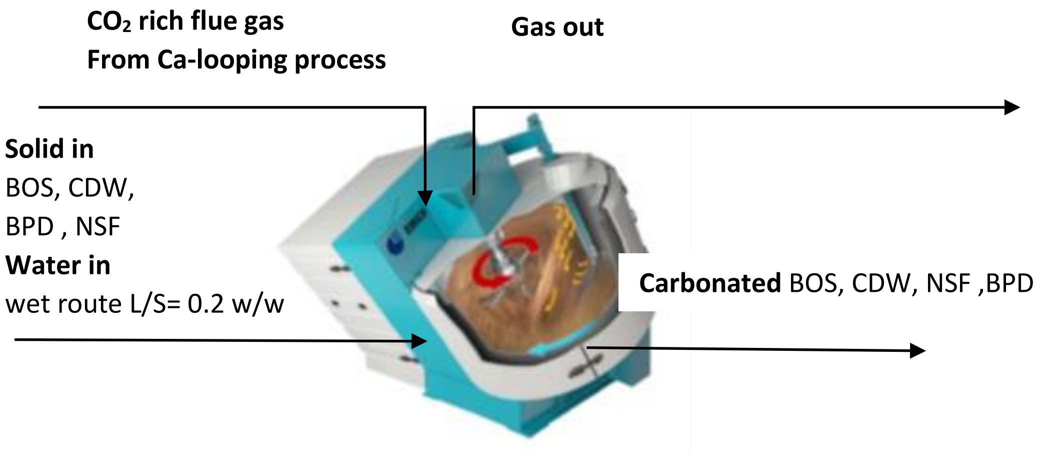


Figure 1.2 Experimental setup №1

Figure 2.2 Experimental setup №2

For process scale-up the experiments were carried out also in a 46 L concrete mixer (CM, technical specifications: engine 230V, ~50hz, 150W, drum capacity 46 L, drum mouth 236 mm, drum speed 29.8 rpm) equipped with gas inlets (Figure 2.2). The experiments were conducted in similar conditions as compared to Eirich EL1 type-mixer, but the material load and gas flows were increased up to 10 times (Table 2.4).

Table 2.4 Samples and operating parameters

	CO_2 %	**Gas flow, l/h**	**Water/solid, ml/g**	**Rotation speed**
Balti Espa	20-70	50-400 2000 (CM)	50/150; 30/150; 1200/6000 (CM)	300-500 3000 (CM)
Balti total	70	200	30/150; 60/300	300
DeSOx	70	100-200	30/150; 60/300	300
Auvere Espa	20-70	50-400	50/150; 60/300; 120/600	300-3000
CDW 2	70	200	30/150	300
Bypass dust	70	200-400	30/150; 90/300	300

The experiments were carried out until CO_2 concentration in outlet gas stabilized on the level of inlet gas.

2.4. Modeling software – ASPEN Plus

ASPEN Plus (Aspentech,2019) is a software package designed to allow a user to build a process model and then simulate the model without tedious calculations. In this work program was use for comparison real state experiments and results what can provide modeling if practical parameters and results will use as the conditions for simulation [36].

The modelling process can be divided by 7 steps:

- Building a Process Flowsheet
- Entering material/heat flows
- entering reaction kinetics
- Entering Process Conditions

- Running Process Model
- Interpreting the Results
- Changing Process Conditions (or error finding) and Rerunning the Model

Building a process flow sheet consists of drawing reactors and material/heat flows same as the experimental setup. Batch reactor is a standard equipment in chemical process industries. It consists essentially of an autoclave provided with mixing and heat transfer devices, as well as with piping connections for feeding the reactants and taking-off the products. Adding flow compositions, operating parameters and reactions kinetics enables us to build a process model and the simulation results are compared with experimental results.

3. Experimental part

3.1. Characterization of wastes

Material characterization includes determining physical, chemical, mechanical and microstructural properties of the materials. This process leads to the higher level of understanding needed to resolve important issues during the experemental part as weel as post analysing.

3.1.1. Phase composition

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The quantative X-ray difraction was carried out via Bruker D8 Advanced at the Department of Geology, University of Tartu.

Table 3.1 Phase composition of oil shale ashes

	EEJ	**EEJ**	**BEJ**	**BEJ**	**DeSOx**	**Enefit280**	**Auvere**	**Auvere**
	Espa	**Total**	**Espa**	**Total**		**Total**	**Total**	**Espa**
Quartz	19.9	17	19.8	14.4	10	6.8	12.2	15.5
Orthoclase	15.5	12.7	16.1	7.7	3.2	8.1	10.9	15.3
Mica	4.7	4.5	4.5	4.4		1.2	4.6	7.1
Calcite	8.1	11.1	7.7	23.8	7.5	63.6	23.1	17
Dolomite				1.7		3		
Hematite	2.4	2	2.3	1.4	1	0.9	1.5	1.7
Lime	12.7	14	12.4	12.6	10.9		18.5	13.5
Portlandite		1.5		1	6		0.7	
Periclase	4.1	5	5.1	5.4	4.4	1.5	2.7	2.8
Anhydrite	11.4	11	9.9	8.8	13	6.3	6.2	8.9
Dicalcium silicate	7.2	8.1	7.6	6.4	21.6	6.3	11.6	11
Wollastonite	1.3	1.1	1.3	1.8	1.1			
Akermanite	8.6	8.2	8.6	7	4.7	0.8	3.5	2.6
Merwinite	3.6	3.8	4.1	3.4	4.6	0.4	4	3.2
Sylvite					1.6			0.5
Hannebachite					10.4			

The phase composition of oil shale ashes (Table 3.1) indicated that the burnt oil shale samples contained a considerable amount lime, portlandite and secondary Ca-silicates, which attribute as potential CO_2 binders.

Table 3.2 Phase composition of concrete demolition wastes (CDW), cement bypass dust (BPD), Blast furnace slag (NSF)

	CDW 1	**CDW 2**	**CDW 3**	**CDW 4**		**BPD**	**NSF**
Quarts	30.7	40.2	34.5	39.8	**Quartz**	5.3	Roentgen amorphous material
Orthoclase	5.2	10.5	12.6	6.2	**Orthoclase**		
Plagiclase	10.6	19.8	15.1	13.4	**Mica**	1.0	
Mica	10	10.3	11.5	6.8	**Calcite**	3.2	
Chlorite	3.9	2.9	6.5	3.5	**Dolomite**		
Kaolinite	0.9	3.4	4	1.6	**Hematite**		
Calcite	23.3	6	8.4	18.9	**Lime**	10.6	
Dolomite	11.5	2.1		7.3	**Portlandite**	41.8	
Cummingtonite		1.4	1.7	1	**Periclase**	0.6	
Hematite	1.2	0.5	1.1	0.8	**Anhydrite**	4.7	
Gypsum	2.4	2.9	4.7	0.8	**Dicalcium silicate**	17.2	
					Wollastonite	4	
					Akermanite	2.3	
					Merwinite	4	
					Diopside	3.9	
					Sylvite	1.3	

The quantitative XRD indicated that the CDW samples (Table 3.2) contained no lime or portlandite as the most active CO_2 binding phases, while BPD contains a large amount of portlandite and enought lime for experiments. NSF sample was roentgen amorphous, therefore the determination of phase composition was not available (Table 3.2.) the material did not contain any free lime of mineral CO_2.

3.1.2. Chemical compsition

The materials were analyzed using XRF spectroscopy (Rigaku Primus II) at the Department of Geology, University of Tartu (Figures 3.1 and 3.2).

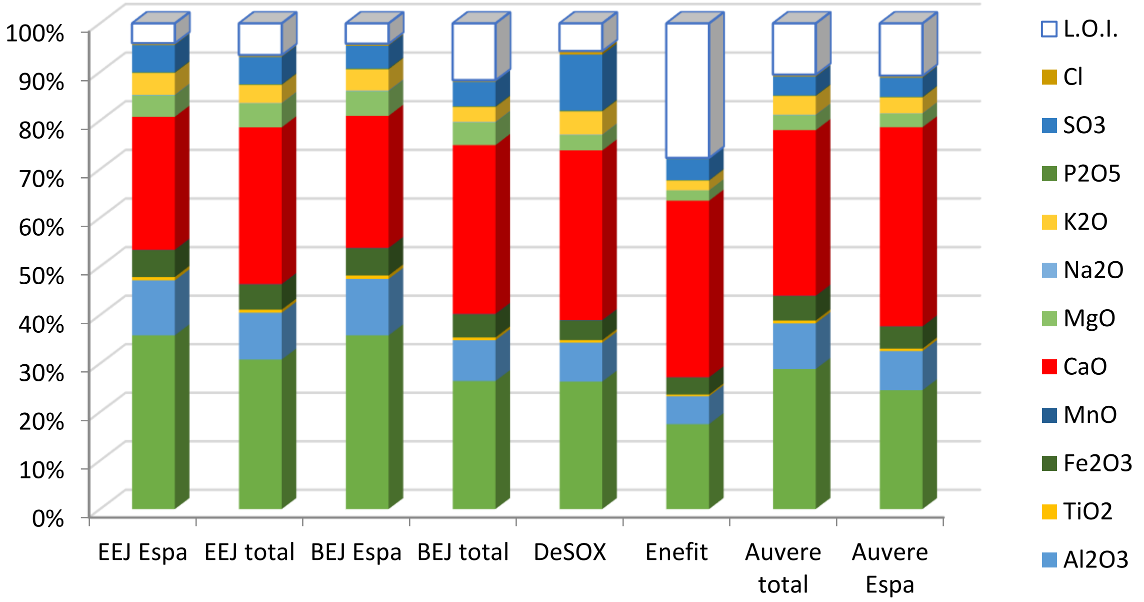


Figure 3.1 Burnt oil shale chemical composition

According to XRF analysis, the BOS (burnt oil shale) samples contained mainly Ca- and Si-compounds.

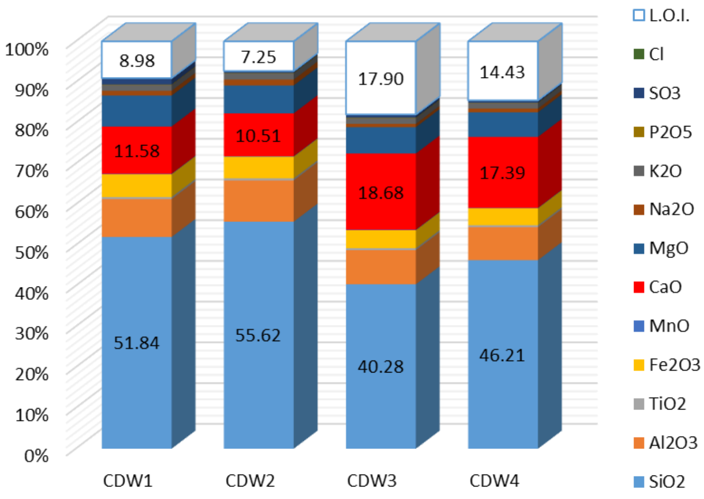


Figure 3.2 CDW chemical composition

Although the chemical composition of CDW showed significant total calcium content XRD indicated that CDW lacked lime, portlandite and Ca-silicates as potential CO_2 binders.

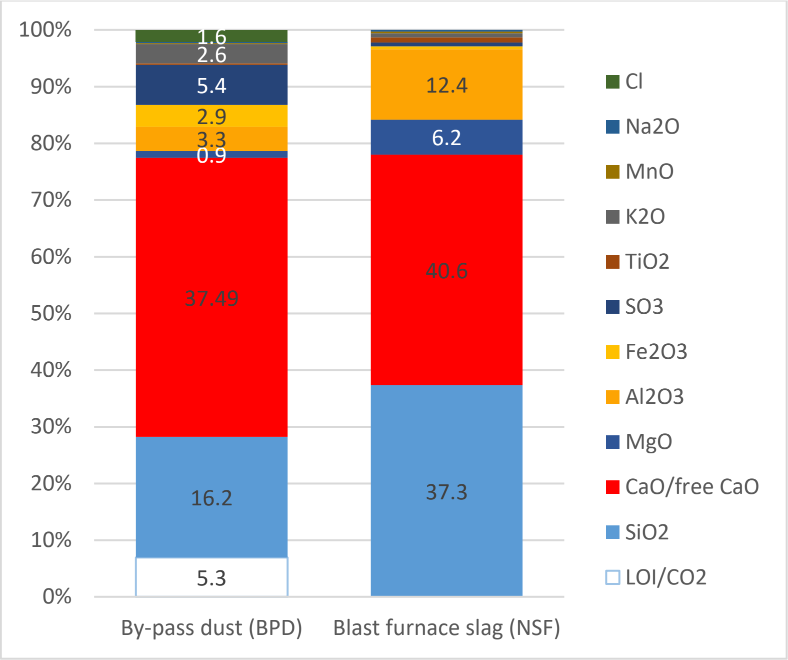


Figure 3.3 BPD and NSF chemical composition

The BPD material contained considerable amount of free lime as lime and portlandite. According to chemical and phase composition BPD could be classified as a very promising material for CO_2 mineralization. The NSF material chemical composition indicates that it consists mainly Ca-silicates and with amorphous composition cannot be attributed as suitable material for carbonation experiments respectively.

3.1.3. Theoretical CO_2 binding ability

Effectiveness of the carbonization process was described by the CO_2 - binding degree (BD CO_2). BD CO_2 shows which part of the theoretical ash- binding capacity is utilized. It was calculated basing on the changes in CO_2 content:

$$BD_{CO2} = \frac{CO_2}{CO_{2max}} \times 100 \tag{3.1}$$

Where CO_2 Is analyticaly determined CO_2 content of the sample. For finding CO_2 max or the maximum possible CO_2 content of the sample calculate via follow equatation [37]

$$CO_{2max} = \frac{CaO \times \frac{M_{CO2}}{M_{CaO}} + CO_2}{100 + CaO \times \frac{M_{CO2}}{M_{CaO}}} \times 100 \tag{3.2}$$

The CO_{2max} calculated on the basis of free lime or CaO and total carbon in initial sample. In this way the more gap between CO_2 in sample and CO_2max is, then more perspectivity carbonization results are expected.

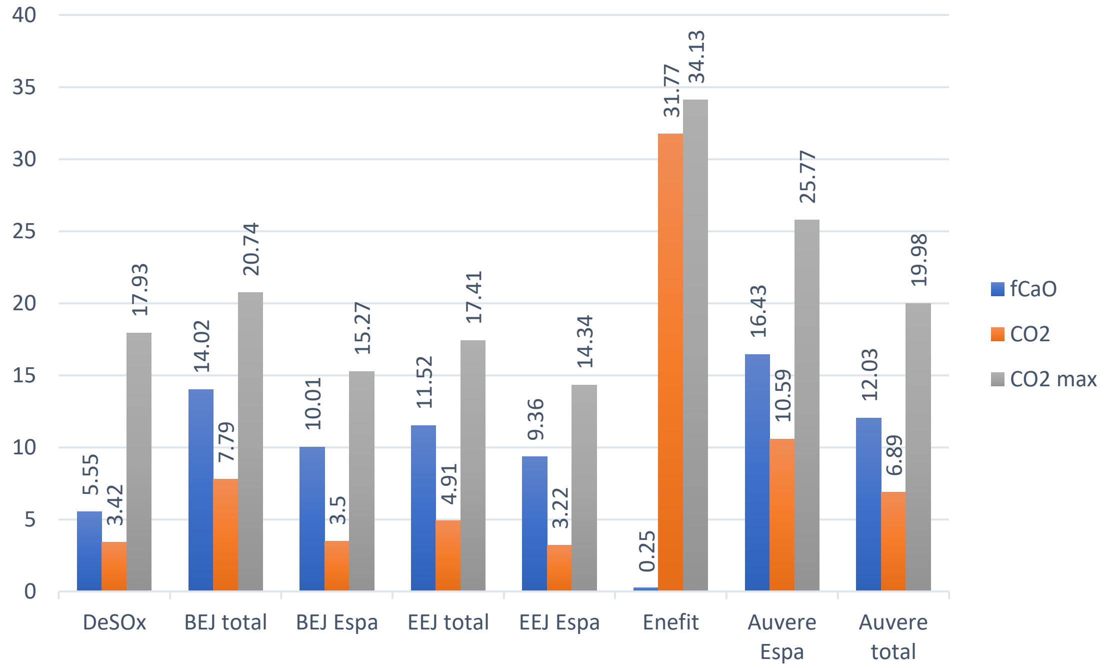


Figure 3.4 Oil shale ash binding ability

Almost all ashes (exluding Enefit) showed good results and thus confirmed that any of them can be used for experimentation (Figure 3.4). In this work we decided to continue experiments with four oil shale ashes BEJ ESPA, BEJ TOTAL, DeSOx and AUVERE ESPA shoved promising CO_2 binding potential.

According to chemical composition, the CO_2 binding ability for CDW is already depleted (Figure 3.5). Theoretical CO_2 binding potential of BPD was very promising according to its high free lime content (Figure 3.5).

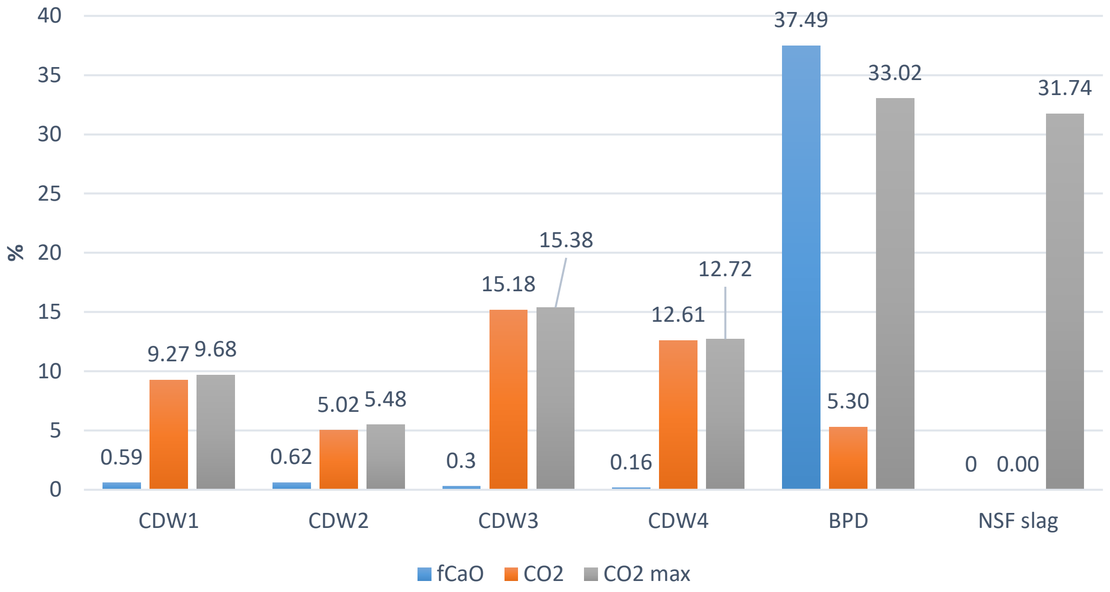


Figure 3.5 CDW, Bypass dust and NSF slag binding ability

3.2. Wet carbonation of oil shale ashes: the effect of operating parameters

The main indicators of the progress on carbonation process are the changes in $CaCO_3$ and free lime concentration in solid phase and CO_2 concentration in the gas phase The experiments were carried out at different operating parameters (gas inlet CO_2 concentration, mixing speed, sample mass and gas flow rate, w/s ratio) parameters in order to build a general picture of their effect on carbonation results. Based on the data obtained, the graphs were constructed b following the composition of solid and gas phase in time. The experemental part starts from changing parameterst one by one to comparison them and to build a general picture of the influence of certain parameters on the system. The best results were used in further experiments with different materials (CDW,BPD, NSF) with focusing on oil shale ashes as the main solid waste type in Estonia

3.2.1. Changes in solid phase composition: $CaCO_3$ and $Ca(OH)_2$ contentent

The most important indicator for carbonation progress are the contents of $CaCO_3$ and residual $Ca(OH)_2$ based on TC and free lime analysis. Due to the large number of samples taken during experiments, the changes in the concentration of these components in time were expressed on graphs.

The effect of rotation speed

First the effect of reactor rotation speed was studied by varying it from 300 – 3000 rpm (Figure 3.6).

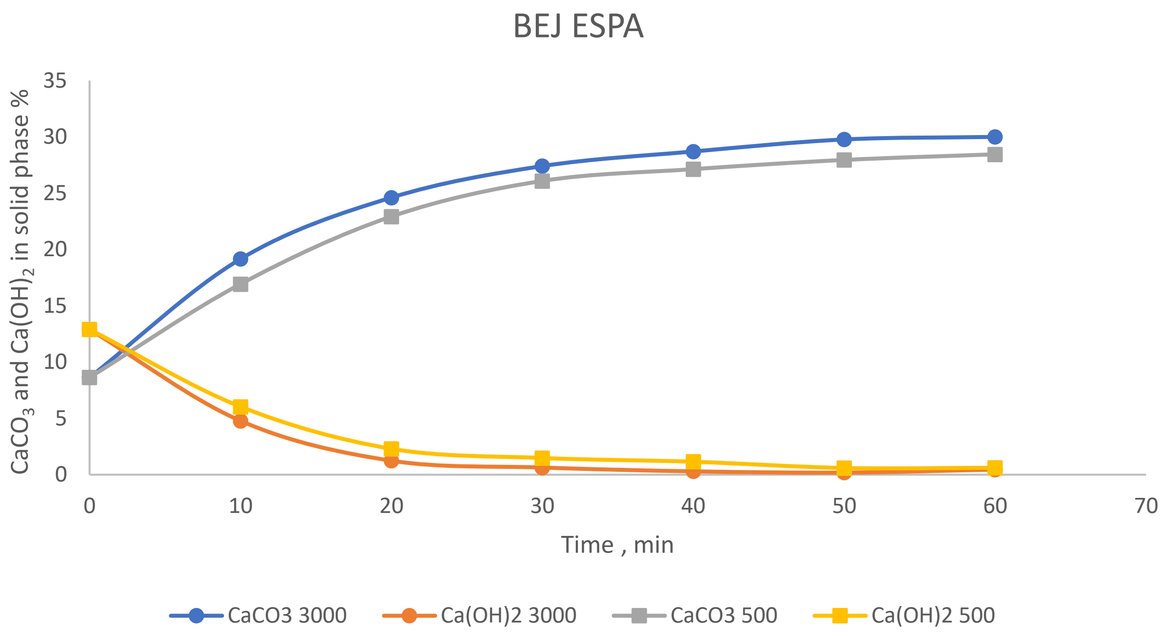


Figure 3.6 The effect of mixing speed. BEJ ESPA with Water/Ash ratio 50/150 , Gas content 20% , Gas flow 50 l/h and rotation speed 500 rpm and 3000 rpm

From the graph it is clear that the rotation speed does not affect notably the carbonation process, since the end of both reactions took about an hour and the cross points were very close.

The water to solid ratio was also evaluated by several tests, which indicated that 0.2 w/w would be optimal to avoid the formation of granules at lower mixing speeds.

The effect of CO_2 concentration in inlet gas

Next step was to change the gas content. We chose 70% CO_2 (in model gas CO_2 is mixed with air) as the lowest CO_2 concentration exiting from CLEANKER Ca-looping pilot and compared it with the CO_2 concentration of the flue gas from convential cement plant (20%).

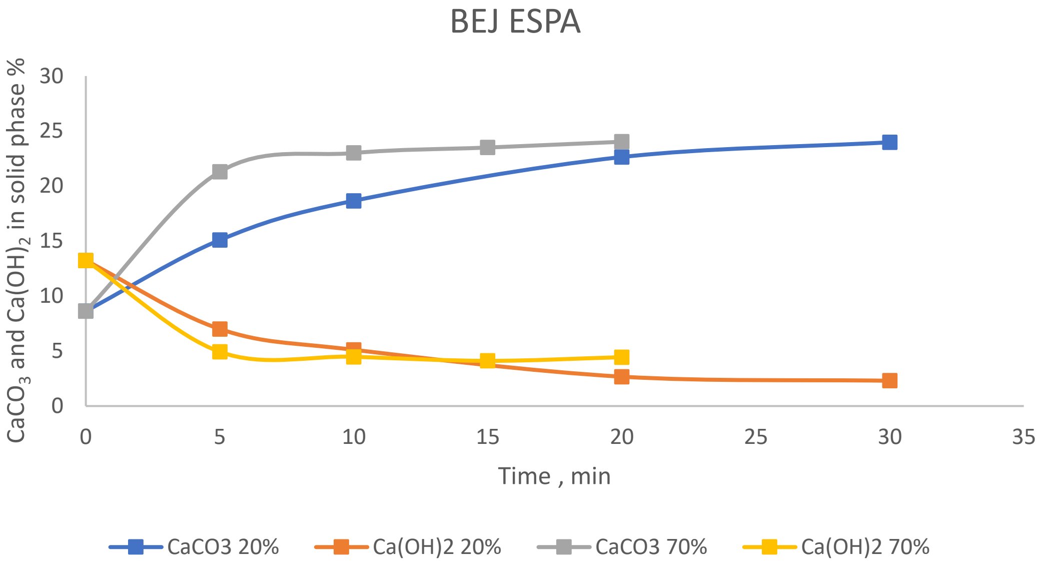


Figure 3.7 The effect of CO_2 gas concentration. BEJ ESPA with Water/Ash ratio 30/150 , Gas content 20% CO_2 and 70% CO_2 , Gas flow 100 l/h and rotation speed 300rpm

The experiments with with different CO_2 concentrations inlet gas, show that at constant flow rate of 100L/h increasing CO_2 concentration from 20% to 70% has a positive effect on carbonation process (Figure 3.7). We have to keep in mind that the amont of CO_2 contacted with solid sample was also higher. On the other hand, the experiments where CO_2 concentration was increased from 20% to 70% but the gas flow rates was regulated accordingly to keep the CO_2 dose costant, the changes in carbonation degree were not that notable.

Experiments were also performed with 100% CO_2 in inlet gas, but as it was impossible to detect the changes of CO_2 concentration in outlet gas, it was not continued.

The effect of gas flow rate

The experiments on studying the effect of gas flow rate indicated that in case the gas flow rate was increased from 100 L/h to 200 L/h to treat 150g BEJ Espa ash was treated with CO_2 containing model gas, the changes in $CaCO_3$ and $Ca(OH)_2$ were identical (Figure 3.8). This indicates that Ca leaching is probably the rate limiting step.

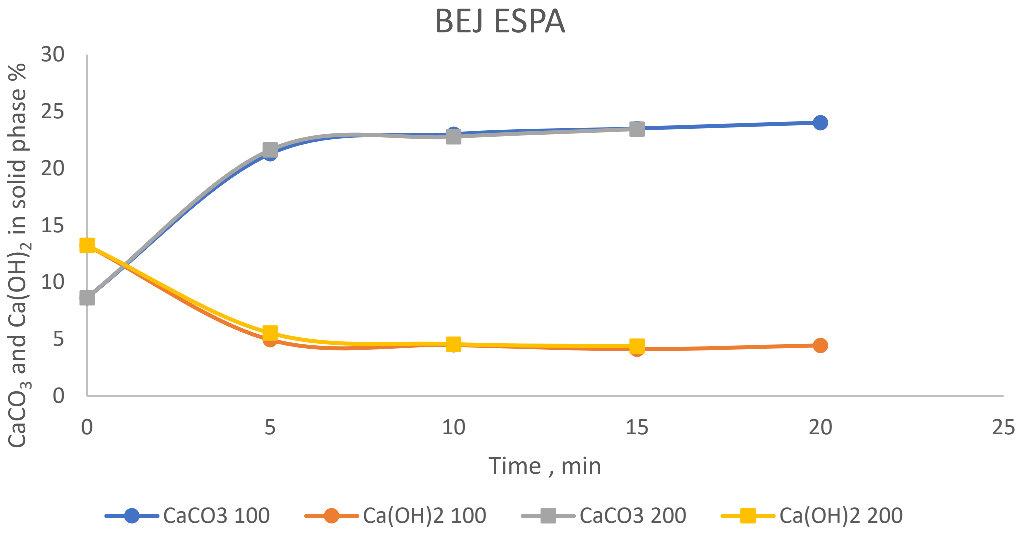


Figure 3.8 The effect of gas flow .BEJ ESPA with Water/Ash ratio 30/150 , Gas content 70% CO_2, Gas flow 100 l/h and 200 l/h and rotation speed 300rpm

Additional tests (Figure 3.9) were conducted increasing gas flow rate from 200 L/h to 400 L/h and also the amont of ash in the reactor (600g Auvere Espa for both experiments).

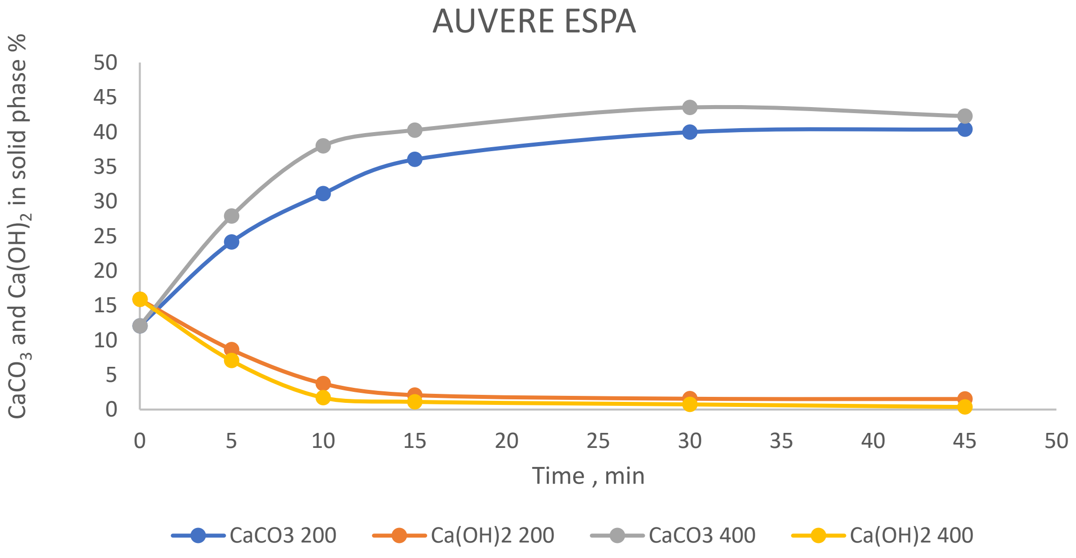


Figure 3.9 The effect of gas flow. Auvere Espa with Water/Ash ratio 120/600 , Gas content 70%, Gas flow 200 l/h and 400 l/h and rotation speed 300rpm

The graph (Figure 3.9) shows visible changes in the $CaCO_3$ and $Ca(OH)_2$ concentrations, which corresponds to an increase in gas flow rate. This means that with an increasing material and gas flows the carbonation process was intesified which was also expressed by rapidly increasing reactor temperature (60-80°C) as both lime slaking and carbonation are wexothermic reactions.

The effect of material and reactor volume ratio

The results from previous experiments were confirmed by increasin the material and reactor võlume ratio from 300 to 600 g/L (Figure 3.10) at constant CO_2 flow of 200 L/h.

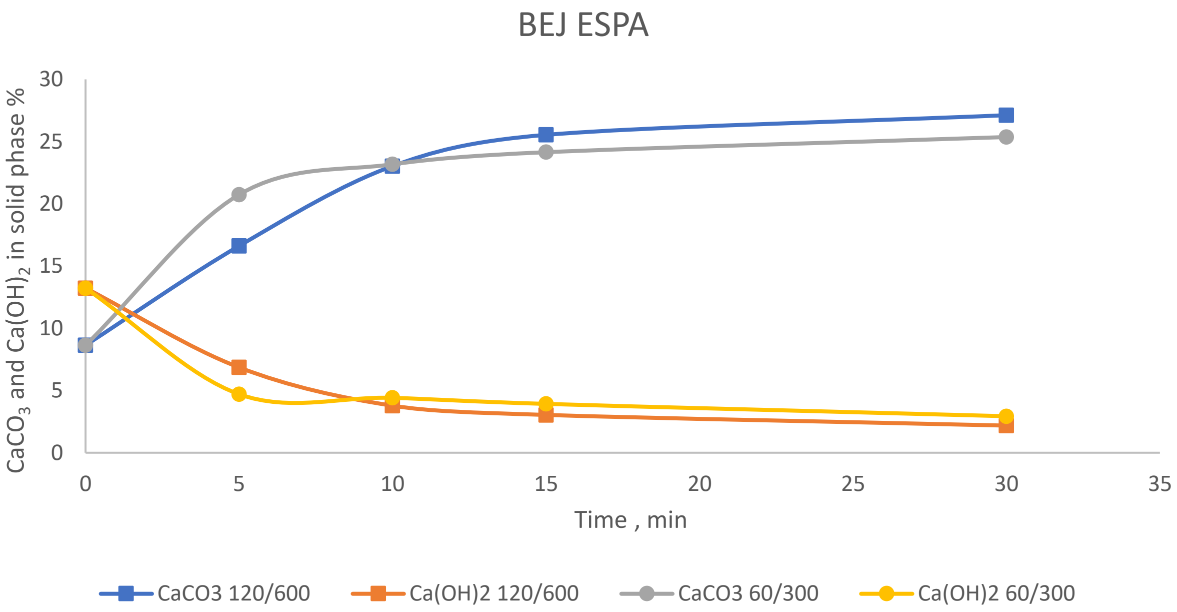


Figure 3.10 The effect of w/s ratio.BEJ ESPA with Water/Ash ratio 60/300 and 120/600 , Gas content 70%, Gas flow 200 l/h and rotation speed 300rpm

Its shown from the gas that although at first free lime is depleted more rapidly in case of 300 g per 1L reactor volume ratio, because there is less material to carbonate, the deeper carbonation was achieved in case of 600 g per 1 L reactor volume.

The effect of different types oil shale ashes

Also, an important indicator for us was how different the results can be when using different types of industrial wastes under the same conditions. In this way we decided to show that these conditions are suitable for all kinds of oil shale ashes from Estonian power plans.

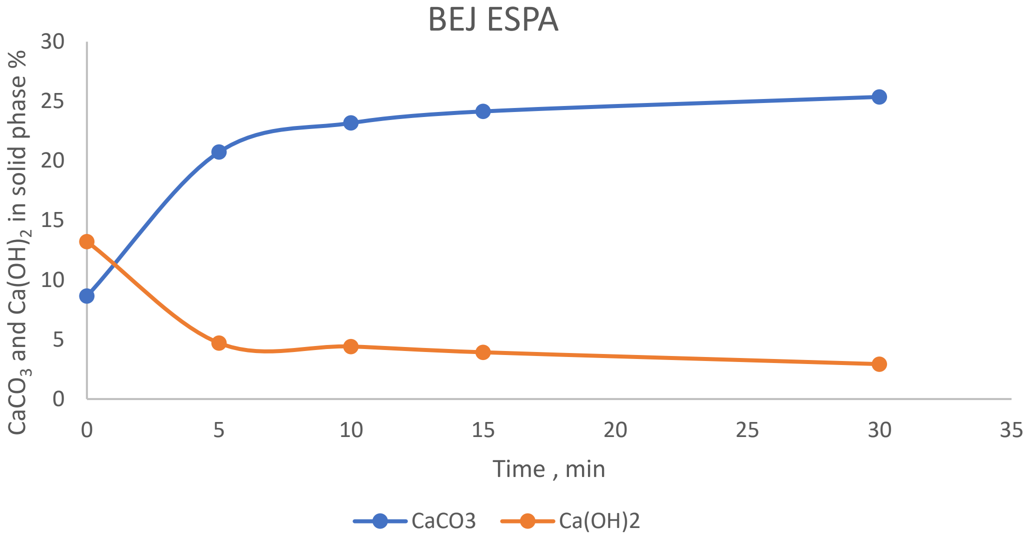


Figure 3.11 BEJ ESPA Water/Ash ratio 60/300 , Gas content 70% , Gas flow 200 l/h and roration speed 300 rpm

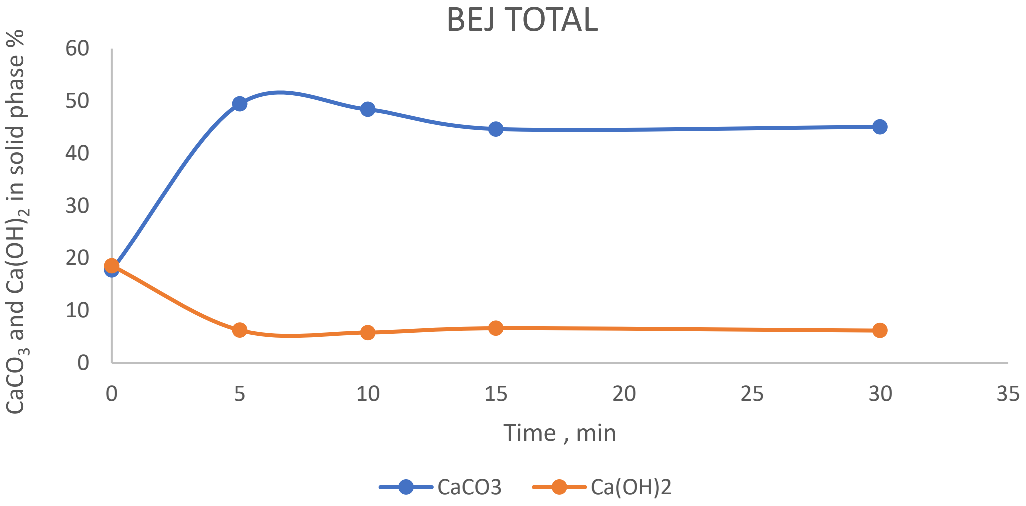


Figure 3.12 BEJ TOTAL Water/Ash ratio 60/300 , Gas content 70% , Gas flow 200 l/h and roration speed 300 rpm

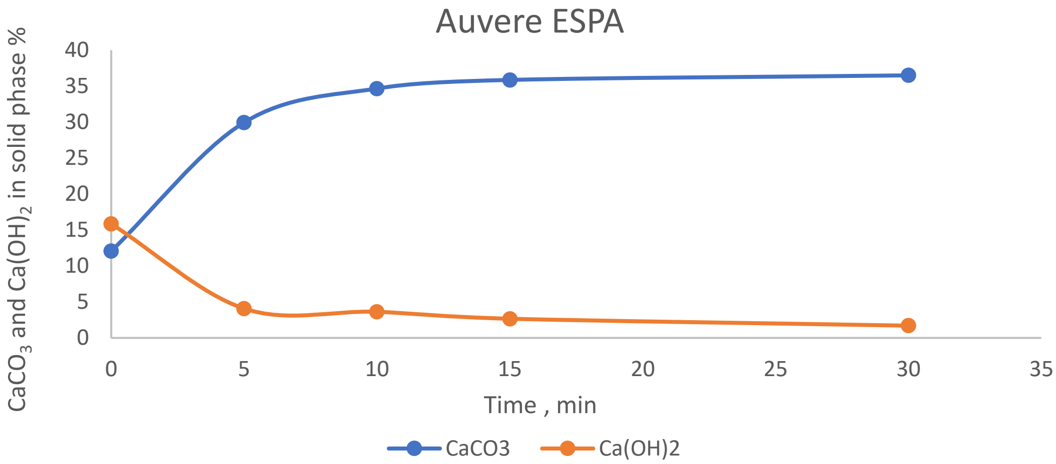


Figure 3.13 AUVERE ESPA Water/Ash ratio 60/300 , Gas content 70% , Gas flow 200 l/h and roration speed 300 rpm

We see that the BEJ Espa, BEJ Total and Auvere Espa have very similar CO_2 binding characteristics (Figures 3.11-3.13), the main reaction occurs during first five minutes of the experiment in the conditions of 300 g ash, and gas flow rate of 200 l/h, as in previous experiments. The free lime is mostly depleted by after 30 minutes. Higher $CaCO_3$ contents in BEJ Total are the result of high initial calcite content (see Table 3.1). The content of free lime does not decrease below 2%.

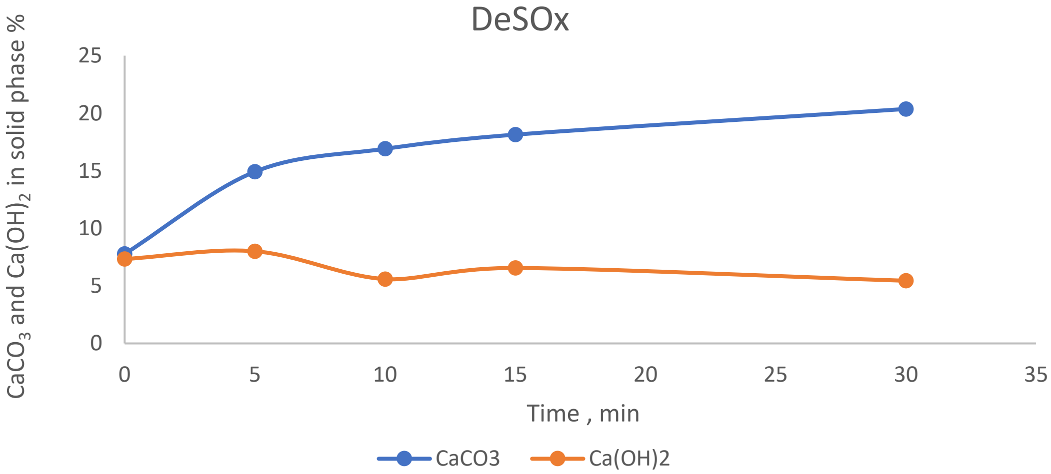


Figure 3.14 DeSOx Water/Ash ratio 60/300 , Gas content 70% , Gas flow 200 l/h and roration speed 300 rpm

The DeSOx ash proved to be slightly different from others, as carbonation is slower and not as deep (Figure 3.14). The contents of $CaCO_3$ and $Ca(OH)_2$ remain respectively lower and higher as compared to the results for CFB ashes. This can be caused by the physical properties of pulverized ashes which are characterized by lower BET specific surface area (1.77 m^2/g as comared to 6.05 m^2/g for Auvere Espa).

Process upscale using 42L concrete-mixer type reactor with oil shale ash

In order to test the wet carbonation method in larger scale the experiment were also carried out in 42L concrete mixer equipped with gas inlets and outlets. Based on this, it was necessary to prove that the assumptions that worked in small volumes are also applicable in large ones. This gives valuable information for process upscale to pilot or even industrial scale.

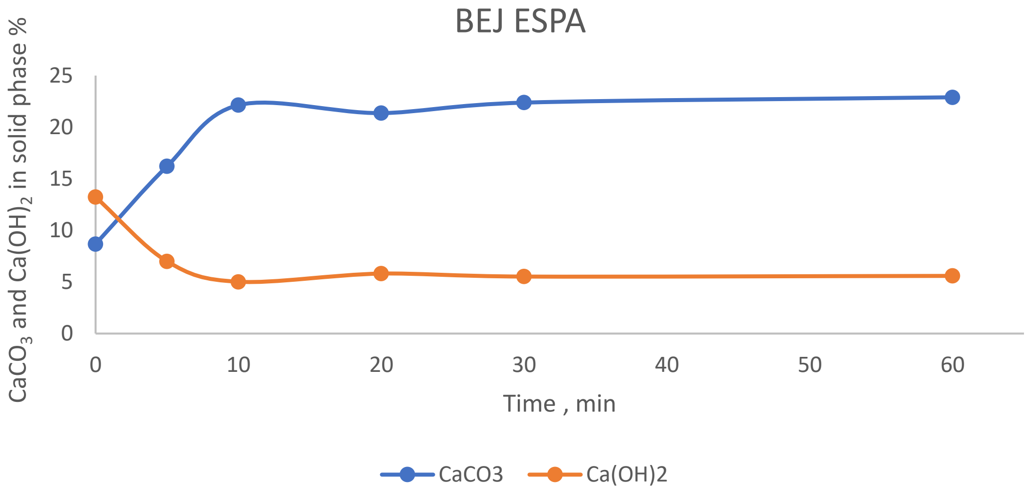


Figure 3.15 BEJ ESPA with Water/Ash ratio 600/3000, Gas content 70%, Gas flow 2000 l/h and rotation speed 300 rpm

On figure 3.15, we see that there are no big changes as compared to Eirich EL1 mixer type reactor. The content of $CaCO_3$ remains lower as compared to Eirich EL1 tests, but can be explained by the less effective mixing due to differences in mixing equipment (Eirich EL1 type mixer is equipped with mixing tool as the concret mixer is just rotating).

Next the sample mass and reactor volume ratio was increased 2 times (Figure 3.16), with no changes in other parameters.

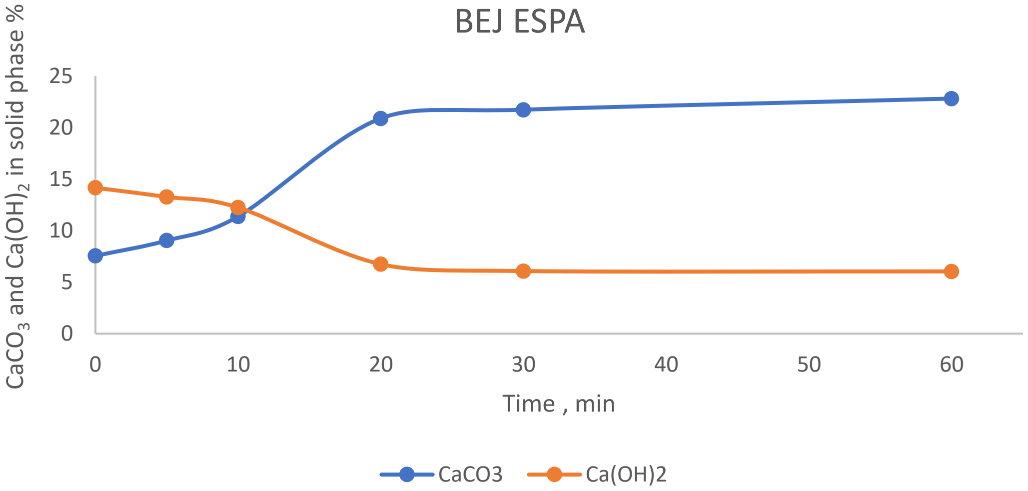


Figure 3.16 BEJ ESPA with Water/Ash ratio 1200/6000, Gas content 70%, Gas flow 2000 l/h and rotation speed 300 rpm

As expected the carbonation takes longer due to lower gas flow rate but the $CaCO_3$ and $Ca(OH)_2$ contents are similar to previous experiment.

3.2.2. Gas phase composition: changes in CO_2 concentration

Another important indicator that enables us to monitor the carbonation even during experiment is CO_2 concentration in outlet gas. The CO_2 concentration was detected continuously but the measurements were taken in a certain interval. On the basis of this data, the graphs were made.

The graph below shows how the content of CO_2 in the gas phase of the reactor change, at three different concentrations: 20%, 70% in 100%, respectively (Figure 3.17). Carbonation occurs wery fast in case of 100% an 70% of CO_2 in inlet gas, as for process takes notably longer if 20% CO_2 in inlet gas is used.

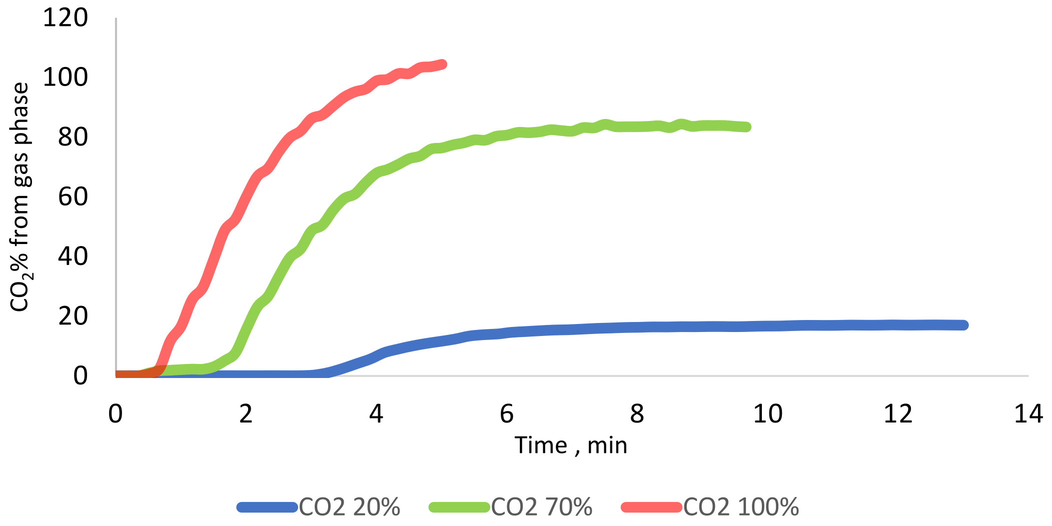


Figure 3.17 Changes in CO_2 concentration in outlet gas from BEJ Espa wet carbonation using 20%, 70%, 100% of CO_2 concentration in inlet gas

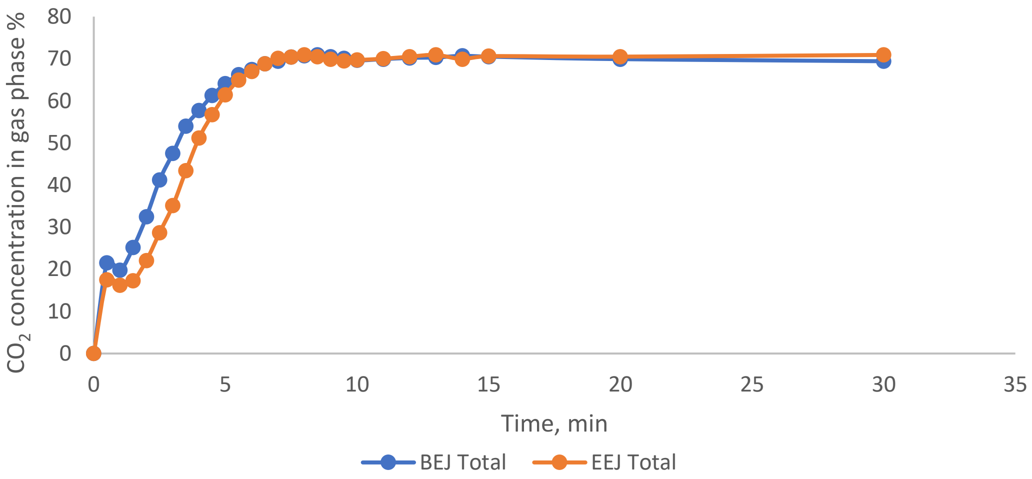


Figure 3.18 Changes in gas phase composition. BEJ Total and EEJ Total with Water/Ash ratio 30/150, Gas content 70%, Gas flow 200 l/h and rotation speed 300 rpm

On the figure 3.18, we see CO_2 concentration in outlet gas for carbonation of two different ashes under same conditions. The two lines are almost identical. So, we see the increase in concentration at the outlet for the first five minutes, after which equilibrium sets in and the gas concentration does not change, and remains at 70%, as much as we fed into the reactor.

Next experiments were carried out increasing sample mass and reactor võlume ratio from 150g per 1L reactor võlume to 300 g (Figure 3.19).

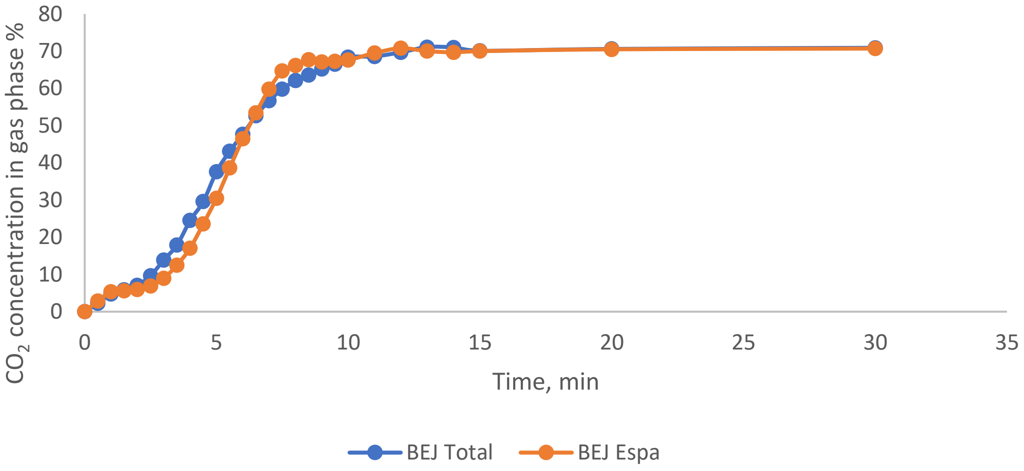


Figure 3.19 Changes in gas phase composition. BEJ Total and BEJ Espa with Water/Ash ratio 60/300, Gas content 70%, Gas flow 200 l/h and rotation speed 300 rpm

In comparison with previous experiments (Figure 3.18), there is a slight slowdown in the increase of CO_2 concentration at the outlet. So, for five minutes, in the first case, the concentration reached 70%, whereas on figure 3.19 by this time the concentration has risen only to 40%. This can be explained by the lower CO_2 dose. But in both cases equilibrium occurred within 10 minutes with the value of 70% CO_2 .

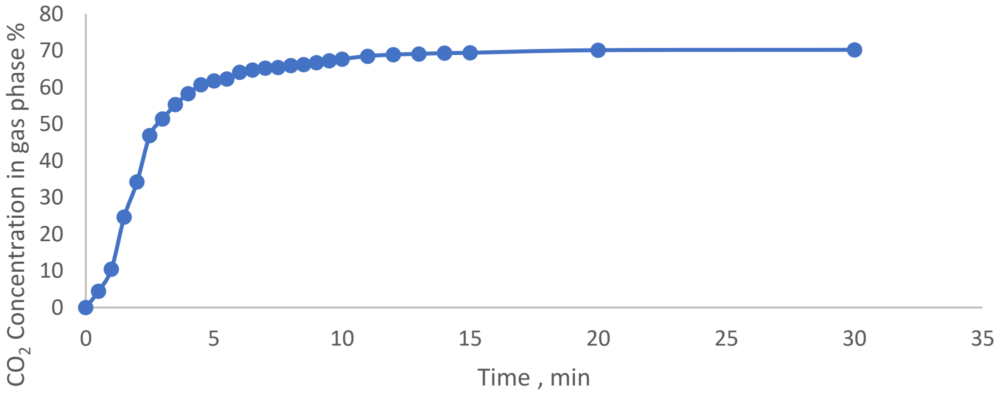


Figure 3.20 Changes in gas phase composition. DeSOx with Water/Ash ratio 60/300, Gas content 70%, Gas flow 200 l/h and rotation speed 300 rpm

Earlier, we saw that this kind of ash (DeSOx) somewhat more difficult to carbonate under same cooperating conditions. From CO_2 concentrations in outlet gas (Figure 3.20) we can see that reaction is over very quickly and CO_2 level stabilizes on 70%, meaning that free lime is probably only partially carbonated.

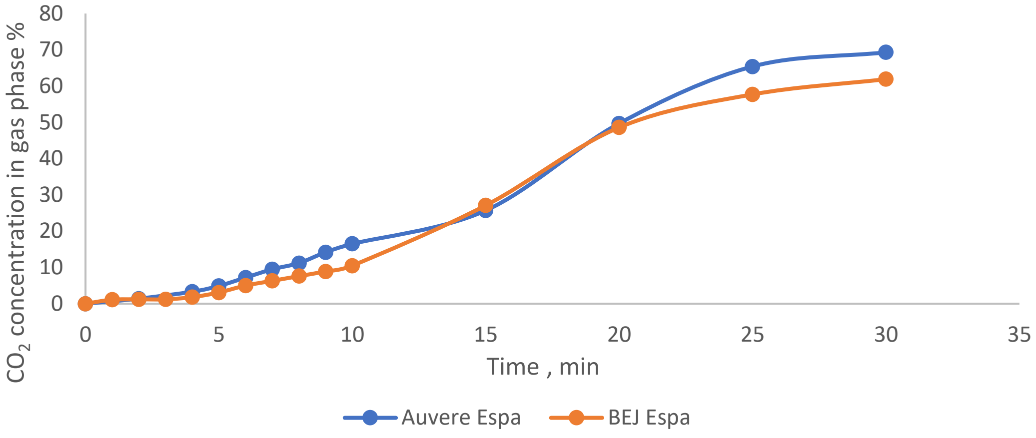


Figure 3.21 Changes in gas phase composition. BEJ ESPA and Auvere Espa with Water/Ash ratio 120/600, Gas content 70%, Gas flow 200 l/h and rotation speed 300 rpm

The ratio of sample mass and reactor volume was increased even further to 600 g per 1L reactor. As expected it aslo contributed to the changes in gas output (Figure 3.22).

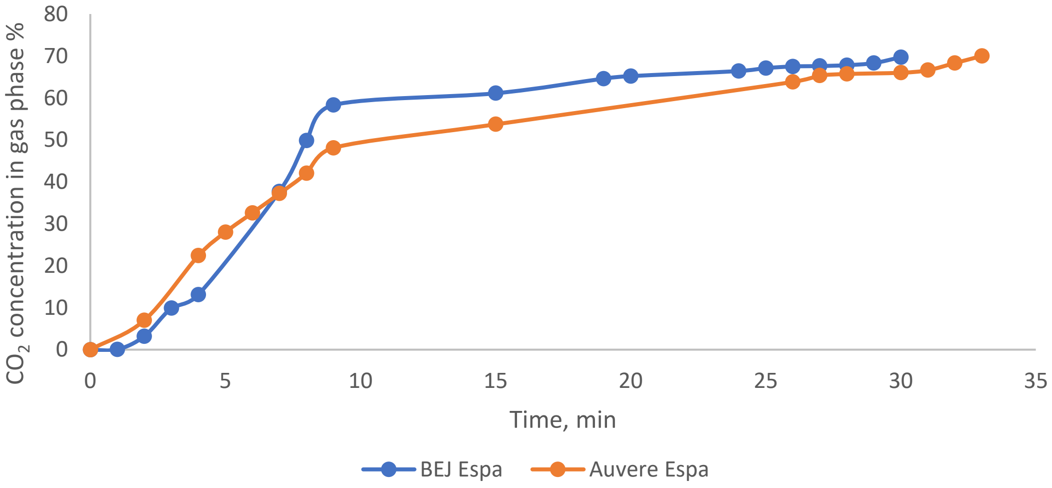


Figure 3.22 Changes in gas phase composition. BEJ ESPA and Auvere Espa with Water/Ash ratio 120/600, Gas content 70%, Gas flow 400 l/h and rotation speed 300 rpm

Increasing aslo gas flow rate to 400 l/h enhaces the carbonation reaction (Figure 3.22). In conclusion we can say that the CO_2 concentration measurements in outlet gas confirmed the results from solid phase analysis.

3.3. Wet carbonation of concrete demolition wastes

The CDW samples showed little promise according to the chemical and phase composition. Tests were carried out with CDW2 sample which also indicated no reactivity towards CO_2 (Figures 3.23 and 3.24)

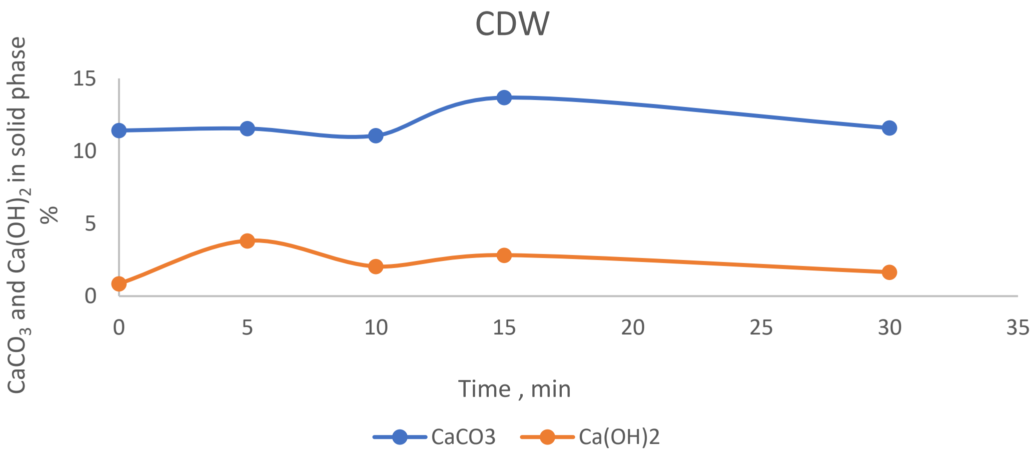
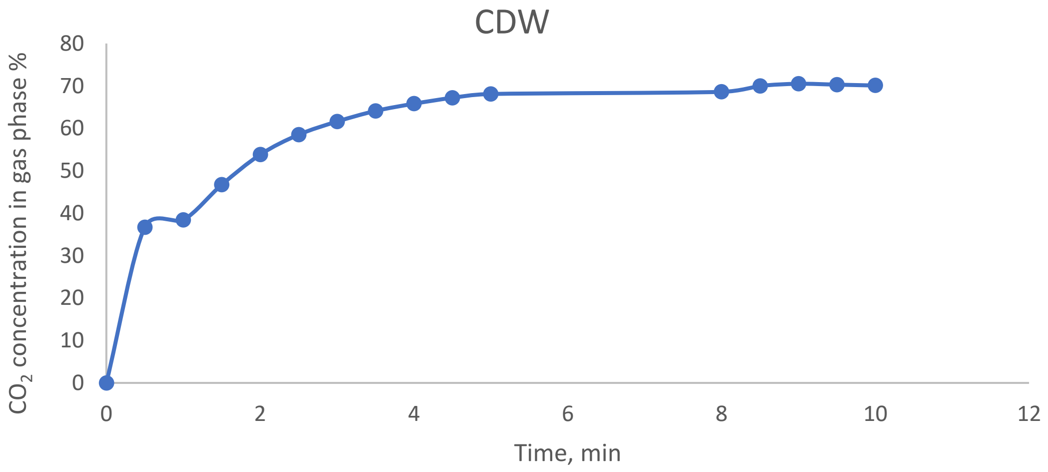


Figure 3.23 Changes in solid phase composition. CDW with Water/Ash ratio 30/150 , Gas content 70%, Gas flow 200 l/h and rotation speed 300 rpm



Joonis 3.24 Changes in gas phase composition. CDW with Water/Ash ratio 30/150 , Gas content 70%, Gas flow 200 l/h and rotation speed 300 rpm

3.4. Wet carbonation of blastfurnace slag

Experiments were carried out also with Blastfurnace slag material with previously studied operating parameters (60/300 w/s ratio, 400 l/h gas flow and 70% CO_2) during a 30 min treatment but unfortunately this type of material was not reactive towards CO_2 in these mild conditions due to lack of fCaO (0.06%) or $Ca(OH)_2$ (0.079%) and total carbon (0.235%) or $CaCO_3$ (1.96%) inside the samples. It was decided not to continue working with this material as it probably needs different operating conditions in order to carbonate the Ca-silicates.

3.5. Wet carbonation of Bypass dust

Last practical session was done with BPD sample that looked very promising according to chemical and phase analysis.

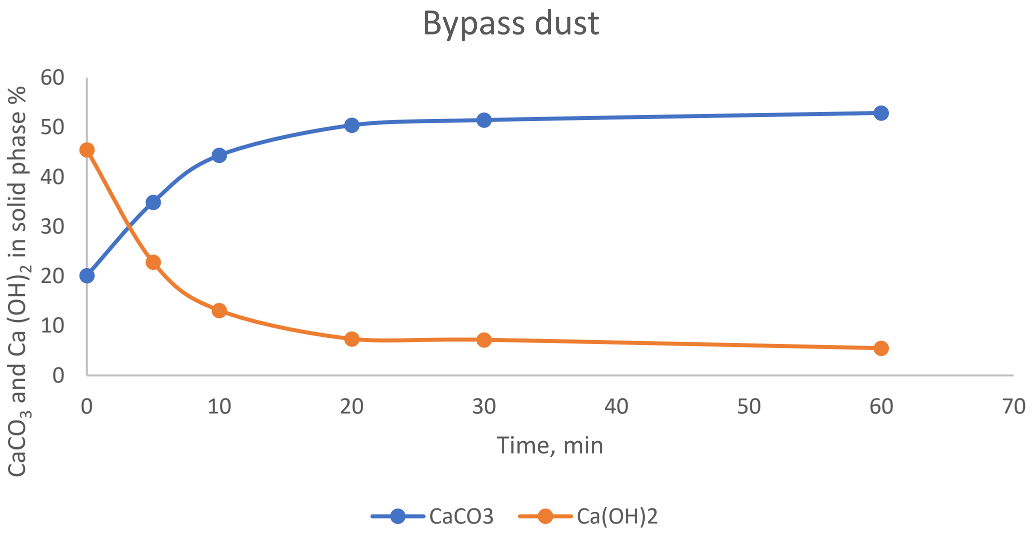


Figure 3.25 Bypass dust with Water/Ash ratio 30/150, Gas content 70%, Gas flow 200 l/h and rotation speed 300 rpm

Figure 3.25 shows that in case of BPD highest CO_2 uptake was achieved (50% $CaCO_3$) although 5% $Ca(OH)_2$ remained unreacted.

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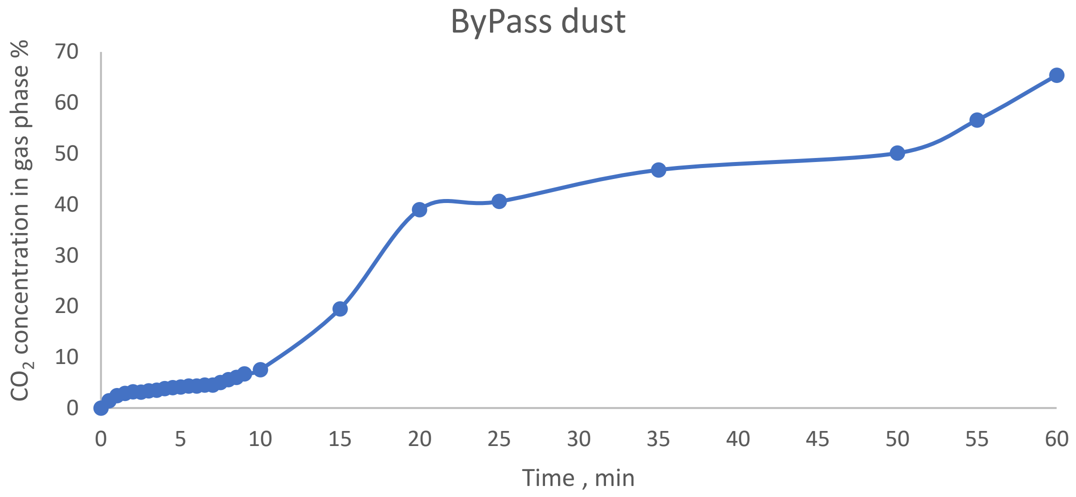


Figure 3.26 Bypass dust with Water/Ash ratio 30/150 , Gas content 70%, Gas flow 200 l/h and rotation speed 300 rpm

The CO_2 concentration from reactor on Figure 3.26 shows that in the beginning CO_2 binding is very active, then steep rise occurs between 10 to 20 minutes after which the CO_2 concentration starts stabilizing on the level of 60-70%. CO_2 measurements in gas phase confirm the results of solid phase composition in Figure 3.25.

As a result, it turned out that BPD is a very good material for mineral carbonation.

4. Modeling

4.1. Model building

In current study, the main idea was to learn how to build a batch model on the basis of experimental results and known reaction kinetics.

In this part, the main steps that directly influenced the simulation and the results obtained were noted: defining chemical components, reaction system and kinetics, physical parameters of the reactor, and recalculation of the unit of measurement.

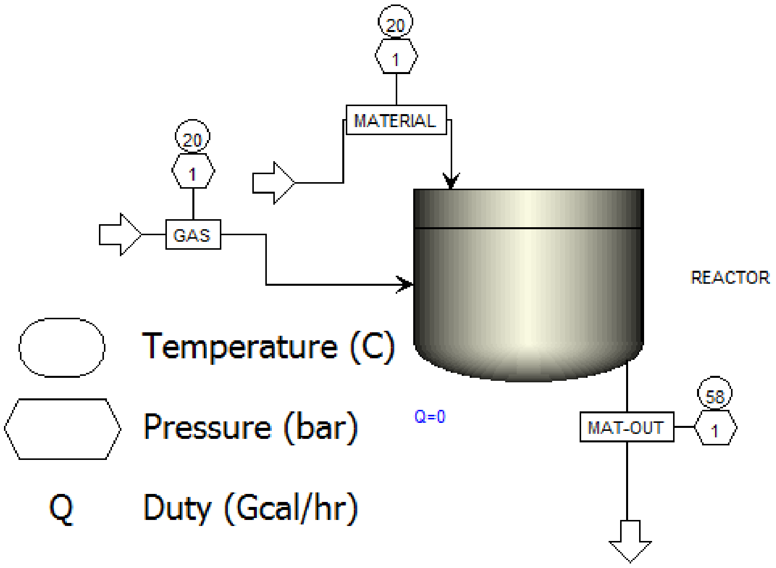
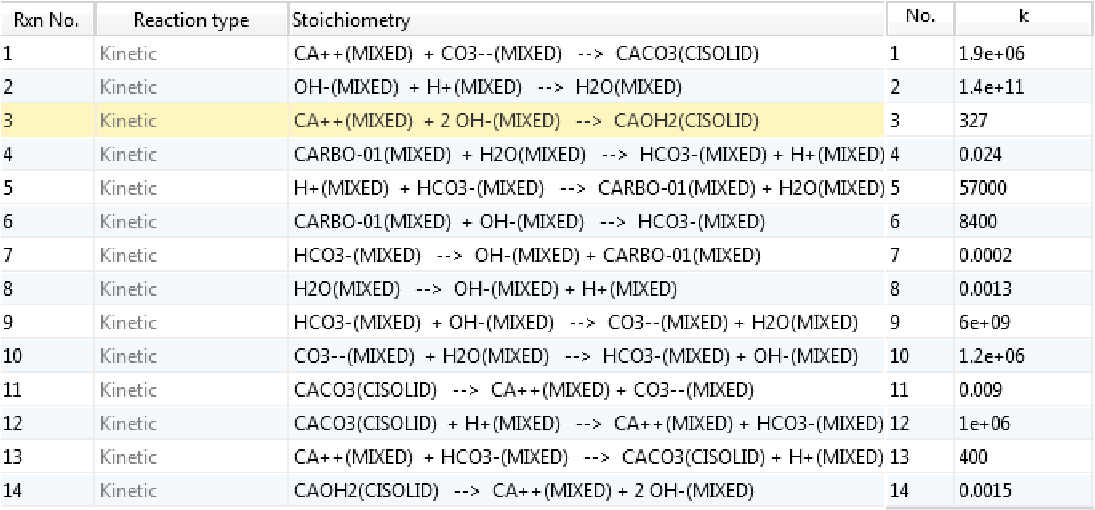


Figure 4.1 The main flowsheet

4.1.1. Chemical reactions

A kinetic model built on previous studies on $Ca(OH)_2$ dissolution [38] and carbonation [39] was implemented within the Aspen Plus simulation platform by inserting the chemical reactions and corresponding kinetic constants (Table4.1) into the Batch reactor model (Figure 4.1).

Table 4.1 Kinetic reactions and reaction rate constants



Rxn No.	Reaction type	Stoichiometry	No.	k
1	Kinetic	CA++(MIXED) + CO3--(MIXED) --> CACO3(CISOLID)	1	1.9e+06
2	Kinetic	OH-(MIXED) + H+(MIXED) --> H2O(MIXED)	2	1.4e+11
3	Kinetic	CA++(MIXED) + 2 OH-(MIXED) --> CAOH2(CISOLID)	3	327
4	Kinetic	CARBO-01(MIXED) + H2O(MIXED) --> HCO3-(MIXED) + H+(MIXED)	4	0.024
5	Kinetic	H+(MIXED) + HCO3-(MIXED) --> CARBO-01(MIXED) + H2O(MIXED)	5	57000
6	Kinetic	CARBO-01(MIXED) + OH-(MIXED) --> HCO3-(MIXED)	6	8400
7	Kinetic	HCO3-(MIXED) --> OH-(MIXED) + CARBO-01(MIXED)	7	0.0002
8	Kinetic	H2O(MIXED) --> OH-(MIXED) + H+(MIXED)	8	0.0013
9	Kinetic	HCO3-(MIXED) + OH-(MIXED) --> CO3--(MIXED) + H2O(MIXED)	9	6e+09
10	Kinetic	CO3--(MIXED) + H2O(MIXED) --> HCO3-(MIXED) + OH-(MIXED)	10	1.2e+06
11	Kinetic	CACO3(CISOLID) --> CA++(MIXED) + CO3--(MIXED)	11	0.009
12	Kinetic	CACO3(CISOLID) + H+(MIXED) --> CA++(MIXED) + HCO3-(MIXED)	12	1e+06
13	Kinetic	CA++(MIXED) + HCO3-(MIXED) --> CACO3(CISOLID) + H+(MIXED)	13	400
14	Kinetic	CAOH2(CISOLID) --> CA++(MIXED) + 2 OH-(MIXED)	14	0.0015

A separate step was to find the dependent constant the reaction rate constant or reaction rate coefficient, *k* in third reaction

$$Ca^{2+} + 2OH^{-} \rightarrow Ca(OH)_2 \tag{4.0}$$

The content of calcium hydroxide $Ca(OH)_2$ in raw ash (for most used BEJ ESPA ash) calculated from experimentally determined free lime content is 10,01%. Knowing the molar masses of components (74g/mol for $Ca(OH)_2$ and 56 g/mol for CaO respectively), finding the percentage of calcium hydroxide is not difficult.

$$Ca(OH)_2\% = \frac{74\ g/mol}{56\ g/mol} \times 10.01\% = 13.23\% \tag{4.1}$$

Knowing that 600 g of oil shale ash (as an example from experiments) is 100%, we found the mass for $Ca(OH)_2$ 13.23%

$$m\ Ca(OH)_2 = \frac{600g \times 13.23\%}{100\%} = 79.38\ g \tag{4.2}$$

And from this part found mols for $Ca(OH)_2$

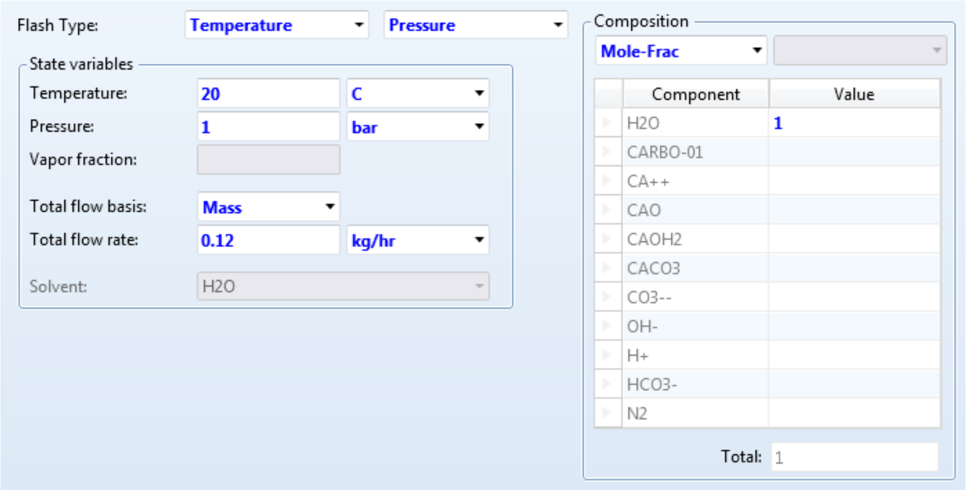
$$n = \frac{79.38g}{74\ g/mol} = 1.073\ mol \tag{4.3}$$

Last stage is finding k for reaction 3 (Table 4.1) by using equitation where concentration expressed with mol/l; therefore, volume of water 120 ml (as an example from experiments) was taken.

$$k = \frac{1.5\times10^{-3}\times\frac{1.073\ g/mol}{0.12l}}{4.09\times10^{-5}} = 327.93\ l(mol * s)^{-1} \tag{4.4}$$

4.1.2. Process parameters

The operating parameters for model reactor were chosen according to experiments as followa: t = 20◦C, P = 1 bar, Q= 0 Gcal/hr (Figure 5.2).



Flash Type: Temperature | Pressure

State variables

Temperature: 20 C

Pressure: 1 bar

Vapor fraction:

Total flow basis: Mass

Total flow rate: 0.12 kg/hr

Solvent: H2O

Composition

Mole-Frac

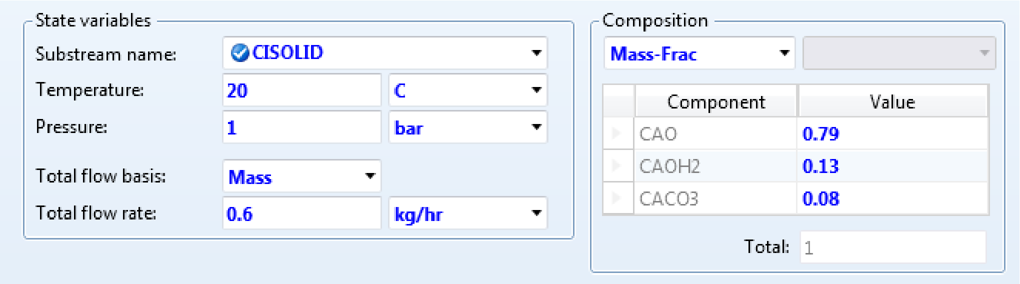
Component	Value
H2O	1
CARBO-01	
CA++	
CAO	
CAOH2	
CACO3	
CO3--	
OH-	
H+	
HCO3-	
N2	

Total: 1

Figure 4.2 Liquid phase

The water was added based on water ash ratio used in experiments (Figure 4.2) composition solid phase imitates the $CaCO_3$ and $Ca(OH)_2$ content in BEJ Espa that was used in experiments, CAO represented the rest presupably inert part of ash (Figure 4.3).

Inlet gas was presented as nitrogen N_2 and CO_2 mixture with the CO_2 concentration of 70% (Figure 4.4).



State variables

Substream name: CISOLID

Temperature: 20 C

Pressure: 1 bar

Total flow basis: Mass

Total flow rate: 0.6 kg/hr

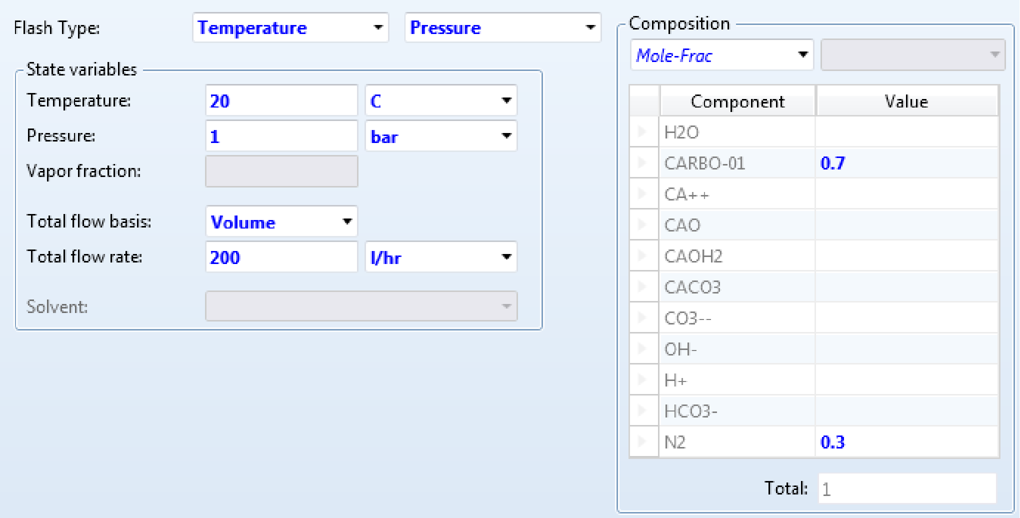
Composition

Mass-Frac

Component	Value
CAO	0.79
CAOH2	0.13
CACO3	0.08

Total: 1

Figure 4.3 Solid phase



Flash Type: Temperature Pressure

State variables

Temperature: 20 C

Pressure: 1 bar

Vapor fraction:

Total flow basis: Volume

Total flow rate: 200 l/hr

Solvent:

Composition

Mole-Frac

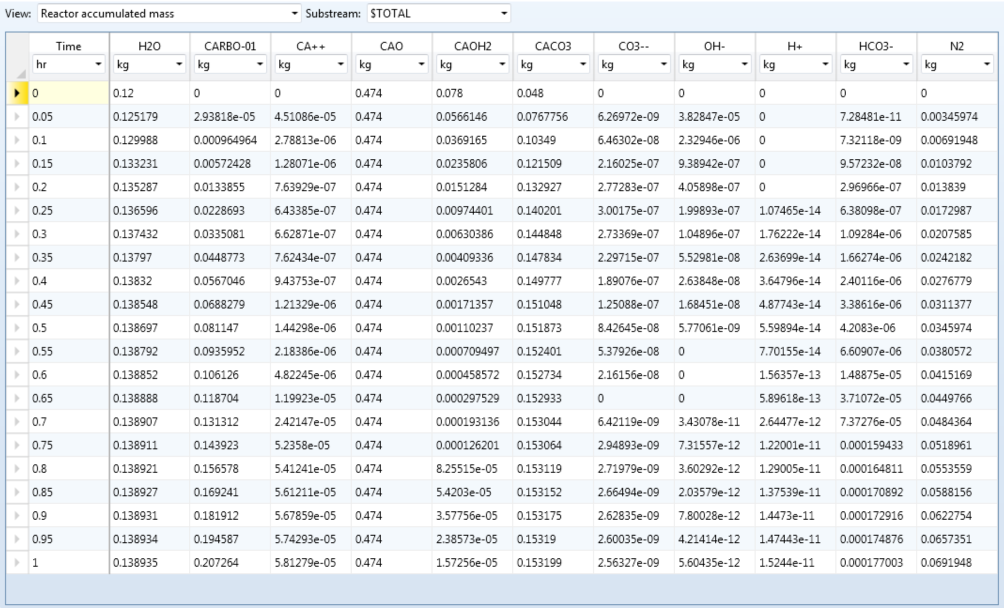
Component	Value
H2O	
CARBO-01	0.7
CA++	
CAO	
CAOH2	
CACO3	
CO3--	
OH-	
H+	
HCO3-	
N2	0.3

Total: 1

Figure 4.4 Gas phase

4.2. Comparison between experimental and simulation

During the simulation, the program produces numerical data for both the reactor components and the thermodynamic and physical state of the system. You can select parameters or you can also immediately analyze whether the values given by the program are correct or problematic. Naturally, to validate the model it should be and compared with the experimental data. Figure 4.5 an example of how the data obtained from the simulation is displayed in the program is expressed. Next, they are transferred to Excel, converted into concetration units to compare with experimental data.



View: Reactor accumulated mass Substream: $TOTAL

Time	H2O	CARBO-01	CA++	CAO	CAOH2	CACO3	CO3--	OH-	H+	HCO3-	N2
hr	kg	kg	kg	kg	kg	kg	kg	kg	kg	kg	kg
0	0.12	0	0	0.474	0.078	0.048	0	0	0	0	0
0.05	0.125179	2.93818e-05	4.51086e-05	0.474	0.0566146	0.0767756	6.26972e-09	3.82847e-05	0	7.28481e-11	0.00345974
0.1	0.129988	0.000964964	2.78813e-06	0.474	0.0369165	0.10349	6.46302e-08	2.32946e-06	0	7.32118e-09	0.00691948
0.15	0.133231	0.00572428	1.28071e-06	0.474	0.0235806	0.121509	2.16025e-07	9.38942e-07	0	9.57232e-08	0.0103792
0.2	0.135287	0.0133855	7.63929e-07	0.474	0.0151284	0.132927	2.77283e-07	4.05898e-07	0	2.96966e-07	0.013839
0.25	0.136596	0.0228693	6.43385e-07	0.474	0.00974401	0.140201	3.00175e-07	1.99893e-07	1.07465e-14	6.38098e-07	0.0172987
0.3	0.137432	0.0335081	6.62871e-07	0.474	0.00630386	0.144848	2.73369e-07	1.04896e-07	1.76222e-14	1.09284e-06	0.0207585
0.35	0.13797	0.0448773	7.62434e-07	0.474	0.00409336	0.147834	2.29715e-07	5.52981e-08	2.63699e-14	1.66274e-06	0.0242182
0.4	0.13832	0.0567046	9.43753e-07	0.474	0.0026543	0.149777	1.89076e-07	2.63848e-08	3.64796e-14	2.40116e-06	0.0276779
0.45	0.138548	0.0688279	1.21329e-06	0.474	0.00171357	0.151048	1.25088e-07	1.68451e-08	4.87743e-14	3.38616e-06	0.0311377
0.5	0.138697	0.081147	1.44298e-06	0.474	0.00110237	0.151873	8.42645e-08	5.77061e-09	5.59894e-14	4.2083e-06	0.0345974
0.55	0.138792	0.0935952	2.18386e-06	0.474	0.000709497	0.152401	5.37926e-08	0	7.70155e-14	6.60907e-06	0.0380572
0.6	0.138852	0.106126	4.82245e-06	0.474	0.000458572	0.152734	2.16156e-08	0	1.56357e-13	1.48875e-05	0.0415169
0.65	0.138888	0.118704	1.19923e-05	0.474	0.000297529	0.152933	0	0	5.89618e-13	3.71072e-05	0.0449766
0.7	0.138907	0.131312	2.42147e-05	0.474	0.000193136	0.153044	6.42119e-09	3.43078e-11	2.64477e-12	7.37276e-05	0.0484364
0.75	0.138911	0.143923	5.2358e-05	0.474	0.000126201	0.153064	2.94893e-09	7.31557e-12	1.22001e-11	0.000159433	0.0518961
0.8	0.138921	0.156578	5.41241e-05	0.474	8.25515e-05	0.153119	2.71979e-09	3.60292e-12	1.29005e-11	0.000164811	0.0553559
0.85	0.138927	0.169241	5.61211e-05	0.474	5.4203e-05	0.153152	2.66494e-09	2.03579e-12	1.37539e-11	0.000170892	0.0588156
0.9	0.138931	0.181912	5.67859e-05	0.474	3.57756e-05	0.153175	2.62835e-09	7.80028e-12	1.4473e-11	0.000172916	0.0622754
0.95	0.138934	0.194587	5.74293e-05	0.474	2.38573e-05	0.15319	2.60035e-09	4.21414e-12	1.47443e-11	0.000174876	0.0657351
1	0.138935	0.207264	5.81279e-05	0.474	1.57256e-05	0.153199	2.56327e-09	5.60435e-12	1.5244e-11	0.000177003	0.0691948

Figure 4.5 Profile results

During the experiment, it was found that the carbonation reaction in the reactor proceeds with changes in CO_2 concentration in outlet gas until reaches equilliblrium state on the level of inlet gas. Thus, the comparison was based on CO_2. The experimental data and simulation were compared on (Figure 4.6) which, whereas the composition of the simulation gas was calculated on the basis of the profile data obtained in the program (Figure 4.5).

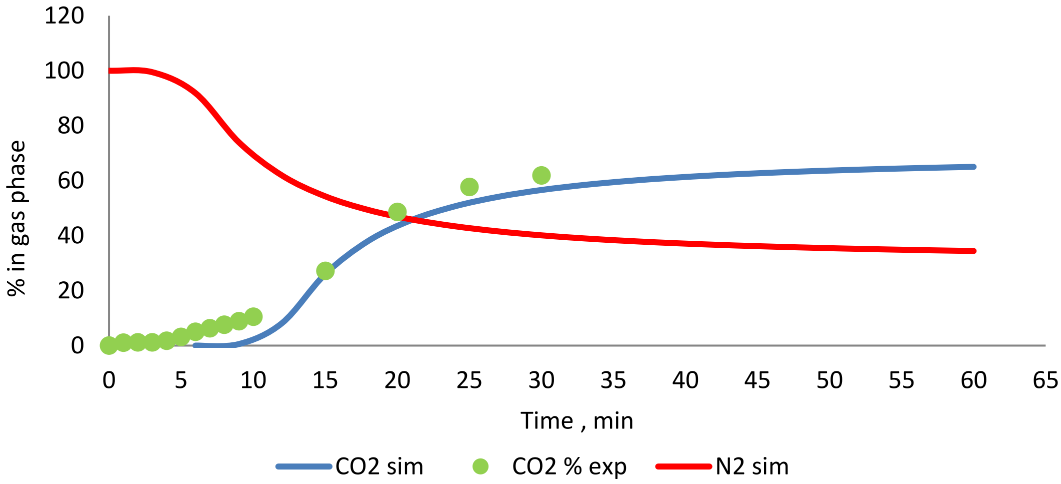


Figure 4.6 Changes in gas composition: simulation vs experimental data. BEJ ESPA Water/Ash ratio 120/600 , Gas content 70% , Gas flow 200 l/h and roration speed 300 rpm

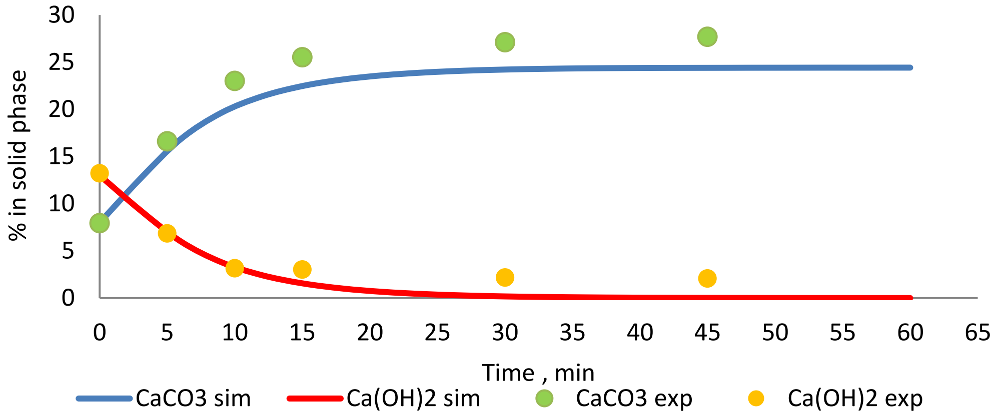


Figure 4.7 Changes in solid phase composition: simulation vs experimental data BEJ ESPA Water/Ash ratio 120/600, Gas content 70% , Gas flow 200 l/h and roration speed 300 rpm

Accuracy of the process simulation was also confirmed by the solid composition such as calcium carbonate and calcium hydroxide. The simulation curve follow the experimental data as seen in figure 4.7.

The results of simulation show that in gas phase the concentration of CO_2 is almost identical with the experimental data. The same picture can be seen in Figure 4.7, simulation results coinside with the experimental cdata of solid phase composition. The model was tested with different ashes indicating that it works best with fine oil shale electrostatic precipitator ashes and BPD that contain lots of free lime. Accordingly, this model can work as prediction for future process upscale. The reactor temperature, ion composition and pH of the reaction mixture can also be derived from simulation results (Figure 4.5).

5. Process upscale and economical evaluation

5.1. Process upscale

During the project, many experiments were carried out resulting correspondingly a large number of samples. The sample data was analyzed and a plan for further actions was drawn up on this data. Also, often during the experiment itself, the features of the processes were identified, which were also considered in planning next steps.

Thus, in this work, knowledge was gradually gained which helped answering the questions asked at the very beginning of the study.

The list of recommendations for process upscale:

- **Selection of a suitable reactor.** In order to guarantee an excellent contact of phases and high CO_2 binding rates we recommend upscaling the CO_2 mineralization process by using commercially available Eirich intensive mixer of 100 – 500 L [40]. The CO_2 mineralization tests with oil shale ashes in a 46 L concrete mixer indicated that this type of apparatus can be used quite effectively for CO_2 mineralization. Therefore, a commercial concrete mixer (500-1000 L) or truck (5000 - 6000 L) equipped with gas inlets and outlets could be used as the CO_2 mineralization pilot.
- **Implementation of moisture and temperature sensors.** Modifications should also include moisture and temperature sensors as well as measures for avoiding the formation of precipitations and dead zones on the walls of the apparatus. At higher temperatures (65-80°C) moisture loss has to be compensated.
- **Implementation of gas analyzer.** The CO_2 gas analyzer should be implemented to measure CO_2 in out-let gas as the main indicator of carbonation efficiency.
- The formation of granules should be avoided by optimizing water to solid ratio in case of different types of wastes. For oil shale ashes 0.2 w/w was the most suitable.
- **Power consumption.** During the experiments, it was observed that the greater the mass of products, the correspondingly more power is needed for the drum and the agitator in the reactor. Also, on the number of revolutions per minute depends on the consumption of electricity. Since it was studied experimentally that the speed does not affect the reaction as a whole, the volumes used in the reactor according to the equipment should be taken into account.

- **Sampling**. Since in any process it is necessary to monitor the quality of the product, the possibility of taking samples is an integral part of the installation. So, we faced the fact that our apparatus did not allow collecting samples without interfering (stopping the reactor) in the process. It is imperative to make access to obtain samples so that it does not interfere with the main process.

5.2. Economical evaluation

As in any other project, one part is the study of the process (in our case, experiments with the material and the study of parameters), the second is the study of the economics of this process. So, it turns out that the two parts of the whole are done at different stages, but their overall assessment gives impetus to the further development of the project.

5.2.1. Opex

The variable operating costs include material utilities consumption such as electricity, natural gas, process water, chemicals, sorbent, etc. The costs of the main utilities and consumables are valuated based on the process energy and mass balance.

So from our side, the volumes of the suitable materials in close locations are most important, but if there is no such data, ohter suitable materials must be found from different contries. The amount of material needed can be determined from the experiments.

Also, process desine include selection of a reactor and suitable process conditions. If there is no such information in literature, our task is to find optimal conditions from lab experiments. Thus, the customer will decide whether the installation we used in the laboratory is suitable for him, and the final installation cost is calculated from this.

Based on the above, the assessment of our part of the work was give the overview about process in lab scale, and it is included in Total direct costs = Equipment cost and installation cost, and ingenering consultancy in Indirect cost (4.5% of Total direct costs). If we look forward Maintenance, insurance and labor costs or fixed opex must be considered to.

5.2.2. Evaluation of project external effects

This work involves several aspects that are part of the economic analysis of the project.

The social factor, when enterprise creates new jobs for the population and the development of infrastructure in the vicinity of the project.

The tax factor, any company pays taxes to the local budget for certain item separately. Taxes associated with the use and emissions of CO_2 and/or with the reuse of CO_2, and the effective use of utilities and consumables cost, give more proses for project.

The environmental factor is undoubted. The above has been described about taxes associated with emissions, but it is worth considering the use of fuel and electricity from green sources, the reuse of industrial waste and of course the utilization of carbon dioxide in the production process. Such decisions give the project a huge plus of approval from both society and the global industry of sustainable development.

Most decisions made by market entities are based on a preliminary assessment of the expected consequences. Individual assessment of the acceptability (efficiency, value) of each investment project is carried out using various methods and considering certain criteria according to the region in which this assessment is carried out.

6. Conclusions

Every year a huge amount of carbone dioxide is emitted into the atmosphere. Most of it originatesfrom anthropogenic sources such as the burning of fossil fuels for heat and power production, as well as in the cement industry. To maintain the sustainable development of our planet, it is necessary to look for any options for reducing emissions of CO_2 into the atmosphere.

It the frames of Cleanker project a mineralization pilot of at least 100 L is planned that uses CO_2 captured from the Ca-looping demo system in Vernasca Cement Plant for carbonating selected types of waste materials, the re-carbonated wastes could in turn be used in concrete casting to produce commercial products. This study focused on laboratory tests and modelling to prove the concept and to find most suitable materials for CO_2 mineralization.

Different types of waste samples from all over the world such as oil shale ashes (BEJ ESPA, BEJ TOTAL, EEJ Total, AUVERE Espa, DeSOx), concrete demolition wastes (CDW1, CDW2, CDW3, CDW4), cement by-pass dust (BPD), blast furnace slag (NSF) were tested in a 1 L Eirich EL1-type intensive mixer as well as in a modified 42 L concrete mixer via wet direct carbonation method in the conditions of 0.2 – 0.3 w/w liquid to solid ratio and CO_2-rich gas flow (20 - 100% CO_2 in air).

The most important indicators for carbonation progress are the contents of $CaCO_3$ and residual $Ca(OH)_2$ and CO_2 concentration in gas phase. The changes of those parameters were followed during experiments and simulation.

The results show:

CO_2 uptake was mainly attributed by the free lime content, which is relatively high (10 - 37%) in oli shale ash and cement by-pass dust samples, but nonexistent in concrete demolition wastes and blast furnace slag. Therefore, selected types of oil shale ashes (BEJ ESPA, BEJ TOTAL, EEJ Total, AUVERE Espa) and BPD could be used as effective sorbents in the proposed CO_2-mineralization process, but CDW and NSF slag were not suitable.

the free lime content could be exhausted with 30 min in the conditions of low range liquid to solid ratio of 0.2 w/w and gas flow of 70% CO_2 in air.

comparing different types of oil shale ash samples indicated that free lime content was almost fully utilized in case of fine electrostatic precipitator ashes (Espa) from CFB boilers, as the free lime in less porous pulverized firing ash (DeSOx) was only partially utilized.

Changing different parameters in EL1-type intensive mixer indicated that increasing material amount per reactor volume and gas flow rates accelerated the CO_2 mineralization process due to improved contact of phases.

Changing different parameters in EL1-type intensive mixer indicated that increasing the mixing speed from 300 rpm to 3000 rpm and CO_2 concentration in gas from 20% to 70% did not affect the process remarkably.

the optimum water solid ratio for oil shale ashes is 0.2w/w.

the CO_2 mineralization of oil shale ashes in a 46 L concrete mixer indicated that this type of apparatus can be used quite effectively for CO_2 mineralization up scale by the means of commercial concrete trucks.

A kinetic model was built to predict the composition of solid and gas phase at given operating conditions. The model followed the experimental results for $Ca(OH)_2$ and $CaCO_3$ contents as well as CO_2 concentration in gas phase contents during carbonation. This model applies well for fine oil shale electrostatic precipitator ashes and cement by-pass dust that contain easily accessible free lime. The model can also be used to predict reactor temperature, ion composition and pH of the reaction mixture.

In conclusion, it can be said that the work was successful and quite voluminous. The work included both experimental work and process modelling, which made it particularly interesting. Cleanker project is an excellent example of the interaction of different countries, institutions and people searching for innovative methods for utilizing CO2 as a step towards more sustainable cement industry.

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