ACCELERATED CARBONATION OF WASTES AND MINERALS

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DECLARATION

I certify that this work has not been accepted in substance for any degree, and is not concurrently being submitted for any degree other than that of Doctor of Philosophy, being studied at the University of Greenwich. I also declare that this work is the result of my own investigations, except where otherwise identified by references, and that I have not plagiarised another's work.

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ABSRACT

Accelerated carbonation technology (ACT) could be used for the stabilisation of hazardous wastes, remediation of contaminated soils and re-use/recycling of various waste streams. ACT has also potential for storing anthropogenic CO_2 emissions into mineral silicates and alkaline waste residues via mineral or waste carbonation. Compared to ocean and geological storage, mineral and waste carbonation offer several advantages such as long-term storage and low monitoring requirements.

Currently, the biggest challenge of mineral carbonation is the low conversion rate of calcium and magnesium-based minerals into thermodynamically stable carbonates under ambient temperature and pressure. Also, literature offers little information about physical techniques or chemical substances that could enhance the efficacy of accelerated carbonation of alkaline wastes.

In this study, various carbonation techniques were applied for increasing the carbonation reactivity of magnesium hydroxide. The experiments were conducted under low temperature and pressure, while the maximum reaction time was 24 hours. Under these conditions the associated costs are kept to a minimum. The possibility of producing monolithic products with value-added was investigated by using blended mixtures of magnesium and calcium hydroxide. These mixtures were cured in carbon dioxide for 7 and 28 days and their physical properties were measured and compared with the properties for normal and lightweight concrete.

Moreover, several alkaline residues were carbonated with the aid of ultrasound and four candidate catalysts (acetic acid, ethanol, sodium hypochlorite and sodium nitrite) and their CO_2 uptake was measured. During sonication the variables: ultrasonic frequency, water content and treatment time were examined, while the applied chemicals were added at three different molarities (0.1 M, 0.5M and 2.5M).

Throughout this work a number of analytical techniques were used for the characterisation of the raw and carbonated materials. These techniques included X-Ray fluorescence, X-ray diffraction, wet laser analysis, total organic carbon analysis and scanning electron microscopy.

The results showed that the CO_2-reactivity of $Mg(OH)_2$ was low due to thermodynamic constraints that inhibited the rapid diffusion of CO_2 into the system. The mixtures composed of pure Mg showed improved compressive strength and bulk density. In addition, sonication at low water content was weak, as there was lack of enough water to facilitate cavitation. On the other hand, at high water content the achieved CO_2 uptake of the products increased by up to four times, as the wet conditions enhanced the cavitation of the solid particles. Finally, it was found that ethanol and acetic acid promoted the hydration rate of CO_2 during accelerated carbonation, while minerals phase analysis did not reveal the formation of toxic by-products.

In conclusion, the findings of this study proved that sonication depends highly on water content and is favoured at wet conditions. Furthermore, acetic acid and ethanol are two chemicals with potential to ameliorate the accelerated carbonation of various industrial wastes without the formation of un-desired or toxic compounds.

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ABBREVIATIONS

ACT	Accelerated Carbonation Technology
APCr	Air Pollution Control Residues
BR	Bauxite Residues
C_3A	Tricalcium Aluminate
CBD	Cement Bypass Dust
CCS	Carbon Capture and Storage
CEM1	Ordinary Portland Cement Type 1
CFA	Coal Fly Ash
CKD	Cement Kiln Dust
C-S-H	Calcium Silicate Hydrate
D	Bulk Density (in kg/m^3)
EU	European Union
F:	Fracture Load (in N)
f_c:	Compressive strength (in MPa)
IPCC	Intergovernmental Panel on Climate Change
LOI	Loss on Ignition
MCT	Mineral Carbonation Technology
MPa	Megapascals
MSWI-BA	Municipal Solid Waste Incineration Bottom Ash
MSWI-FA	Municipal Solid Waste Incineration Fly Ash
p	Pressure (in MPa)
PSD	Particle Size Distribution
SEM	Scanning Electron Microscopy
SS	Steel-making Slag
TOC	Total Organic Carbon
WCT	Waste Carbonation Technology
W/S	Water/Solid Ratio
XRF	X-Ray Fluorescence
XRD	X-Ray Diffraction
WA_{24}	Water absorption after immersion for 24 hours (% of the dry mass)

1 INTRODUCTION

1.1 Background

The adverse impact of human activity on global climate is now beyond doubt (Parmesan et al., 2013). In addition to the increase of CO_2 concentration in the atmosphere, the reliance on the disposal of high volumes of hazardous wastes to landfill also presents serious implications for human health and the environment (Nabhani et al., 2013).

Strategies to control anthropogenic CO_2 emissions involve meeting national-term targets, improvement in energy efficiency, alternative fuels, 'greener' industrial processes and the adoption of targeted tax schemes and integrated environmental policies, such as IPPC (IPCC, 2005, IPCC, 2011, IPCC, 2013).

By way of example of tax-based initiatives, the local government of Alberta, Canada, introduced a carbon offset tax where large emitters are charged CAD15 (USD13) per tonne of CO_2 with proposals to increase this tax to CAD40 (USD35), in order to generate more revenue (Gunning et al., 2014).

The progress towards a "green" society is slow, mainly due to government inertia and the investment required for energy efficiency, coupled with the slow integration of renewables into the energy supply mix. In addition, the disaster in Fukushima in 2011 has raised serious concerns over the future of nuclear energy for electricity generation (Stohl et al., 2012).

Recently, the method of Carbon Capture and Storage (CCS) has considered beneficial for tackling the CO_2 release into the atmosphere from large emitting points such as coal and power stations, and industrial plants. The routes to CCS involve the capture, transportation and subsequent storage of CO_2 in appropriate geological and ocean sites, or the storage as carbonates/bicarbonates via mineral carbonation technology (MCT) (Sanna et al., 2013). The biggest "issue" of mineral carbonation is the low conversion rate of minerals into stable carbonates under ambient temperature and pressure or at rapid reaction time due to thermodynamic constraints, and thus, the associated costs of this method are high.

However, it is not widely recognised that high volume alkaline waste streams can sequester CO_2, via a process known as waste carbonation technology (WCT). The similarity of wastes to natural silicates is often overlooked and if waste carbonation can be widely achieved, then there is potential to manage significant amounts of CO_2 by this method (Renforth et al., 2011).

Except for immediate measures for CO_2 mitigation/utilisation, the necessity of handling the disposal of wastes is also becoming urgent, since higher landfill taxes and stricter regulations imposed by national governments. In the EU, the disposal of wastes is regulated by the European Commission, through the directive 2000/532/EC. This lists the hazardous wastes affecting humans' health and the environment. Landfill taxes have been introduced by the majority of European Governments and range from €17 (USD21) to €130 (USD160) per tonne, depending on the type of waste and national legislation (CEWEP, 2011). In China and the US similar measures are expected in the near future.

An effective technique for combining carbon emissions with minerals or waste residues is accelerated carbonation technology (ACT), which in the past has been successfully applied for contaminated land remediation, stabilisation of hazardous wastes and re-use/recycling of industrial waste-streams (Fernández Bertos et al., 2004). Although the topic of accelerated carbonation is well studied, literature offers little knowledge about physical and chemical accelerators that could potentially enhance the reaction and increase the final yield.

The primary aim of this study was the development of more effective carbonation systems, systems with increased yield, under moderate temperature and pressure and quicker reaction time. Under these conditions the associated costs are kept to a minimum and thus, the processing of large amounts of minerals or wastes is cost-effective. For this purpose, various carbonation techniques and candidate catalysts were applied, following selection based on the literature. Another aim was to explore the possibility of producing monolithic products with added-value from magnesium-based materials. The physical properties of the newly formed products were measured and compared with the properties for normal and lightweight concrete.

1.2 Aims

The overall hypothesis of this study was the enhancement of accelerated carbonation of wastes and minerals by using physical and chemical techniques. In this section, a description of the key aims of this study is presented:

- Economic assessment of mineral and waste carbonation.
- Estimation of carbon sequestration potential of seven “common” alkaline residues.
- Increase the conversion rate of $Mg(OH)_2$ into $MgCO_3$ by testing various carbonation techniques at moderate reaction conditions.
- Possibility of producing monolithic products with value-added from magnesium-rich materials.
- Estimation of physical properties of the newly-formed monolithic products and comparison with the properties for normal and lightweight concrete.
- Accelerated carbonation of “reactive” waste residues under ambient temperature and pressure. Comparison between experimental and theoretical CO_2 uptakes.
- Enhancement of accelerated carbonation by using ultrasound.
- Effect of ultrasound on mineral composition, morphology and particles size
- Effect of sonication time on the CO_2 uptake.
- Enhancement of accelerated carbonation by using chemical accelerators.
- Identification of toxic by-products after chemical acceleration.

1.3 Structure of thesis

The structure of this thesis was divided into 8 chapters describing the methods, input materials, experimental results, and discussion of the main findings formed as a summary of conclusions.

In Chapter 2, key previous studies on accelerated carbonation were critically reviewed. The work was mainly focused on the carbonation background and mechanism, variables affecting CO_2 diffusivity and reactivity, and microstructural changes after treatment. Also, the techniques of mineral and waste carbonation were evaluated by comparing their potential with other sequestration methods (geological and ocean storage) in terms of costs and processing routes. In addition, the annual production and maximum sequestration capacity of seven alkaline wastes was estimated. Finally, an appraisal of companies specialising in CO_2 utilisation and production of carbonated/valorised products with added-value was made via an analysis of their process routes.

The materials, analytical methods and a summary of carbonation methods used in this study are presented in chapter 3.

Experiments on mineral carbonation were conducted in chapter 4. Pure $Mg(OH)_2$ was carbonated via ambient, ultrasonic, pressurised and water vapour carbonation and the CO_2 uptakes were measured and compared with those of $Ca(OH)_2$. Also, a product development study was made in order to explore the possibility of producing monolithic products with added-value from magnesium based materials.

In chapter 5 seven alkaline wastes and wollastonite were carbonated under ambient temperature and pressure and at various water concentrations. The experimental CO_2 uptakes were compared with the theoretical uptakes derived from the Steinour formula. The elemental and mineral composition of the input and materials was analysed by X-ray fluorescence and X-ray diffraction respectively.

The effect of sonication on CO_2 uptake is described in chapter 6. The most reactive materials found in chapter 4 were carbonated again but in the presence of an ultrasonic field (35 KHz) for 1 hour. Further sonication experiments lasting up to 8 hours were conducted to assess the effect of sonication time on the recorded yield. The difference in mineralogy amongst the un-treated, non-sonicated and sonicated samples was studied by qualitative/semi-quantitative X-ray diffraction and the morphology of the sonicated samples was analysed by scanning electron microscopy. Finally, the change in particles size during sonication was estimated by wet laser analysis.

In chapter 7 the effect of four chemical accelerators on CO_2 uptake was studied. For the same reactive wastes identified in chapter 5, carbonation with acetic acid, ethanol, sodium hypochlorite and sodium nitrite was conducted. The samples that showed that highest CO_2 uptake were analysed by X-ray diffraction in an attempt to identify any toxic by-products.

In the final chapter (chapter 8) a discussion of the results, the main conclusions and suggestions for future work are presented.

Included in the appendices are the published papers produced by this research.

2 LITERATURE REVIEW

2.1 Introduction

This chapter examines the relevant literature surrounding the background of accelerated carbonation, the reaction mechanism, important variables affecting the CO_2 diffusivity and reactivity and microstructural changes observed for the carbonated products.

Also, the basic principal and effects of ultrasound during the sonication of calcium-rich materials are presented by summarising relevant works and identifying important parameters such as ultrasonic power, amplitude and sonication time.

Previous studies suggested that the rate and extent of accelerated carbonation could be increased by enhancing the hydration rate of CO_2. The latter can be achieved by applying organic or in-organic chemical substances that catalyse the reaction. In this chapter, a number of relatively cheap and non-toxic "candidate" catalysts are proposed.

In addition, an economic assessment of mineral and waste carbonation was done by reviewing appropriate metrics (sequestration capacities, costs etc.), and the sequestration potential of seven "common" alkaline residues was estimated. Finally, an appraisal of commercially active or close to commercialisation companies, specialising in CO_2 utilisation and formation of valorised/carbonated products was done by comparing their processing routes and technology.

2.2 Accelerated Carbonation Technology

2.2.1 Carbonation Background

Natural carbonation is known to have detrimental effects on cementitious systems and occurs when atmospheric carbon dioxide reacts with alkaline ions found on the systems surface (Van Ginneken et al., 2004). Due to the low partial pressure of atmospheric CO_2 (0.03%), the gas diffusion is slow and for that reason the process typically lasts from months to years (Bukowski and Berger, 1979).

Concrete is the most common building material composed primarily of aggregate, ordinary Portland cement and water. It is extremely strong in compression pressure but relatively weak in tension. Thus, the construction industry replaced concrete with reinforced concrete, which contains steel bars and various fibres in its mixture (Katzer and Domski, 2012). In reinforced concrete the containing cement forms a protective alkaline layer (at pH at least 10.5), mainly portlandite, protecting the steel from corrosion. Natural carbonation causes durability issues, since atmospheric carbon reacts with reinforced concrete and destroys this layer by lowering the pH value. (Roy et al., 1999).

Despite the negative effects of carbonation on concrete structures, the same method could have beneficial effects regarding the utilisation of wastes or minerals comprising calcium, magnesium and ferrite ions. The reaction can be accelerated by increasing the partial pressure of CO_2, and it is completed within hours or even minutes (Johnson et al., 2003).

This accelerated version of carbonation is known as accelerated carbonation technology (ACT) and it offers economically attractive solutions for the stabilisation of hazardous wastes, remediation of contaminated soils, and re- use /recycling of various waste streams (Tarabadkar and Melton, 2006, Liu et al., 2006, Barnard et al., 2005). Informative studies have also been done in heavy metals leaching reduction techniques, focusing on the reduction and removal of heavy metal traces prior to landfilling and according to environmental regulations (Van Gerven et al., 2005, Sicong et al., 2011, Gunning, 2010, Garrabrants et al., 2006, Etoh et al., 2006).

2.2.2 Carbonation Mechanism

The reaction mechanism of accelerated carbonation involves three main steps: the hydration of carbon dioxide, the ionisation of carbonic acid and the precipitation of calcium carbonate (Li et al., 2007). The relevant reactions are shown in equations (2.1)-(2.3).

$$H_2O + CO_2 \rightarrow H_2CO_3 \tag{2.1}$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-} \tag{2.2}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \tag{2.3}$$

In a previous study (Maries, 2008) the reaction mechanism was considered as a cyclic process with 9 subsequent steps through all the physical states (gas, aqueous, solid). A description of these steps and their physical state are shown in Table 2.1.

The overall carbonation rate depends on the solvation and hydration of CO_2, the two slowest steps of the process. If any of the nine steps is blocked then the whole reaction stops and no gas diffusion is taken place. During secondary carbonation some calcium silicate hydrates (C-S-H) are decalcified slowly to calcium carbonate. Secondary carbonation is as important as the primary, since the reaction of calcium silicate hydrate increases the concentration of $CaCO_3$.

Table 2.1: Detailed description of accelerated carbonation mechanism (Maries, 2008)

Step	Name	State	Description
1	Diffusion of CO_2	gas	Amount of carbon dioxide is diffused into the air.
2	Permeation of CO_2	gas	Carbon dioxide passes through the cementitious surface.
3	Solvation of CO_2	gas/aqueous	Solvation of CO_2 in the aqueous pores of the system. High internal surface area favours the reaction.
4	Hydration of CO_2	aqueous	Carbon dioxide reacts slowly with water and forms carbonic acid.
5	Ionisation of carbonic acid	aqueous	The formed carbonic acid ionised instantaneously into H+, HCO_3^-, $CO_3^=$.
6	Dissolution of C-S-H phases	aqueous	All the calcium silicates phases dissolve rapidly and extensively.
7	Nucleation of $CaCO_3$	aqueous /solid	Formation of calcium carbonate
8	Precipitation of $CaCO_3$	solid	Initially, all the three polymorphs of calcium carbonate are present, until due to the T and humidity only calcite is formed.
9	Secondary carbonation	solid/gas	Some calcium silicates may be produced during step 4 and decalcified later than primary carbonation.

2.2.3 Carbonation Variables

The efficiency of accelerated carbonation depends on the CO_2 diffusivity and reactivity. Both are determined by variables that eventually indicate the final yield. The latter is quantified by the amount of CO_2 that is bound into the carbonated products, also known as CO_2 uptake. The theoretical maximum CO_2 uptake can be estimated by the Steinour formula (Fernández Bertos et al., 2004), which is a function of calcium oxide, sulphur trioxide, sodium oxide and potassium oxide.

$$CO_2\% = 0.785\left(CaO - 0.7SO_3\right) + 1.09Na_2O + 0.93K_2O \tag{2.4}$$

On the other hand, the experimental or actual CO_2 % uptake is a function of the initial and final CO_2% and can be measured by calcimetric or thermo-gravimetric analyses according to equation 2.5 (Baciocchi et al., 2009a).

$$CO_{2UPTAKE}\% = \frac{CO_{2FINAL}\% - CO_{2INITIAL}\%}{100 - CO_{2FINAL}\%} * 100 \qquad (2.5)$$

In Figure 2.1 all the variables influencing CO_2 reactivity and diffusivity are presented, while Table 2.2 summarises their optimum values found in previous studies focusing on the carbonation of concrete and ordinary Portland cement.

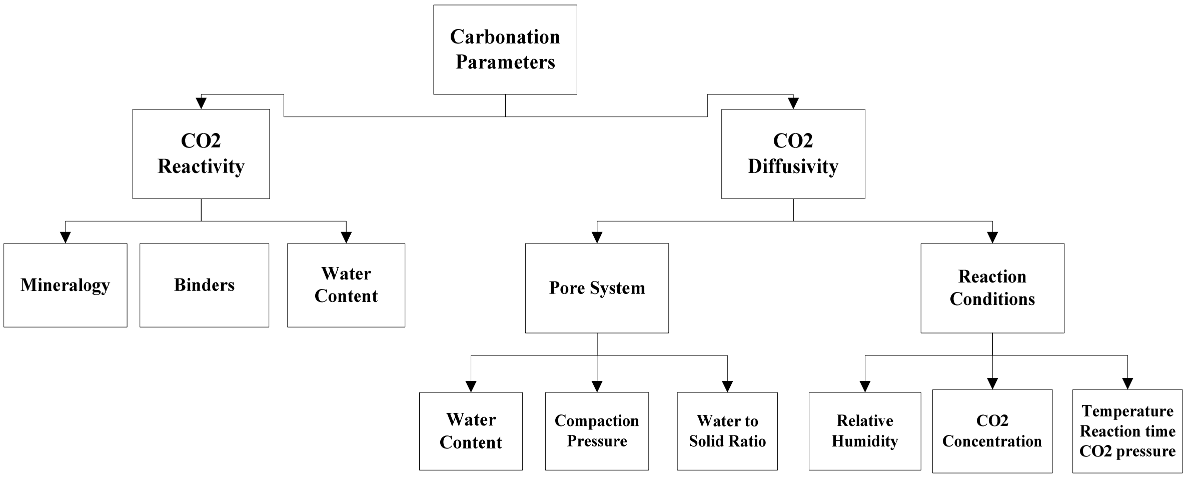


Figure 2.1: Categories of carbonation variables

Mineralogy

The presence of calcium and aluminium is crucial in order to achieve effective carbonation (Balayssac et al., 1995), while high concentration of calcium oxide promotes the reactivity and diffusivity of CO_2 (Johnson, 2000). Also, the precipitation of calcium carbonate is favoured by the presence of Cu, Ni, Pb, Zn, Cd, Fe and tricalcium aluminate (C_3A) (Lange et al., 1996a). On the other hand, the existence of specific organics and anions may retard the reaction as they inhibit the diffusion of CO_2 into the system (Lange et al., 1996b). Finally, calcium to silicon ratio is another important factor of the reaction and the optimum value was estimated between 1.33 and 1.50 (Black et al., 2008).

Binders

Binders are optionally used in materials to increase their calcium content. Portland cement is a common binder due to its relatively low cost and high calcium concentration. For cost-effectiveness binders should not exceed 20% of the total mixture (Barnard et al., 2006).

Water Content

CO_2 penetrates the system when there is enough water on the pores surface to promote the gas diffusion. Completely dry pores prevent CO_2 from entering the system (Criado et al., 2005), whereas excess water blocks the pores and hinders the reaction (Soroushian et al., 2004).

Water-to-solid ratio

Water to solid ratio (w/s ratio) expresses the weight of solid compared to liquid (usually water) in a particular mixture. It is known that accelerated carbonation is favoured at dry conditions and the optimum w/s ratio ranges between 0.1 and 0.3 (Fernández Bertos et al., 2004). At higher w/s ratios the CO_2 penetration is restricted by the low permeability of the mixture and often unstable products are formed (Johnson, 2000, Barnard et al., 2005, Liu et al., 2001).

CO_2 partial pressure

The concentration of carbon dioxide (CO_2%) is an important variable affecting the final CO_2 uptake. During the reaction, the concentration of CO_2 may take values from 0.03% (atmospheric) up to 100% (Jerga, 2004, Cultrone et al., 2005, El-Turki et al., 2007) and thus, the value 50% can be chosen as the lower benchmark. However, a previous study on treatment of incineration bottom ashes showed that effective carbonation of these ashes can be achieved at 10% and 20% (Van Gerven et al., 2005).

CO_2 pressure

Increased carbon dioxide pressure results in better CO_2 diffusivity and thus more successful carbonation (Anthony et al., 2000). A previous literature finding suggested that under slightly elevated pressure (0.2 MPa) the reaction yield increased considerably (Barnard et al., 2005). When supercritical carbon dioxide is used (between 5 MPa and 20 MPa), the achieved CO_2 uptake increases significantly, while the precipitation of calcium carbonate is improved (Domingo et al., 2006, Hidalgo et al., 2006). However, carbonation under supercritical pressure requires special equipment and thus, the associated costs are higher.

Table 2.2: Variables and optimum values of accelerated carbonation

Variables	Category	Optimum	Description
Mineralogy	Mineralogy	1.33-1.50	Apart from Ca/Si ratio, the overall mineralogy of the waste form affects the carbonation rate. The presence of heavy metals and aluminate substances enhances the rate of $CaCO_3$ precipitation. On the other hand, the reaction is inhibited by organics and anions (Lange et al., 1996b, Lange et al., 1996a, Johnson, 2000, Black et al., 2008).
Binders	Binders	up to 20%	Binders are mixed with wastes that do not contain high amounts of calcium, in order to accelerate the reaction and increase the total CO_2 uptake (Barnard et al., 2006).
Water content	Pore system	n/a	CO_2 penetrates the system when there is enough water on its surface. Excess water results in slower gas diffusion (Soroushian et al., 2004, Criado et al., 2005).
Water-to-solid ratio	Pore System	0.1-0.3	For every carbonated waste system a different ratio is optimum. Previous studies indicate that the optimum w/s ratio ranges between 0.1 and 0.3 (Johnson, 2000, Liu et al., 2001, Fernández Bertos et al., 2004, Barnard et al., 2005).
Relative humidity	Reaction conditions	50-70%	RH% can be considered as a measure of water content. Typically, relative humidity should not exceed 80% because the pores are blocked and CO_2 diffusion decreases (Criado et al., 2005, Hills et al., 1999, Russell et al., 2001, Sanjuán and del Olmo, 2001).
CO_2 concentration	Reaction conditions	>50%	Better gas diffusivity is achieved by higher CO_2 concentration (Cultrone et al., 2005, El-Turki et al., 2007, Jerga, 2004, Van Gerven et al., 2005).
Temperature	Reaction conditions	up to 333 K	The reaction rate increases with temperature increase. The upper temperature limit is 333 K, where physical limitations decrease the penetration ability of CO_2 (Liu et al., 2001, Maries, 2008).
Reaction time	Reaction conditions	24 hours	Normally, accelerated carbonation is completed within a couple of hours. After 24 hours the reaction can be considered complete (Marina Sanchez and Miranta Martinez, 2010).
CO_2 partial pressure	Reaction conditions	0.2 MPa	Partial pressure is an important variable during carbonation. The CO_2 uptake is proportional to pressure however, higher pressure results in higher costs (Anthony et al., 2000, Barnard et al., 2005, Domingo et al., 2006, Hidalgo et al., 2006).

Temperature

Accelerated carbonation is an exothermic process and during the initial stages of the reaction there is an instant temperature rise of approximately 293 K (Maries, 2008). The reaction rate increases with temperature up to 333 K, where the rate decreases due to physical limitations of CO_2 diffusion and CO_2 solubility in water at elevated temperatures (Liu et al., 2001).

Relative Humidity

Relative humidity (RH %) is determined by the water content and it usually varies between 50% and 70% (Hills et al., 1999, Russell et al., 2001, Sanjuán and del Olmo, 2001). At RH over 80% the pores are blocked and CO_2 permeability decreases. At RH% less than 25%, CO_2 cannot react with the system, as there is not enough water to promote the reaction (Criado et al., 2005).

Reaction Time

Under ideal conditions accelerated carbonation proceeds rapidly and the treated materials can be fully carbonated within hours or even minutes. Thus, it can be assumed that after 24 hours of treatment almost all the reactants are fully carbonated (Marina Sanchez and Miranta Martinez, 2010).

2.2.4 Microstructural Changes

Accelerated carbonation alters the microstructure of the carbonated materials by changing their physical and chemical characteristics. The majority of scientific works that refer to these changes were based on carbonation of concrete in building structures. Table 2.3 summarises all the known effects, their type and their trend of change, while Figure 2.2 depicts the carbonation zones according to their local pH value.

Physical

A common physical effect is the decrease of macro-porosity due to the formation of $CaCO_3$ molecules, which fill the pores of the system and reduces its overall free space (Ngala and Page, 1997, Hyvert et al., 2010, Bouchaala et al., 2011, Tong et al., 2012). The reduction of macro-porosity results in permeability reduction up to five orders of magnitude (Sanjuán and del Olmo, 2001, Borges et al., 2010), and the final product shows improved weight, strength and bulk density, the extent of which depends on its physical characteristics.

Microstructure

In contrast to macro-porosity that is reduced after the reaction, the micro-porosity of the system increases as the calcification of the feedstock promotes the formation of additional nano-pores (Anstice et al., 2005, Castellote and Andrade, 2008, Dias, 2000, Lawrence et al., 2007, Rostami et al., 2012). The amount of additional nano-pores depends on the variables of the reaction and the physical properties of the reactant. Another microstructural change is the modification of the pores size, which can be observed clearly by scanning electron microscopy and other analytical techniques.

Chemical

A notable chemical effect of carbonation is the pH reduction up to 4 values (Dinakar et al., 2007, Khaitan et al., 2010, McPolin et al., 2007). According to shrinking core model of wet particle carbonation, carbon dioxide penetrates the materials surface and tends to create a carbonated thick layer around the unreacted core, altering the local pH. The reaction can be described by three distinguishable zones found in the carbonated structure (Figure 2.2): fully carbonated with $pH < 9$, partly carbonated zone: with $9>pH>11.5$ and un-carbonated zone where the $pH > 11.5$ (Chang and Chen, 2006).

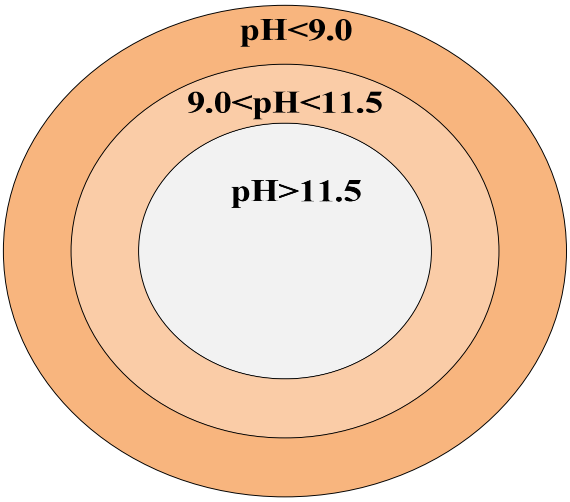


Figure 2.2: Carbonation zones according to local pH value

Table 2.3: Effects of carbonation upon cementitious systems

Effect	Type	Trend
Bulk density	Physical	Increase depends on the desired product
Macro-porosity	Physical	Decrease up to 15%
Micro-porosity	Micro-structural	Increase
Permeability	Physical	Decrease up to 5 orders of magnitude
Pore size distribution	Micro-structural	Modified
pH	Chemical	Decrease up to 4 units
Strength	Physical	Increase depends on the desired product
Weight	Physical	Increase depends on the desired product

2.3 Chemical and Physical Accelerators

The rate and extent of accelerated carbonation can be increased by enhancing the hydration rate of carbon dioxide or the precipitation rate of calcium carbonate. The former can be achieved by chemical compounds and the latter by physical means such as ultrasound.

2.3.1 Chemical Accelerators

The hydration of carbon dioxide proceeds in two stages, following the reactions below:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3^- \Leftrightarrow H^+ + HCO_3^- \tag{2.6}$$

$$CO_2 + OH^- \Leftrightarrow H_2CO_3^- \tag{2.7}$$

Below pH 8 the effect of the second reaction is negligible compared to the first one. Between pH 9 and 10 the effect of both reactions is equivalent, while at pH above 10 the overall rate of hydration is controlled by the second reaction (Roughton and Booth, 1938).

At large scale, candidate catalysts for the acceleration of CO_2 hydration should have high capacity of CO_2 uptake, regeneration capability and high absorption rate (Sharma and Danckwerts, 1963). Effective chemical accelerators can be divided into two main categories. The first category includes oxyanions in the metal state, which contain oxygen atoms without proton removal, while the second involves oxyanions in non-metal state containing at least a lone pair of electrons (Dennard and Williams, 1966).

Previous workers studied the effect of various inorganic compounds and found that in an alkaline environment (pH>8) hypobromous acid, chlorine, hypochlorous acid, sulphite and selenite increased the rate of carbon dioxide hydration. However, the majority of those catalysts raise environmental concerns due to their toxicity, and their high cost prevents potential application in large scale (Kiese and Hastings, 1940).

Sodium hypochlorite and sodium sulphite, two relatively cheap and nontoxic chemical substances, were found to increase the degree of hydration, the percentage of CO_2 uptake and eventually the rate of accelerated carbonation. The increase was favoured at relatively dry conditions (w/s=0.25) and sodium sulphite was proved more effective than sodium hypochlorite (Gunning, 2010).

In another study, several organic and in-organic chemical substances were tested as potential catalysts for the hydration of CO_2 during the carbonation of cement. The CO_2 uptake was continuously recorded as the experiments conducted inside a "eudiometer". The results suggested that the additives: nitrite, acetate, hypochlorite and ethanol increased the CO_2 uptake of cement and further research will prove whether these chemicals could catalyse the accelerated carbonation of wastes and minerals (Maries and Hills, 2013).

2.3.2 Ultrasonic Irradiation

Except for chemical accelerators, the reaction yield could be increased by applying physical techniques such as ultrasonic irradiation also known as sonication. The basic principal of sonication is cavitation.

Cavitation refers to the formation, development and collapse of small bubbles (cavitation bubbles) in liquids, resulting in high pressures and temperatures. Sonication decreases particle size and increases the dissolution ability of the sonicated solids especially for particles with high surface area (Lu et al., 2002). The process requires an aqueous medium, in order to allow energy to be transmitted properly between the device and the treated solid (Rao et al., 2007). Ultrasonic waves can be generated by ultrasonic baths or ultrasonic probes.

Ultrasound is known to affect the precipitation rate of $CaCO_3$ and the overall rate of carbonation. Under ideal ultrasonic conditions the formation of $CaCO_3$ increases (Nishida, 2004), while sonication at high values of amplitude (Watt/density) showed significant particles size reduction (Kojima et al., 2010).

Precipitated calcium carbonate (PCC) is a product with added-value as it is widely used in detergents, paint, plastics, pulp paper and textile industries (López-Periago et al., 2010). The three crystal polymorphs of $CaCO_3$ are calcite, aragonite and vaterite. At ambient conditions the most thermodynamically stable polymorph is calcite, which consists of rhombohedra crystals, while aragonite crystals are found in orthorhombic formation. Aragonite is favoured under elevated temperatures and pressures and is converted naturally to calcite after thousands of years. Vaterite is the least thermodynamically stable polymorph of $CaCO_3$, with hexagonal crystals, and is transformed instantaneously into either calcite or aragonite (Price et al., 2010).

A previous study suggested that the ultrasonic treatment of calcium-rich materials in magnesium chloride solutions resulted in the precipitation of aragonite close to absolute purity (99.6%) even under ambient temperature and pressure (Santos et al., 2012). Table 2.4 summarises key works on sonication of calcium-rich materials.

Table 2.4: Previous studies on sonication of calcium-rich materials

Materials	Frequency (kHz)	T (°C)	P (MPa)	Time (min)	Major Findings
Alumina and silica particles	20	20	0.1	0-60	The particle size of alumina and silica particles decreased, and particle surfaces were smoothed. The dissolution of particles was 7-20 times higher compared to non-sonicated solutions (Lu et al., 2002).
FBC ashes[a]	N/a	20-80	0.1	5-60	Ultrasound found to promote carbonation, to allow access to un-reacted calcium oxide and to reduce the particle size of the products (Rao et al., 2007).
$CaCl_2$, $NaHCO_3$	24	30	0.1	0-30	Ultrasonic treatment accelerated the precipitation of calcium carbonate. However, neither the morphology nor the sizes of calcium carbonate crystals were affected (Nishida, 2004).
$CaCl_2$, $(NH_4)_2CO_3$	20,40	-	0.1	5	Treatment decreased the size of vaterite crystals and narrowed the width of particle size distribution (Kojima et al., 2010).
$(Ca(OH)_2)$	42	40	13	10-60	Outstanding conversion of calcium hydroxide to calcite, increase of carbonation rate (up to 89%), and no important morphological changes (López-Periago et al., 2010).
Steelmaking slags	24	50	0.1	0-240	The CO_2 uptake of steel slags increased, the particle size decreased, and sonicated particles showed eroded morphology (Santos et al., 2010).
kaolinite	20	20	0.1	600-4500	Particle-size reduction can be controlled by sonication power, time of treatment, and w/s ratio. Ultrasound increased the structural disorder and surface area of the particles (Franco et al., 2004).
Aluminium oxide particle	24	10-50	0.1	0-10	Higher breakage of particles. Breakage rate was higher during the initial stages of sonication (Raman and Abbas, 2008).
$(Ca(OH)_2)$, CaO	42	40	13	20, 60	Ultrasound ameliorated the carbonation kinetics and increased the yield of calcium carbonate (López-Periago et al., 2011).
$CaCl_2$, $NaHCO_3$	20	10-30	0.1	19-76	Sonication enhanced the formation of calcite, and changes on the morphology of calcite were recorded (Price et al., 2010).
$(Ca(OH)_2)$, $MgCl_2 \cdot 6H_2O$	24	24-70	0.1	30-120	Ultrasound along with magnesium chloride ions found to enhance the formation of pure aragonite crystals at ambient conditions (Santos et al., 2012).
$CaCl_2 \cdot H_2O$, $NaHCO_3$	20	70	0.1	20-120	Remarkable effects on aragonite morphology (Zhou et al., 2004).
$CaCl_2$, Na_2CO_3	40	30	0.1	10	Sonication resulted in bigger crystals of calcite and vaterite, while their morphological variety was large: from rhombohedral to spherical and flower-like crystals (Stoica-Guzun et al., 2012).

There are also various studies referring to more effective carbonation in the presence of ultrasonic fields. Sonication found to ameliorate the dissolution rate of CO_2 in water

(López-Periago et al., 2010), and the CO_2 uptake of steel-making slags increased by 2.8% to 8.1% (Santos et al., 2010).

Important parameters of sonication are: time of treatment, weight of sample, power and temperature (Franco et al., 2004). Improved ultrasonic power is known to enhance the particles breakage by creating a better cavitation environment and longer sonication times result in higher levels of breakage at temperature range between 298 K and 310 K (Raman and Abbas, 2008).

2.4 Carbon Capture and Storage (CCS)

Carbon capture and storage is projected to utilise up to 60% of overall anthropogenic carbon emissions (Dooley et al., 2009). The process of CCS involves three steps (Praetorius and Schumacher, 2009):

1) The removal and capture of CO_2 from specific locations.

2) Transportation to proper storage sites.

3) CO_2 long term storage.

Large quantities of carbon are emitted by coal and gas plants, where three capture technologies are used: Post-combustion capture, Pre-combustion capture and Oxy-combustion capture (Gibbins and Chalmers, 2008). The transportation of carbon dioxide can be achieved onshore or offshore by pipelines, water carriers or a combination of these. After transportation the captured CO_2 can be stored in appropriate geological and ocean sites (Svensson et al., 2004). The overall cost of carbon capture and compression is USD20-95/tonne, while the costs for geological and ocean storage are USD5-10/tonne and USD5-30/tonne respectively (Adams and Caldeira, 2008).

In Europe, a large-scale demonstration of CCS centred upon the Drax coal-fired power station in the UK has been given the go-ahead. This 'White Rose' CCS project will see CO_2 transported in a pipeline for permanent storage in the North Sea in depleted oil wells

(About the White Rose CCS Project, 2014). Alternatively to geo- and ocean storage, mineral carbonation involves the production and disposal of environmentally benign minerals that are stable over geological timescales. Potential feedstock for MCT involves minerals comprising calcium and magnesium ions such as wollastonite, basalt, olivine and serpentine. The reaction is thermodynamically favourable and the final products are stable. The potential storage capacity exceeds 10,000 Gtonnes at an average cost of USD100-120/tonne CO_2 (Goldberg et al., 2001, Lackner, 2002, Lackner, 2003).

Table 2.5 overviews the available carbon capture and storage technologies, their advantages/disadvantages, estimated capacity and likely costs.

Table 2.5: Overview of CCS technologies

Technology	Advantages	Disadvantages	Capacity^a (Gtones)	Cost^b (USD)	Ref
Geological storage	1. Established technique 2. Low storage cost 3. Positive/indifferent public perception 4. More eco-friendly than ocean storage	1. High risk of CO_2 leakage from the aquifers 2. Requires continuous monitoring, increasing the long term cost 3. Many countries lack appropriate storage sites	1800	5	(Harvey et al., 2012, Shukla et al., 2010)
Ocean storage	1. High capacity 2. Global availability of oceans, seas, deep lakes 3. No monitoring requirements	1. High environmental risk 2. Higher cost than geo-storage 3. Negative/hostile public perception	10000	18	(Adams and Caldeira, 2008)
Mineral carbonation	1. Environmentally benign long term storage 2. Exothermal reactions 3. Wide availability of natural feedstocks	1. High sequestration and transportation costs 2. Pre-treatment of silicates 3. Unsecure future potential	>10000	120	(Goldberg et al., 2001, Lackner, 2002, Lackner, 2003)

a: maximum estimated capacity
b: average sequestration cost

2.5 Mineral Carbonation Technology (MCT)

2.5.1 Mineral Carbonation Background

Despite the controversy regarding the high associated costs and energy requirements, mineral carbonation is considered a promising sequestration method in countries lacking depleted oil and gas fields or countries with large availability of natural silicates such as Finland, USA and Australia.

Mineral carbonation involves the formation of stable carbonates and bicarbonates which are chemically equivalent to calcite, magnesite and dolomite (Olajire, 2013). Natural abundant silicates such as: peridotite, serpentine, olivine, wollastonite, gabbro and basalt, are used as feed stocks and can be found in rocks and mining ores. After appropriate treatment the carbonated products may be used as paper fillers and coating materials (Sanna et al., 2012b, Teir et al., 2010). The carbonation reactions (2.8-2.12) of calcium and magnesium oxides, wollastonite, olivine and serpentine are shown below (Huijgen and Comans, 2003).

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \Delta H = -179 \text{kJ/mol} \qquad (2.8)$$

$$MgO + CO_2 \rightarrow MgCO_3 \qquad \Delta H = -118 \text{kJ/mol} \qquad (2.9)$$

$$CaSiO_4 + CO_2 \rightarrow CaCO_3 + SiO_2 \qquad \Delta H = -90 \text{kJ/mol} \qquad (2.10)$$

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 \qquad \Delta H = -89 \text{kJ/mol} \qquad (2.11)$$

$$Mg_3SiO_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \qquad \Delta H = -64 \text{kJ/mol} \qquad (2.12)$$

All the reactions are exothermic and no energy is added to the system. However, slow kinetics, low yield under mild conditions, heat pre-treatment of silicates adversely impact on the cost of the processing (Maroto-Valer et al., 2005). Also, the cost of transportation accounts for 77-94% of the total costs involved in MCT (Renforth, 2012).

During the mining of silicate ores, the cost of grinding, crushing and milling must also be considered. It is estimated that, in order to be applied at industrial scale, the maximum cost of mineral carbonation should range between USD20 and USD30 per tonne of CO_2

(Lackner, 2002). Indicative costs of wollastonite and serpentine were estimated at USD200 and USD126-185 respectively (Lackner, 2002, Kakizawa et al., 2001).

2.5.2 Carbonation of Mineral Residues

Mineral sequestration can be achieved close to emitting plants (ex-situ MCT), or via direct diffusion of CO_2 into rocks containing calcium and magnesium ions (in-situ MCT) (Gadikota et al., 2014).

The ex-situ carbonation of feed-stock occurs in three stages (Prigiobbe and Mazzotti, 2011): 1) Thermal and mechanical pre-treatment of the mineral; 2) The reaction of CO_2 with ions of Ca^{2+} and Mg^{2+} accompanied by energy release; 3) The disposal/reuse of the final carbonated products. Ex-situ processing facilitates the efficient management of the carbonation process and maintenance of the 'quality' of the carbonated products (Bodénan et al., 2014, Gerdemann et al., 2004, Soong et al., 2012).

One of the biggest challenges of ex-situ processing is the distance that often exists between CO_2 emitters and the location of mineral sources, as invariably they do not coincide. The need for handling large quantities of CO_2 and mineral silicates impacts negatively on the costs of material transportation. Thus, the location of bespoke carbonation plants should be as close to the natural mineral resources as possible.

Previous workers (Picot et al., 2011) investigated candidate locations around the world, which combine coal-fired plants emitting more than 1 Mtonne of CO_2, with available minerals within a distance of 300 km. The regions identified are located at Botswana, China, South Africa, Russia, Kazakhstan, and around isolated places in Northern Europe, USA and Australia. Unfortunately, there is lack of mineral availability in industrial regions with vast carbon emissions, raising the transportation costs considerably.

However, although ex-situ processing is the preferred option, the slow kinetics (unless powder is used), the heat-induced pre-treatment of feed-stock and elevated reaction conditions have turned attention towards in-situ treatments i.e. the carbonation of mineral reserves located in the geosphere (Kelemen et al., 2008). The application of in-situ mineral carbonation involves the reaction of ions of Ca^{2+} and Mg^{2+} with supplied carbon dioxide to form products such as calcite, dolomite, magnesite and siderite. CarbFix is a research project worthy of note, using CO_2 emitted from a geothermal plant in Iceland. The mineral 'host' is basalt, a silicate rich in calcium, magnesium and ferrite ions (Matter et al., 2009). The installation consists of a CO_2 separation plant and injection facility, with a 3 km pipeline for the carbon transportation and monitoring systems. The current overall capacity of CO_2 injection is estimated at 2.2 ktonnes CO_2/per year (Matter et al., 2011) and it can reach 60 ktonnes at overall cost of USD66/tonne of CO_2 sequestrated (Ragnheidardottir et al., 2011). Although the CO_2-sequestration capacity of basalt is higher compared to other minerals, mainly olivine and serpentine, this rock is rich in silica (up to 50% w/w) and this oxide is known to have a neutral effect during accelerated carbonation (Gunning et al., 2010b).

In the Samail ophiolite (Oman), it is estimated that approximately 0.1 Mtonnes of CO_2 per year react naturally with peridodite and form solid carbonate reaction products. The potential for reaction with carbon dioxide may reach 1 Gtonne, if accelerated carbonation is applied under elevated temperature and pressure (Kelemen and Matter, 2008, Streit et al., 2012). Other relevant research has been made at Mount Keith Nickel Mine in Canada, Linnajavri in Norway and various locations in Italy (Beinlich et al., 2012, Boschi et al., 2010, Dipple et al., 2008, Wilson et al., 2014).

Table 2.6 shows the optimum conditions and estimated costs for carbonating basalt (Ragnheidardottir et al., 2011), olivine, serpentine and wollastonite (Gerdemann et al., 2007).

Table 2.6: Optimum conditions and relevant costs for various minerals

feed-stock	Method	T (K)	P_{CO2} (MPa)	USD/ton CO_2	USD/kWh
basalt	in-situ	-	-	66[a]	0.05
olivine	ex-situ	458	15	54	0.06
serpentine	ex-situ	373	4	250	0.26
wollastonite	ex-situ	428	11.5	91	0.09

a: estimation based on full utilisation of carbon emissions from Hellisheidi plant (CarbFix project) (Ragnheidardottir et al., 2011)

2.5.3 Routes for Mineral Carbonation

The routes for mineral carbonation could be classified into two main categories: direct and indirect. During the direct route, silicates react with gaseous or aqueous CO_2 in a single step, without the extraction of calcium or magnesium ions (Priggiobbe et al., 2008); whereas the indirect route involves more than one step, followed by ion extraction. The approach to direct and indirect carbonation may vary, and each category has particular advantages and disadvantages presented in detail in Table 2.7.

Table 2.7: Routes for direct and indirect carbonation

Route	Description	Advantages	Disadvantages	Cost (USD/tonne)
Gas-solid	Gas-solid treatment is the simplest route for mineral carbonation. Particulate metal oxides react directly with CO_2, producing high temperature steam and electricity. Depending on the feed-stock, under ambient pressure the optimum temperature range for the reaction is considered to be between 433 K and 683 K (Sipilä et al., 2008, Lackner et al., 1997, Baciocchi et al., 2009b).	1) Simplicity of the method 2) Production of steam 3) Mining integration potential	1) Slow reaction 2)Thermodynamic constraints 3) Industrially unfeasible	
Aqueous	Aqueous carbonation involves mixing (minerals) with a liquid medium such as bicarbonate/salt ($NaHCO_3$/NaCl), before the reaction with CO_2. Bicarbonate acts as a catalyst during the reaction process, while salt creates saline environment where silicates are generally more soluble. Formic acid, citrate, disodium oxalate, oxalate and EDTA ligands have also been explored in various studies to increase mineral dissolution rates. For serpentine-derived silicates the optimum temperature is 458 K, whereas for olivine is 428 K at the optimum pressure of CO_2 of 18.5 MPa. The overall cost of aqueous route was estimated between USD50 and USD100 /tonne of CO_2 (Huijgen and Comans, 2003, Sipilä et al., 2008, O'Connor et al., 2000, Chen et al., 2006, Ghoorah et al., 2010, Bonfils et al., 2010, Krevor and Lackner, 2008, Krevor and Lackner, 2009, Bobicki et al., 2012, Bonfils et al., 2012, Gerdemann et al., 2004).	1) Satisfactory conversion rates 2) High degree of carbonation 3) No chlorine addition	1) High energy requirements 2) Addition of extra chemicals 3) Negligible heat integration potential 4) No recycling 5) High carbon sequestration costs	50-100
HCl extraction	In HCl extraction hydrochloric acid is used to extract ions of Ca+ and Mg+ from a silicate matrix. The sequestration cost of the method is estimated at over USD188/tonne of CO_2 (Lackner, 2003, Huijgen and Comans, 2003, Huijgen and Comans, 2005a).	1) Recoverable reactants 2) Defined and fully comprehensive mechanism	1) High energy requirements 2) Ineffective for alkaline metals 3) Expensive acid	>188
Acetic acid extraction	Similarly to HCl extraction, the use of acetic acid is an alternative option, although more research has to be carried out to prove its efficiency. An approximate cost estimation of processing CO_2 via the acetic acid extraction route is €63 (USD85) /tonne CO_2 (Kakizawa et al., 2001, Huijgen and Comans, 2005a, Teir et al., 2007b, Teir et al., 2007a).	1) Less energy intensive than HCl 2) Less expensive than HCl	1) Non- proven economic feasibility 2) Higher recoverability needs to be applied	78
Molten Salt	Another potential solvent is molten salt (such as $MgCl_2 \bullet 3.5H_2O$) at T=573 K and P < 3 MPa, which is less energy intensive than hydrochloric acid. However, molten salt extraction has almost been abandoned, as this solvent is extremely corrosive causing operational problems and undesirable by-products (Bobicki et al., 2012).	1) Less energy intensive than HCl	1) Extremely corrosive 2) Undesirable by-products	
Ammonia extraction	In the ammonia extraction route, ammonium salts are used to promote the reaction between the silicates and CO_2. Previous workers (Kodama et al., 2008) proposed a two-step extraction process by using NH_4Cl and the results showed that calcium selectivity was reached 99%. In another study (Wang and Maroto-Valer, 2010) ammonium bisulfate (NH_4HSO_4) was applied in a direct and less energy demanding reaction at 373 K.	1) High purity carbonates 2) Good kinetics 3) Recoverable reactants	1) High current costs 2) More research needs to be done	

2.5.4 Magnesium Silicates

A group of silicates with particular interest due to its large availability around the globe is serpentines. They contain around 40% of MgO, and they can be found in ultramafic rocks or mining tailings. Direct carbonation of serpentines leads to the formation of magnesium carbonate ($MgCO_3$) following the reaction below (Huijgen and Comans, 2003):

$$Mg_3SiO_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \qquad \Delta H = -64 kJ/mol \qquad (2.13)$$

The effective conversion of serpentine into magnesite via direct carbonation requires elevated temperatures over 1173 K and supercritical CO_2 pressure. In a previous study a three-step production of magnesite through the separation of magnesium oxide from serpentine ores (step 1), hydration of the free magnesium oxide (step 2) and subsequent carbonation of magnesium hydroxide (step 3) was proposed (Zevenhoven et al., 2008b). The relevant reactions of the three steps are shown below:

$$Mg_3Si_2O_5(OH)_4(s) \rightarrow 3MgO(s) + 2SiO_2(s) + 2H_2O \qquad (2.14)$$

$$MgO(s) + H_2O \rightleftarrows Mg(OH)_2(s) \qquad (2.15)$$

$$Mg(OH)_2(s) + CO_2 \rightleftarrows MgCO_3(s) + H_2O \qquad (2.16)$$

The carbonation of brucite, the mineral form of magnesium hydroxide, produces various mineral phases of $MgCO_3$, depending on the reaction conditions. Magnesite and hydromagnesite are products with added-value since they can be used as mineral fillers in paper and pigments or flame retardants in electrical and electronic parts (Montes-Hernandez et al., 2012). However, under ambient temperature and pressure and low reaction times, the precipitation of both magnesite and hydromagnesite is inhibited by the selective precipitation of low value hydrated magnesium carbonates, mainly nesquehontite (Hänchen et al., 2008, Zhao et al., 2009).

Various studies have been made on brucite carbonation focusing on optimum reaction conditions and appropriate accelerators for the enhancement of the precipitation magnesite/hydromagnesite under moderate temperature and pressure. Table 2.8 summarises the most notable recent works on carbonation of $Mg(OH)_2$.

At the moment, the main challenges of mineral sequestration of serpentines are the low conversion rate of brucite into $MgCO_3$ at mild conditions, and the high costs associated with the method. Further research should focus on chemical and physical accelerators that might favour the precipitation of $MgCO_3$ at competitive costs. In addition, the value of the carbonated products should be evaluated. In a previous study (Gunning et al., 2009), accelerated carbonation of wastes showed that products with improved physical properties, suitable for sustainable concrete blocks, were created via a carbon negative process. Ideally, large amounts of flue gas (15% CO_2 concentration) emitted from big mining fields could be utilised with magnesium rich tailings coming from the same mine and commercially valuable products could be produced (Jung et al., 2004).

The analysis of mineral sequestration economics showed that the method cannot be applied at large scale without further research focusing on less energy demanding rocks handling/processing and more efficient reactions at lower operating conditions. In the next section a similar analysis for waste carbonation was also made, and the findings suggested that this method is more feasible due to lower costs and less energy demands.

Table 2.8: Previous studies on carbonation of brucite

Year	Particles size(µm)	T (K)	p (MPa)	t (min)	Details/Results	Ref
2008	n/a	298,393	0.1,0.3, 10	up to 1200	At p=0.1 MPa and T=298 K only nesquehontite precipitated. The presence of hydromagnesite was first recorded at p=0.3 MPa and T=393 K, and within 5-15 h it transformed into magnesite. At elevated pressure and temperature the reacted brucite formed magnesite in a few hours.	(Hänchen et al., 2008)
2010	<150	Amb	1.5	30-150	Brucite extracted directly from a mining pit was mixed with deionised water and HCL. After 150 min the samples containing deionised water precipitated 95% nesquehontite, and approximately 98% of the initial brucite reacted. On the other hand, samples with HCL precipitated 78% of nesquehontite, while 30% of brucite remained unreacted.	(Zhao et al., 2009)
2010	75-125	773	2.85	30	Brucite from nickel mine tailings was carbonated in a pressurised fluidised bed reactor. At T=773 K and P=2.85 MPa the conversion of $Mg(OH)_2$ into $MgCO_3$ was 26% after 30 min. The study showed that the presence of water had negative effects on the reaction.	(Fagerlund et al., 2010)
2011	125-425	773	2	10	Both commercial and serpentine derived brucite was carbonated in a pressurised fluidised bed reactor. The carbonation degree was 50% after 10min in the reactor. Longer carbonation time (20 min) showed no additional carbonation. Different particle size fractions did not affect the efficiency of the reaction.	(Fagerlund et al., 2011)
2011	20-32	323, 348	8.2	up to 6900	Natural brucite was reacted with dry and wet CO_2 in a high pressure X-ray diffraction reactor. Samples carbonated by anhydrous CO_2 showed no reactivity at the desired temperatures (323 K and 348 K) However, the addition of water increased significantly the reactivity of $Mg(OH)_2$. At 323 K the initial brucite was completely converted into nesquehontite, while at 348 K magnesite was the predominant mineral phase.	(Schaef et al., 2011)
2012	2-40	ambient	0.1	up to 11880	Slurries comprising high purity pulverised brucite were carbonated with different CO_2/N_2 mixtures at ambient conditions. At 10% CO_2 after 198hours the final efficiency of the reaction was 43%. At 50% CO_2 after 56 hours the conversion was 51%. Finally, at 100% after of 72 hours of carbonation the yield was 44%.	(Harrison et al., 2012)
2012	<150	up to 673	up to 1.5	60	Commercial brucite was reacted in the presence of steam with low and high pressure CO_2 in a TGA analyser and a high pressure vessel respectively. Steam enhanced the reaction kinetics at elevated pressures, aiding conversion of $Mg(OH)_2$ to $MgCO_3$.	(Fricker and Park, 2013)

2.6 Waste Carbonation Technology (WCT)

As an alternative to minerals extracted from the geosphere, solid wastes from bauxite processing, cement dusts, coal fly ash, steel-making slags and incineration ashes can be reacted with carbon dioxide (Araizi et al., 2013). These wastes have a highly alkaline nature containing high amounts of Ca^{2+} and Mg^{2+}, and their availability is widespread around the world. Due to their alkalinity they cause serious implications to humans' health including respiratory symptoms, weak ventilatory function various lung diseases, irritation of eyes, skin and throat, respiratory tract, cardiovascular deaths and in some cases arsenic poisoning and cancer (Clancy et al., 2002, Kakooei et al., 2012, Yao et al., 2015) In the EU, their disposal to landfills is expensive or difficult, since they present serious environmental and health issues. According to Directive 2000/532/EC, these wastes are generated during "harmful" activities including thermal, incineration, pyrolysis and combustion processes.

Table 2.9: Characterisation of wastes according to Directive 2000/532/EC

Waste	Main Category	Code	Sub-category	Code
Bauxite residues	Wastes resulting from exploration, mining, dressing and further treatment of minerals and quarry	01	Wastes from further physical and chemical processing of metalliferous minerals	01 03
Cement kiln dust	Inorganic wastes from thermal processes	10	Wastes from manufacture of cement, lime and plaster and articles and products made from them	10 13
Coal fly ash	Inorganic wastes from thermal processes	10	Wastes from power stations and other combustion plants	10 01
MSWI bottom ash	Wastes from waste treatment facilities, off-site waste water treatment plants and the water industry	19	Wastes from incineration or pyrolysis of waste	19 01
MSWI fly ash	Wastes from waste treatment facilities, off-site waste water treatment plants and the water industry	19	Wastes from incineration or pyrolysis of waste	19 01
Steelmaking slags	Inorganic wastes from thermal processes	10	Wastes from the iron and steel industry	10 02
Waste concrete	Construction and demolition wastes (including road construction)	17	Concrete, bricks, tiles, ceramics, and gypsum-based materials	17 01

This process is known as waste carbonation technology and the most significant advantage, compared to MCT, is the absence of rock handling/processing and the general proximity of these residues to point sources of anthropogenic CO_2 (Shu-Yuan Pan et al., 2012). Also, during processing the hazards associated with the waste, such as high pH or contaminant mobility can often be managed, facilitating the re-use, as for example, an alternative to virgin stone in construction, or in higher value raw materials (Dri et al., 2013, Zhang et al., 2013). A number of the high volume waste streams with potential for WCT are identified in Table 2.9.

2.6.1 Bauxite Residues (Red Mud)

'Red mud' is the solid waste produced by the Bayer process when alumina is extracted from bauxite ores. The transport, re use and disposal of red mud is extremely difficult due to its high alkalinity (pH>13) and elevated sodium concentration (Johnston et al., 2010). It is estimated that the total amount of red mud stock-piled is 2.7 Gtonnes worldwide, increasing by 120 Mtonnes per year (3.7 Mtonnes in the EU and 1 Mtonne in the UK) (Gunning, 2010, Power et al., 2011, Poulin et al., 2008, Association, 2010). The carbonation of bauxite residues can be achieved by neutralisation involving the reaction of aqueous solutions of red mud with carbon dioxide and Na_2CO_3, $NaHCO_3$ and H_2CO_3 as the final products (Sahu et al., 2010, Renforth et al., 2012). The carbonation capacity of the process is estimated at 53 kg of CO_2/tonne of red mud (Yadav et al., 2010).

2.6.2 Cement Kiln Dusts

The world-wide manufacture of cement produces large-scale CO_2 emissions. Residues from cement manufacture have a chemistry that will facilitate carbon uptake, the fact that they result from the calcination of limestone notwithstanding. Cement kiln dust (CKD) is formed during cement treatment at high temperature (around 1673 K) and it is a mixture of fine particles, unburned and part-burned raw materials and other elements. Many cement manufacturing processes involve CKD recycling, however, the degree of recycling depends on various parameters including dust composition and alkali content/standards (Huntzinger and Eatmon, 2009, Huntzinger et al., 2009, Gunning et al., 2010b). Historically, large amounts of CKD are landfilled and represent a potential resource for reacting with CO_2. The production of cement using alternative fuels has meant that in some cases cement kiln dusts are ‘contaminated’ and require disposal, but invariably remain suitable for carbonation.

Depending on the type of cement kiln, 250-300 kg of cement kiln dust is formed per tonne of cement. CKD production is estimated at 990 million tonnes worldwide (3.6 Gtonnes cement are produced annually), with 208 Mtonnes produced in the EU and 8.5 Mtonnes in the UK (Schneider et al., 2011, Hoenig et al., 2007, British Geological Survey, 2005, Van Oss, 2011). The CO_2-binding capacity was calculated by Huntzinger et al. at 11.5 % w/w, i.e. 115 kg CO_2 can be stored for every tonne of CKD (Huntzinger et al., 2009). Other workers estimated the sequestration capacity at 9% w/w and 1.5% w/w respectively (Grandia et al., 2010, Gunning et al., 2010b).

2.6.3 Coal Fly Ash

Coal fly ash (CFA) is produced from the burning of coal at various plants, and energy production from combusting this fuel is a major contributor to global warming. CFA is composed of metal oxides, such as: SiO_2, Al_2O_3, FeO_3, CaO, MgO, K_2O, Na_2O and TiO_2. The burning of anthracite and bituminous coal typically produces Class F fly ash, while the burning of lignite and sub-bitunimous coal forms Class C fly ash. The latter contains a higher CaO and displays a CO_2-reactivity that is significant (Blissett and Rowson, 2012, Muriithi et al., 2013). CFA is typically used as building material, due to its pozzolanic nature and unique properties (Wee, 2013). Where high CaO containing CFA is available, there is great potential to capture CO_2 with minimal handling and transport costs (Sun et al., 2012) whilst mitigating the effects of CFA on the environment. The annual total emissions of coal ash were estimated at 600 Mtonnes worldwide, 90 Mtonnes in the E.U, and 6 Mtonnes in the U.K (Montes-Hernandez et al., 2009, Feuerborn, 2005) .

Studies on CFA’s CO_2 binding capacity showed dependency on composition and carbonation reaction temperature and pressure. The CO_2 binding capacity of CFA containing 4% w/w CaO was found to be 26 kg/tonne of ash (Montes-Hernandez et al., 2009), whereas a mixture of brown coal fly ash and brine, varied from 3.6 to 7.2

kg/tonne. Under ambient temperature the maximum binding capacity of CO_2 was found to be 8 kg/tonne of ash (Jo et al., 2012). However, a previous worker (Sun et al., 2012) carbonated high CaO- and MgO-containing brown coal fly ash derived from Latrobe Valley in Australia with acetic acid leachate, and found that the sequestration capacity of the system could reach 264 kg of CO_2/tonne of ash.

2.6.4 MSWI Bottom Ash and APCr

The treatment of municipal solid wastes from incinerators produces two waste streams: bottom ash and air pollution control residues (APCr) or fly ash (Yang et al., 2012). The former represents 80% of the total incineration residue and is composed of aluminium silicates and metal substances, such as Ca, Cr, Ni, Cu, Zn. During incineration these metals due to their relatively high weight head towards the bottom of the incinerator. On the other hand, APCr is a mixture of lighter substances, mainly fly ash, lime and pure carbon, representing 20% of the solid waste arising from incineration (Fernandez Bertos et al., 2004). Bottom ashes are invariably used in road pavement construction, glass and ceramics, and in agriculture and waste water treatment (Lam et al., 2010, Li et al., 2006). The presence of heavy metals is a concern, and an accelerated carbonation treatment-step has been shown to be a promising management option (Sakita et al., 2006, Shimaoka et al., 2006, Cornelis et al., 2006, Santos et al., 2013a).

In Europe around 9 million tonnes of bottom ash are produced annually, with 10% of this originating in the UK (Pecqueur et al., 2001, Sanna et al., 2012a). These ashes have potential to form stable carbonated products (Li et al., 2007), with a sequestration capacity between 247 kg/tonne and 475 kg/tonne for bottom ash, and between 30kg/tonne and 120 kg/tonne for the APCr (Clarens et al., 2010, Rendek et al., 2006, Jianguo et al., 2009). The world production of MSWI ash is estimated to be 100 Mtonnes/year (Reijnders, 2007).

2.6.5 Steelmaking Slags

Steel manufacture generates slag, comprised of calcium, iron, silicon, aluminium, magnesium and manganese oxides. These residues are highly alkaline (pH=12) and when they react with carbon dioxide, stable products comprising carbonates are produced (Bonenfant et al., 2008, Santos et al., 2013b). Moreover, slag production is around 400 Mtonnes worldwide (Worldsteel Association, 2010), with 45 Mtonnes in the EU (Euroslag, 2012) and 5.2 Mtonnes in the UK (Böhmer et al., 2008). Their carbon-uptake potential is promising whilst transportation costs are negligible, assuming the CO_2 can be captured.

The rate of carbonation of steel slag depends on temperature and particle size. The generalised reaction involves the leaching of anions into aqueous solution, followed by precipitation of calcium carbonate (Huijgen and Comans, 2005b, Chang et al., 2011). Indicative costs of carbon sequestration via steel slags were given by Huijgen et al. (Huijgen et al., 2007) who proposed processing at p=3.55 MPa and T=451 K and an overall cost of USD95/tonne of CO_2. The maximum sequestration capacity of steel slag waste was estimated between 227 and 300 kg of CO_2/ tonne of slag despite extensive research on the use of solvents, including ammonium salts, for process enhancement and increased calcium carbonate precipitation (Baciocchi et al., 2010, Eloneva et al., 2008, Eloneva et al., 2010).

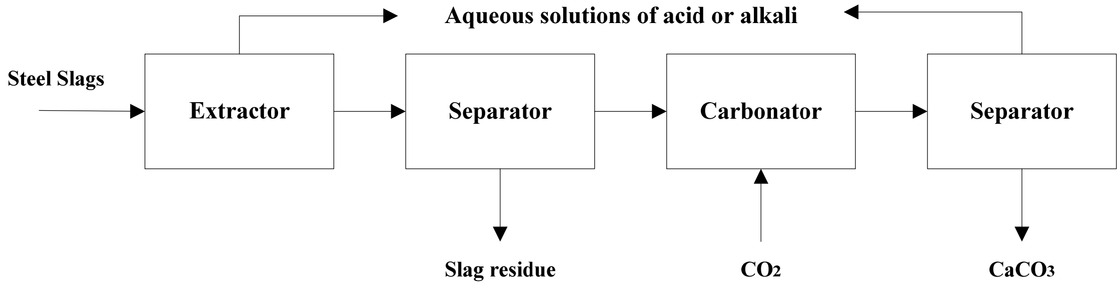


Figure 2.3: Sequestration concept of steelmaking slags

2.6.6 Waste Concrete

Waste concrete has potential to be used as feedstock in WCT, as it contains cementitious phases derived from Portland cement, at 10-20% w/w. Construction and demolition waste (C&D) is also typically CO_2 reactive (Galan et al., 2010). The maximum carbon uptake of waste concrete was estimated at 165 kg of CO_2/tonne, (Teramura et al., 2000), while the cost of processing concrete waste was calculated at USD38/tonne CO_2, excluding any revenue from sale of the carbonated products (Yamasaki et al., 2006) (see Figure 2.4).

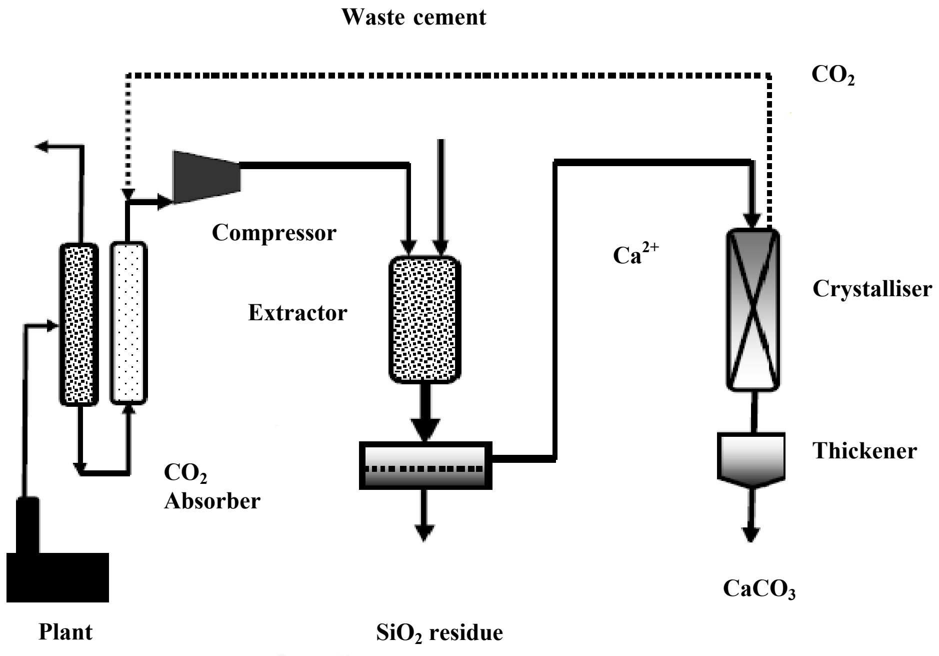


Figure 2.4: CCS of a power plant using cement waste as feedstock (Yamasaki et al., 2006)

Access to up-to-date data on waste volumes is fairly difficult due to the lack of a universal waste regulation. However, available data between 2007 and 2011 indicated that it is possible to sequester up to 1 Gtonne of CO_2 by carbonating 7 alkaline residues found widespread around the world (Table 2.11). Although this number is low compared to the sequestration potential of geologically derived minerals, and of the oceans, the carbonation of wastes is already an established technique. WTC ensures the utilisation of both CO_2 and solid waste residues (arising from the same plant) without additional transportation and monitoring costs. The average cost of WCT, based on steel slags and waste cement treatment, is estimated at USD67/tonne of CO_2 which is considerably lower than MCT. Furthermore, process operating conditions including temperature and pressure are generally lower, requiring less energy intensive processing. However, the complexity of waste systems and the frequent presence of heavy metals and radioactive elements in some residues necessitate pre-treatment, which may increase the cost of handling and processing these wastes. Finally, in many countries the regulation of waste does not lend itself to treatment and valorisation at this time, and this is an impediment to utilising waste for the sequestration of CO_2 gas.

Table 2.10: Alkaline residues suitable for waste carbonation

Waste	Annual world production in million tonnes	Year	Sequestration capacity in kg CO_2/tonne of waste	Max potential CO_2 utilised (MTonnes)	Min potential CO_2 utilised (MTonnes)	T (K)	P (MPa)
Bauxite residues	120	2011	53	6.36	6.36	ambient	0.35
Cement kiln dust[a]	990	2011	15-115	113.85	14.85	ambient	0.1-0.2
Coal fly ash [74-78]	600	2009	8-264	158.4	4.8	ambient-363	0.1-4
MSWI bottom ash[b,c]	80	2007	247-475	38	19.76	ambient	1.7
MSWI fly ash[b]	20	2007	30-120	2.4	0.6	ambient	0.3
Steelmaking slags	400	2010	227-300	120	90.8	451	3.55
Waste concrete[d]	3600	2011	165	594	594	353	3.0
Total[e]	**4790**			**1033.01**	**731.17**		

a: For every tonne of cement, 0.25-0.30 tonnes of kiln dust are produced. Thus: 0.275×2800=770Mt

b: The annual production of municipal incineration ashes is estimated at 100Mt. If we assume that 80% comes as bottom and 20% as fly ashes then the respective figures would be 80Mt and 20Mt

c: Ambient T and P are assumed

d: Figures refer to cement production. Every tonne of concrete contains typically 10% cement

e: Max and min potential CO_2 utilised was estimated by multiplying the world annual production of the waste residues by the highest and lowest sequestration capacities found in literature

2.7 Commercial Applications

It is worth noting that several commercial companies process various types of waste otherwise disposed, in order to form products with value, including, aggregates and secondary building materials. be transported. Table 2.11 presents data on these commercial/near commercial companies and their processes, using data/ metrics (CO_2 utilised, products value, energy penalty) taken from two reports from Carbon Sequestration Leadership Forum (Carbon Sequestration Leadership Forum, 2012, Carbon Sequestration Leadership Forum, 2013), companies web-sites and other information sources.

Table 2.11: Summary of ventures applying mineral and waste carbonation

Name	Activities and Technology	Raw Materials	Key Process Steps	Output materials	Projected CO_2 Utilisation (Mtonnes/year)	Projected Cost (USD/tonne of product)	Development Stage
Calix	Calix's technology focuses on CCS and subsequent gas reaction with minerals (i.e. magnesium hydroxide) for the formation of high value commercial products useful in agriculture, building and construction, power and water industry. Recently, Calix has expanded in Europe by purchasing the intellectual rights of Novacem process (Calix, 2012).	1. Limestone 2. Dolomite 3. Magnesite 4. Kaolin 5. Gypsym 6. Diatomite 7. Bauxite	1. Minerals Grinding 2. Minerals heat pre-treatment 3. Calcination 4. Separation of the products	1. Steam 2. Magnesium Oxide 3. Semidolime 4. Metakaolin 5. Organic Phosphate	2-23	100/tonne of lime	Pilot scale
CCC	Cambridge Carbon Capture (CCC) applies accelerated carbonation in terms of mineral sequestration. The company's main plan is the mineralisation of magnesium and calcium silicates to carbonated products, along with generation of zero carbon electricity. Its technology is proven at laboratory scale and CCC is currently seeking for industrial partner to commercialise the process (Cambridge Carbon Capture, 2014b, Cambridge Carbon Capture, 2014a).	1.Silicate minerals/wastes 2. Flue gas	1a. Digestion of the process fluids 1b. Carbon capture & power generation unit 2. Carbonation 3. Regeneration of the process fluids	1. Silica by-products 2. Carbon free electricity 3. Carbonate materials	50-1000		Laboratory scale
Carbon8	Carbon8 has undertaken pilot-demonstration work on contaminated soil, and a number of industrial waste streams including cement-production residues. The company has utilised landfill gas emissions for waste materials. Its first commercial operation utilises CO_2 captured from sugar refining, to produce 60,000 tonnes pa of manufactured aggregate from carbonated MSWI APCr. The process is carbon positive -44kg of CO_2 /tonne of product (Carbon8, 2014, Gunning et al., 2013).	1.Alkaline wastes 2. CO_2 3. Reagents	1. Pre-treatment of waste powders 2. Mixing of carbonated product 3. Pelletising 4. Aggregates production	1. Aggregates	0.003-0.009[1]	10-18[1] (aggregates)/tonne of CO_2	Commercially active
Carbon Engineering	Carbon Engineering is a Canadian company working on the commercialisation of direct air capture (DEC) and production of high quality carbon dioxide, which can be used for enhanced oil recovery, algae growth in industrial-scale ponds, and synthesis of liquid hydrocarbons. Although the current cost of capture of air ranges between USD50-2000/tonne, Carbon Engineering technology could ensure costs of USD100/tonne with energy	1.Atmospheric air 2. Energy 3. Chemicals	1. Air capture 2. Separation of CO_2 via air contractor 3. Regeneration cycle	1. Pure CO_2		100/tonne of CO_2	Pilot scale

	consumption of 11kWh/tonne CO_2 (Carbon Engineering Technology, 2014, Holmes et al., 2013).						
CO_2 Solutions	CO_2 Solution's technology utilises the enzyme catalyst carbonic anhydrase for removing carbon from flue gases at emitting plants. Enzymes were found to accelerate the removal process at relatively low cost and low environmental impact. At the moment a pilot plant utilises 5.5kTonnes of CO_2 per year (CO2 Solutions, 2014, Penders-van Elk et al., 2012, Penders-van Elk et al., 2013).	1. Flue gas 2. Low energy solvents	1. CO_2 Absorption 2. Enzyme catalysis 3. Thermal heating	1. Pure CO_2	0.0055		Pilot scale
ICS	The novelty of ICS approach is that integrates the flue gasses capture step with the carbonation of silicate minerals. Thus, carbon dioxide does not require pure gas treatment, reducing its total energy requirements. The company estimates the overall cost per tonne of CO_2 sequestrated at US$50, while it is possible to utilise at least 90% of carbon dioxide emissions of a power plant (Hunwick, 2009, Hunwick, 2010).	1. Flue gas 2. Mineral silicates	1. Capture of flue gas 2. Extraction/ transport/treatment of mineral silicates 3. Carbonation 4. Storage	1. Mineral Carbonates	24	50 / tonne of CO_2	Pilot scale
Recmix	Recmix is commercially active, processing stainless steel-slag, including by autoclave, to produce aggregates, fillers for concrete and asphalt and blocks (Recmix, 2014).	1. Stainless steel slag 2. CO_2	1. Granulation of steel slag 2. Mixing 3. Carbonation 4. Shaping and curing of carbonated streams	1. Aggregates 2. Concrete/asphalt fillers 3. Artificial aggregates			Commercially active
Solidia	Solidia's two main products, solidia cement and solidia concrete, are manufactured similarly to ordinary Portland cement and concrete but with the merit of up to 70% less carbon footprint. Solidia concrete can be used in paving stones, concrete blocks and roof tiles. During the initial stages of concrete production in both processes the same materials and the same equipment are used. However, during curing step solidia utilises CO_2 instead of water, resulting in lower curing time and concrete with improved characteristics. The energy requirements are estimated at 3.8GJ/tonne of cement (Solidia Technologies, 2014).	1. Solidia cement 2. CO_2	1. Kiln treatment 2. Mixing with water 3. Curing with CO_2 4. Shaping of concrete	1. Solidia concrete			Commercialising

1:Actual

2.8 Conclusions

The reduction of anthropogenic CO_2 emissions and harmful waste-streams prior to landfilling is necessary in order to mitigate environmental impacts and maintain the sustainability of the planet. Governments consider following the example of Alberta, Canada, and imposing carbon taxes to heavy industry and electricity suppliers. Moreover, landfill regulations have tightened up in many parts of the world, and the penalties are now affecting a wide range of the market.

A technique which combines CO_2 mitigation and waste management is accelerated carbonation technology (ACT), which has particular advantages such as rapid reaction completion, high yield at ambient temperature and pressure and proven applicability. The mechanism of ACT is fully established and the reaction efficacy depends on several variables affecting CO_2 diffusivity/reactivity comprising the mineralogy of the treated materials, water content, relative humidity, CO_2 partial pressure and concentration and reaction conditions.

However there is limited previous work regarding physical and chemical techniques (accelerators) which could further increase the reaction yield at ambient conditions. Various organic and inorganic substances are candidate catalysts such as sodium sulphate, sodium hydroxide, acetate, ethanol, and nitrite, as they are known to promote the hydration rate of carbon dioxide. Also, the application of ultrasound could have beneficial effects on the achieved yield, as this method is known to promote precipitation rate of calcium carbonate.

The development of more effective ambient carbonation systems is crucial for the handling/processing of vast amounts of feed-stock. Under ambient temperature and pressure the associated costs are kept to a minimum. Cost-effective handling/processing is necessary for the commercialisation of mineral and waste carbonation, two promising methods of carbon capture and storage (CCS).

CCS is considered the preferred option for storing captured CO_2 in appropriate geological locations and in extracted minerals. From the available CCS methods, mineral carbonation ensures the long-term sequestration of CO_2 in calcium and magnesium silicates, and the potential to sequester in excess of 10,000 Gtonnes of CO_2 cumulatively in stable carbonate products. However, this technique is currently expensive at USD100-120/tonne CO_2, conversion rates remain low, and there are large distances between major CO_2 emitters and potential geological storage sites. Therefore, the commercial application of mineral carbonation will remain uncertain until costs can be reduced to be competitive with geological and ocean storage, at USD5 and USD18 per tonne of CO_2 respectively.

Waste carbonation has obvious short-term advantages: processing is easier (many suitable bulk wastes are finely particulate in nature), handling and transport procedures are largely in place, and waste and CO_2 are often located together as a result of being produced by the same industrial process. Thus, the cost of processing and transportation are likely to be lower as these wastes are generally treated with CO_2 emitted from the same plant. The average cost of waste carbonation of steel slags and waste cement is estimated at USD38-95/tonne of CO_2, with a potential for reduction if carbonated products with value can be manufactured.

This study of 7 alkaline process wastes has shown that approximately 1 Gtonne of CO_2 may be sequestered each year. Although this figure represents only a small fraction of the annual anthropogenic emissions or what needs to be sequestrated to mitigate climate change, waste carbonation is a reality, being processed commercially as products with value. For example, Carbon8 and Recmix produce carbon negative construction materials that would otherwise be disposed to landfill. The production of manufactured aggregate by waste carbonation technology in the UK is cost effective and the manufacture aggregates are utilised in concrete construction blocks that are certified as ‘carbon negative’, thus contributing to the UK government’s target for sustainable housing.

The commercial prospects for MCT and WCT are both positive if costs can be controlled, and there are several other companies either commercially active or near-market with processes utilising waste CO_2. However, as is often the case, the further development of WCT and the production of new products utilising CO_2 very much depend on market potential and the willingness of governments to establish enabling legislation, such as stricter environmental regulations, a favourable tax environment, and a meaningful ‘price’ on carbon managed by this process. As future regulatory change is widely expected, an increase in commercial investment, leading to the diversion of larger quantities of waste from landfill and the sequestration of far greater quantities of carbon dioxide than has hitherto possible can be anticipated.

In the next chapter the input materials, analytical methods and a summary of the applied carbonation techniques are presented.

3 MATERIALS AND METHODS

3.1 Introduction

This chapter summarises the standard analytical methods used in this work including X-ray fluorescence, X-ray diffraction, total organic carbon analysis, wet laser diffraction and scanning electron microscopy. Also, a brief overview of the applied carbonation techniques is given. Detailed descriptions accompanied by schematic diagrams and photos of each technique are discussed in the next chapters.

In addition the selected input and reference materials and chemicals are presented. Finally, the statistical measures (i.e. mean, standard deviation, standard error) used for the interpretation of experimental data are explained.

3.2 Materials

The selected materials were divided into two categories: wastes and minerals. For each category a reference material was used: ordinary Portland cement type 1 (CEM 1) for wastes and calcium hydroxide for minerals. The input wastes comprising bauxite residues (BR), cement bypass dusts (CBD), coal fly ashes (CFA), MSWI fly ashes (APCr), MSWI bottom ashes (BA) and steel slags (SS), while the tested minerals comprising wollastonite (WOL) and three commercial grades of magnesium hydroxide classified according to their particles size (2 μm, 18 μm and 255 μm). The treated materials are summarised in Table 3.2.

Also, organic and inorganic chemical substances were added to carbonation systems in order to assess their impact on the reaction yield. The selected chemicals included acetic acid, ethanol, sodium hypochlorite and sodium nitrite and they were mixed with aqueous solutions in three different molarities (0.1M, 0.5M and 2.5M). A detailed description and common industrial uses of chemical are given in Chapter 7.

Table 3.1: Input wastes, minerals and reference materials used in this study

Material	Category	Description
Cement (CEM)	Reference	Ordinary Portland cement (or cement) is the main compound of concrete manufacture. Concrete is the ultimate building material, generating around 5% of the total global carbon emissions (Bobicki et al., 2012). Cement is a blended mixture of lime, silica alumina and iron, and its predominant mineral phases are alite, belite, aluminate and ferrite (Gagg, 2014).
Air pollution control (APCr)	Waste residue	Air pollution control is the top waste stream (around 20% of the total) from incineration process. It is mixture of fly ash, lime and pure carbon. This waste due to its complex and toxic mineralogy (presence of heavy metals and hazardous substances) cannot be easily disposed to landfills without prior treatment or expensive penalties (Ecke et al., 2003).
Bauxite residues (BR)	Waste residue	The bauxite residues or alternatively red mud is the waste product of the Bayer process during aluminium extraction from bauxite ores. It is extremely alkaline containing concentration of aluminium, iron and sodium (Johnston et al., 2010).
Cement bypass dust (CBD)	Waste residue	Cement kiln dusts are formed during cement manufacture and they are composed of fine particles, unburned and part-burned raw materials and various other elements (Huntzinger et al., 2009). Typically 1tonne of cement production forms 250-300 kg of CKD. Cement dusts cause serious implications to human's health especially respiratory symptoms and ventilatory function (Fell et al., 2003).
Coal fly ash (CFA)	Waste residue	CFA is formed from coal burning and its chemical composition includes various metal oxides such as SiO_2, Al_2O_3, FeO_3, CaO, MgO, K_2O, Na_2O and TiO_2. CFA is responsible for contamination of soils and groundwater, air pollution and contribution to Global Warming (Nyambura et al., 2011).
MSWI bottom ash (BA)	Waste residue	Represents the predominant waste-stream (up to 80%) coming from the incineration of municipal solid wastes. Is mainly composed of aluminium silicates and metals such as: Ca, Cr, Ni, Cu, and Zn. After appropriate treatment bottom ashes can be used in road pavement construction, glass and ceramics and in waste water treatment (Li et al., 2014).
Steel-making slags (SS)	Waste residue	The main by-product of steel production process, comprising calcium, iron, aluminium, magnesium, manganese and other heavy metals. Due to its high alkalinity (high pH) pre-treatment prior to disposal is required (Santos et al., 2013b).
Calcium Hydroxide	Reference	Inorganic compound with chemical formula $Ca(OH)_2$, usually obtained as white powder after the reaction of calcium oxide and water. $Ca(OH)_2$ has many applications including the construction, chemical, food and dental industry.
Magnesium hydroxide	Mineral	Magnsieum hydroxide is the product of hydration of calcium oxide. The latter is the main component of serpentines which account for a large percentage of silicates found in rocks and mining ores (Huijgen and Comans, 2003). $Mg\ (OH)_2$ when reactes with CO_2 leads to the formation of magnesite and hydromagnesite, two high value products that can be used as mineral fillers in paper and pigments or flame retardants in electrical and electronic parts (Montes-Hernandez et al., 2012).
Wollastonite (WOL)	Mineral	Wollastonite is a calcium mineral ($CaSiO_3$) containing small amounts of iron, magnesium and manganese. Due its properties and unique crystallography, wollastonite is widely used in heat-insulating ceramics, metallurgy, automobile and paint industry (Demidenko et al., 2001).

3.3 Methods

3.3.1 Carbonation Techniques

The input materials were carbonated predominantly via carbonation under ambient temperature and pressure (baseline-ambient carbonation) and under an ultrasonic field (ultrasound). However, carbonation experiments were also conducted at slightly elevated temperatures (water vapour carbonation) and pressures (pressurised carbonation). An overview of the applied carbonation techniques are shown in Table 3.2. Detailed descriptions, schematic diagrams and images of each technique are presented in the relevant experimental chapters.

Table 3.2: Summary of carbonation techniques used in this study

Technique	Description
Carbonation under ambient temperature and pressure	Samples exposed to a continuous flow of humidified carbon dioxide under ambient temperature and pressure.
Carbonation under pressure	Samples exposed to humidified carbon dioxide at elevated pressure (0.2 MPa). The treatment time was 24 hours.
Carbonation with ultrasound	Samples exposed to a continuous flow of humidified carbon dioxide at ambient temperature and pressure under an ultrasonic field.
Carbonation with water vapour	Samples exposed to a continuous flow of carbonic acid vapour at ≈373 K.

3.3.2 X-Ray Fluorescence

Chemical composition is an important parameter for the evaluation of the reactivity to CO_2 of a candidate material, as the presence of particular elements results in increased yield. For example, high initial concentration of Ca usually indicates effective carbonation (Johnson, 2000). In this work, quantitative elemental analysis of the input materials was performed by X-Ray fluorescence (XRF) spectrometry.

During XRF analysis, each individual element of a particular sample emits a characteristic x-ray radiation with discrete energy. The latter could be quantified by measuring the relative intensity, and by using appropriate software the % concentration of each element can be determined.

The biggest advantage of XRF in terms of elemental analysis is the simple preparation required for the analysed samples. In this study, 10 grams of dried material were mixed with 2.5 gr of CEREOX Licowax C Micropowder inside medium size bags. Then, the mixtures were taken to a press to become homogeneous pellets, and the formed pellets were analysed by an XRF spectrometer Bruker S4 Explorer.

The device generated x-rays from a rhodium source operating at 50 kV nominal high voltage and 50 mA nominal current. The pellets were analysed for 15 min and the data interpretation was done by using the software Specrta plus (version 2.0.28). Finally, the loss of ignition (LOI) was estimated by the difference between 100% and the sum of the measured concentrations of each identified element.

3.3.3 X-Ray Diffraction

Similarly to chemical composition, the mineralogy of a candidate residue determines the final CO_2 uptake. Reactive mineral phases such as calcite, lime and portlandite promote the reaction rate, while other mineral phases such as anhydrite have an neutral effect upon the carbonation yield (Gunning et al., 2010b).

X-Ray Diffraction (XRD) is the ultimate technique for analysing crystalline phases in solid samples. During the analysis a sample is illuminated with x-rays of a fixed wave-length and the intensity of the reflected radiation is recorded using a goniometer. The data is then analysed for the reflection angle and estimation of the inter-atomic spacing (D value in Angstorm units 10^{-10} m). The intensity is measured to discriminate the various D spacings and the results are to identify possible matches.

Pressed powder tablets were prepared for quantitative XRD analysis. The un-treated and treated materials were ground to around 40 microns by using an agate mortar and pestle. The received powders were then pressed into silica sample holders and with the aid of a glass side a smooth surface was created.

The analysis was performed on a Bruker D8 Advance, fitted with a Siemens K710 generator running at 40kV voltage and 40mA current and a copper anode. The tablets were analysed between 5-65° 2θ in 0.02° steps each lasting 0.4 seconds.

The generated diffractograms were interpreted by using DIFFRACplus EVA software (Bruker AXS). The X-ray fluorescence data import function in EVA was used to filter the phase-database to aid identification. As carbonation results in both the consumption and the growth of new minerals, a shift in peak heights of the phases can be observed. DIFFRACplus EVA allows one trace to be subtracted from another; hence any differences in peak heights can be readily observed.

3.3.4 Total Organic Carbon Analysis

CO_2 uptake represents the amount of carbon dioxide that has been absorbed by the products during carbonation and it is used for the quantification of the reaction yield. The CO_2 uptake can be measured by using total organic carbon analysis (TOC), which estimates the concentration of total organic carbon in a specific mixture.

In this study, a TOC analyser consisting of two modules was utilised: the IL 550 TOC-TN module used for analysing liquid samples and the HSC1300 module for the analysis of solids samples. The HSC1300 module incorporates a high temperature furnace where the solid samples are burnt and release their carbon content. The selected operating parameters of the furnace were: furnace temperature=1253 K, pressure=0.4 MPa, maximum integration time =180 sec and stability= 7.

Prior to analysis a calibration curve was required. Any compound decomposing below 1273 K can be used as the calibration medium. In this analysis calcium carbonate was the chosen medium due to its large availability and low cost. For the generation of the curve, 6 calibration standards of $CaCO_3$ with different weights ranging from 0-50 mg (0 mg, 10 mg, 20 mg, 30 mg, 40 mg, and 50 mg) were analysed in the furnace. The validation of the curve was performed by analysing triplicates of $CaCO_3$ with known carbon concentration (120000mg/kg) and the measured carbon concentrations were compared with the known value. The same calibration curve was used for consequent measurements as long as the daily factor remained between 0.8-1.2. The daily factor expresses the change of status of the analyser from day to day due to different room temperature and pressure or different concentration of the incoming oxygen.

Between 25 mg and 50 mg of each un-treated and carbonated material were weighted in clean and dried ceramic tubes and then inserted into the furnace for around 4 min. The software (OmniToc) expressed the data as total carbon concentration and conversion to CO_2 concentration was done by multiplying the values obtained by the ratio of the atomic mass of CO_2 (44 gr) to atomic mass of C (12 gr).

3.3.5 Particles Size Distribution

The particles size was measured by wet laser diffraction analysis. Laser diffraction is based on the diffraction theory of Fraunhofer which states that the intensity of light scattered by a particle is directly proportional to its size. On the other hand, the angle of the laser beam and particle size have an inversely proportional relationship and thus, when the laser beam increases the particles size decreases and vice versa.

Particle size measurements were performed with a Mastersizer MS2000. The device was fitted with a wet sample delivery module (Hydro MU) which transports the material in suspension (in water), and a dry module (Scirocco 2000), which carries the sample in a stream of air. In this study all the analyses were done by using this method.

The tested materials were soaked in water for 24 hours and immediately before analysis, the dispersed sample was agitated by manual stirring, and added drop by drop to the sample holder on the wet module, until the degree of laser obscuration was between 10 and 20%. The circulating pump speed was set at 2500rpm, the refractive index (RI) of the material at 1.520, and the RI of water at 1.330.

3.3.6 Scanning Electron Microscopy

The method of scanning electron microscopy (SEM) produces images by scanning a specific sample with a focused beam of electrons. When the diffused electrons interact with the individual atoms of the samples they generate detectable signals which provide information about the surface topography and composition.

A few milligrams (between 2 mg to 5 mg) of the un-treated and treated materials were placed, with the aid of a small brush, on 12 mm spectro-carbon tabs and then upon stainless steel specimen studs with 32 mm diameter. The analysis was performed on a JEOL JSM-5310LV microscope equipped with an Oxford Instruments Energy Dispersive Spectrometer (EDAX).

The electron source operated at 20 kV nominal voltage and the sample surface was maintained at a working distance between 10 and 12 mm from the detectors to provide a balance between high resolution and depth of field. Images of the blocks were taken by using the backscattered electron (BSE) detector, coupled with chemical analysis using the EDAX. Oxford Aztec software was used for image acquisition and chemical analysis.

3.3.7 Variability and experimental error

To verify the reliability of the data set, each experiment was repeated three times. The variability of the final results was estimated by using two common statistical measures: standard deviation and standard error.

The dispersion of data around the mean was measured by using the standard deviation following the equation below:

$$\sigma = \sqrt{\frac{\sum\left(x - x_{mean}\right)^2}{N}} \tag{3.1}$$

Where

x: each experimental value
x_{mean}: the mean of the values
N: the number of values (3 in this study)

The level of dispersion of data from the mean was estimated by the standard error which is a function of the standard deviation and the number of the experimental values as shown in equation 3.2:

$$SE = \frac{\sigma}{\sqrt{3}} \qquad (3.2)$$

In the following chapter magnesium hydroxide and calcium hydroxide were carbonated via different carbonation techniques and the achieved CO_2 uptakes were recorded. Also, non-standard cylinders of Mg/Ca were formed and their physical properties were measured.

4 ACCELERATED CARBONATION OF MAGNESIUM HYDROXIDE

4.1 Introduction

The most common group of magnesium-based silicates is the serpentines, which usually contain up to 40% magnesium ions in the form of MgO. The direct carbonation of serpentine leads initially to the formation of $Mg(OH)_2$ and subsequently to $MgCO_3$. However, under mild temperatures and pressures the conversion rate of $Mg(OH)_2$ into $MgCO_3$ is low as a result of thermodynamic constraints that inhibits the reaction.

The main aim of this chapter was the testing of various carbonation techniques (summarised in Chapter 3) for increasing the carbonation reactivity of $Mg(OH)_2$. The applied techniques included carbonation under ambient temperature and pressure, carbonation with ultrasound, carbonation under pressure and water vapour carbonation. The yields obtained for magnesium hydroxide were compared with those for calcium hydroxide, which was used as the reference material. The effective conversion of $Mg(OH)_2$ into magnesium carbonate at moderate temperature, pressure and reaction time is necessary, for reducing the costs associated with mineral carbonation technology (MCT).

Also, a product development study was conducted by preparing non-standard demoulded cylinders (40 mm x 40 mm) of $Mg(OH)_2/Ca(OH)_2$ mixed at five different concentrations, in order to assess the possibility of producing monolithic products with added-value. The cylinders were cured with carbon dioxide for 7 and 28 days and their CO_2 uptake was estimated by Total Organic Carbon analysis (TOC).

The key mineral phases of the mixtures were identified by qualitative/semi-quantitative X-Ray diffraction and their compressive strength, bulk density and water absorption were determined by appropriate tests. Finally, the results were compared with the physical properties for normal-strength and lightweight concrete.

4.2 Materials and Methods

4.2.1 Materials

Three commercial grades of $Mg(OH)_2$ (Lehmann & Voss) and one grade of $Ca(OH)_2$ (Calcium hydroxide, 99%, extra pure, ACROS Organics™) were purchased for the purpose of this study.

Each grade of magnesium hydroxide was classified according to its particles size: 2 μm, 18 μm and 255 μm. Calcium hydroxide was used as the reference material due to its wide availability, simple mechanism, and its significant reactivity with carbon dioxide.

The input hydroxides were pure and received as fine powders and thus, no grinding or oven-drying was required before treatment

4.2.2 Methods

4.2.2.1 Ambient and Ultrasonic Carbonation

Carbonation under ambient conditions and carbonation with ultrasound were conducted in a similar experimental set up, which is shown in Figure 4.1 consisting of:

a) A CO_2 chamber where pure (99.9%) carbon dioxide was entered the system,
b) A rota meter to control the flow-rate,
c) An aspirator to humidify the incoming gas,
d) A water bath (Camlab, 150-300W) which can also generate an ultrasonic field 35 kHz containing up to 10 plastic tubes in series
e) A condenser to maintain a constant temperature

The reaction temperature and pressure were kept constant at T=293 K, p=0.1 MPa respectively, the carbon dioxide concentration (C_{CO_2}) was set at 100% and the flow-rate at 0.2 L/min.

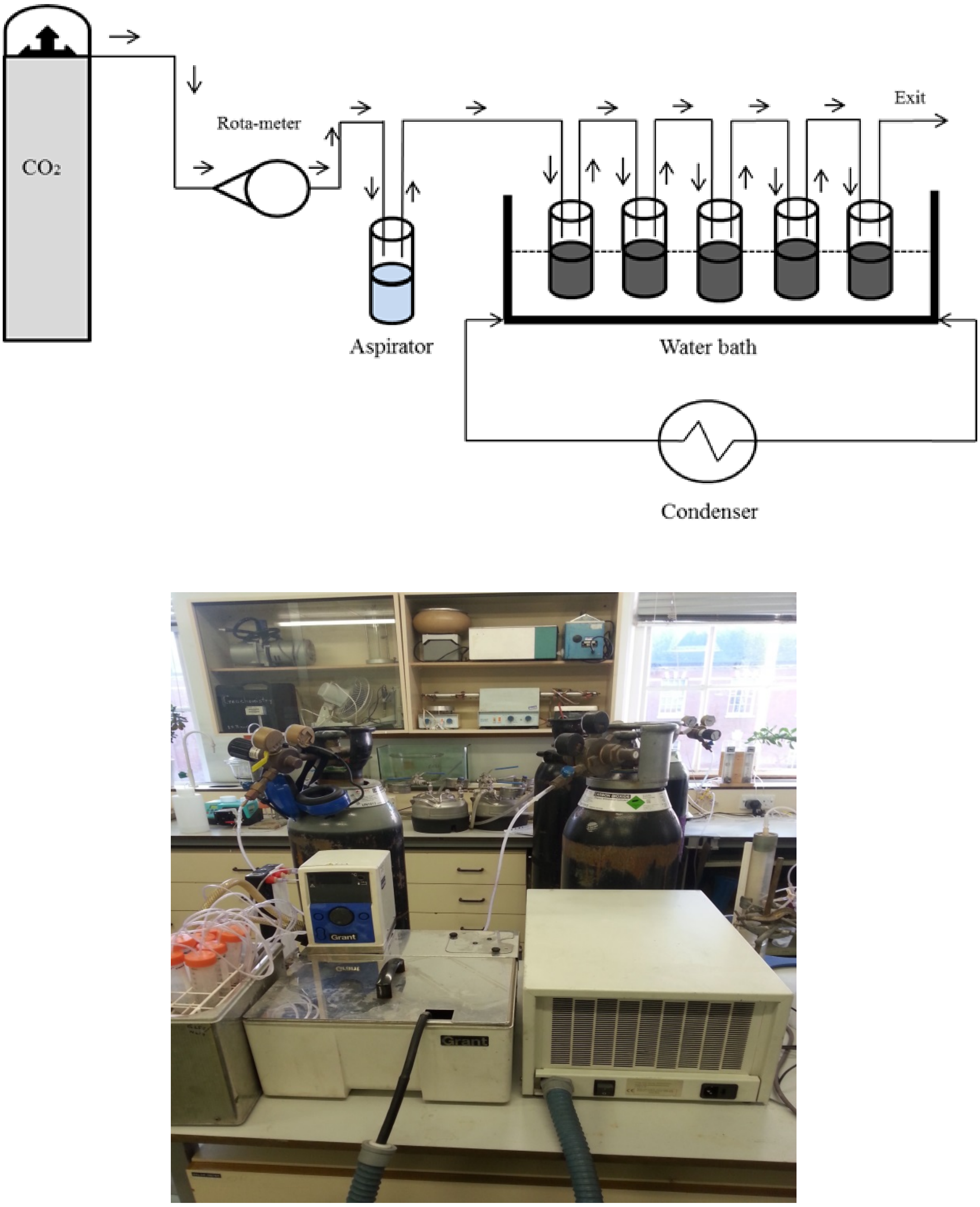


Figure 4.1: Schematic diagram and image of ambient /ultrasonic carbonation

4.2.2.2 Pressurised Carbonation

Experiments inside a pressurised chamber were conducted and the treatment time increased to 24 hours. Calcium hydroxide and the Grade 018 were carbonated by this technique. The apparatus is shown in Figure 4.2.

The samples were placed inside a pressure-tight reaction chamber containing a saturated salt solution to maintain constant humidity. The chamber was connected to a pressured-regulated supply of pure carbon dioxide. At the beginning of the experiment, the chamber was flushed with carbon dioxide to ensure that any air present was purged. The chamber was then pressurised, and the reaction proceeded in a static atmosphere, with pressure constantly maintained.

4.2.2.3 Water-vapour Carbonation

The last carbonation technique investigated was water vapour carbonation, where the reaction proceeded with the aid of steam. The treatment lasted 6 hours and the temperature was constantly measured during the experiment. The apparatus is shown in Figure 4.3. Carbon dioxide was bubbled through a flask of boiling water on a hotplate. Carbonic acid vapour exited the flask and passed through a reaction tube containing the calcium or magnesium hydroxide powder.

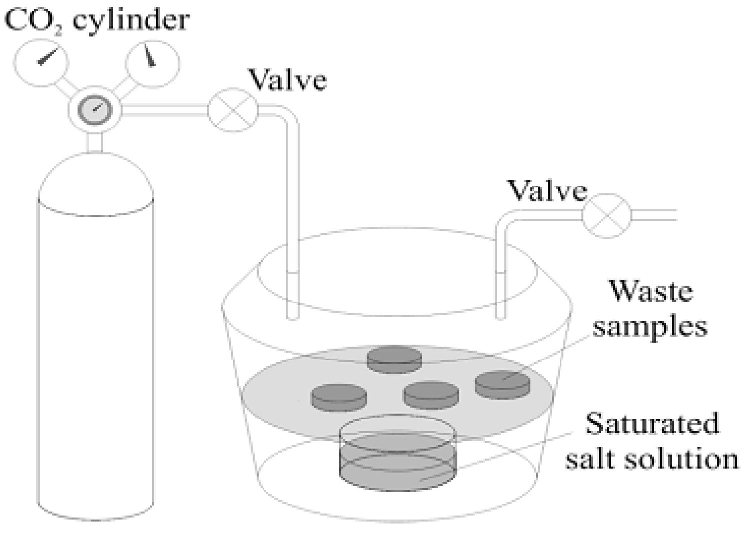


Figure 4.2: Schematic diagram of pressurised carbonation

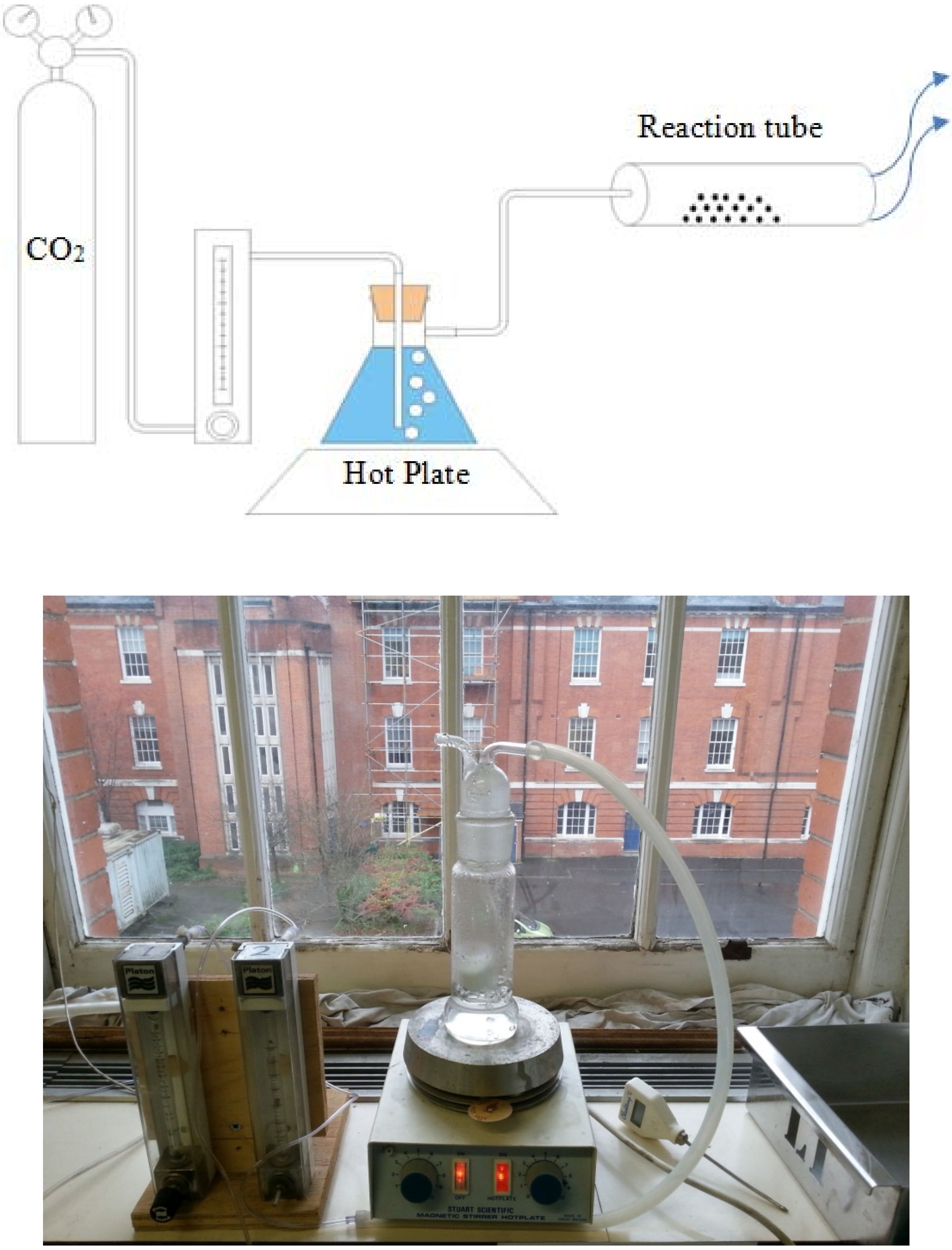


Figure 4.3: Schematic diagram and image of water vapour carbonation

4.2.2.4 Product Development

The possibility of producing monolithic products with added-value from Mg/Ca mixes was studied by preparing cylinders of wetted powders compacted into 40 mm diameter x 40 mm height moulds. The de-moulded cylinders were placed in a carbonation reaction chamber (see Figure 4.4). A continuous flow of humidified carbon dioxide gas passed through the chamber containing the cylinders, which were removed after 7 and 28 days, and their carbon dioxide uptake was measured.

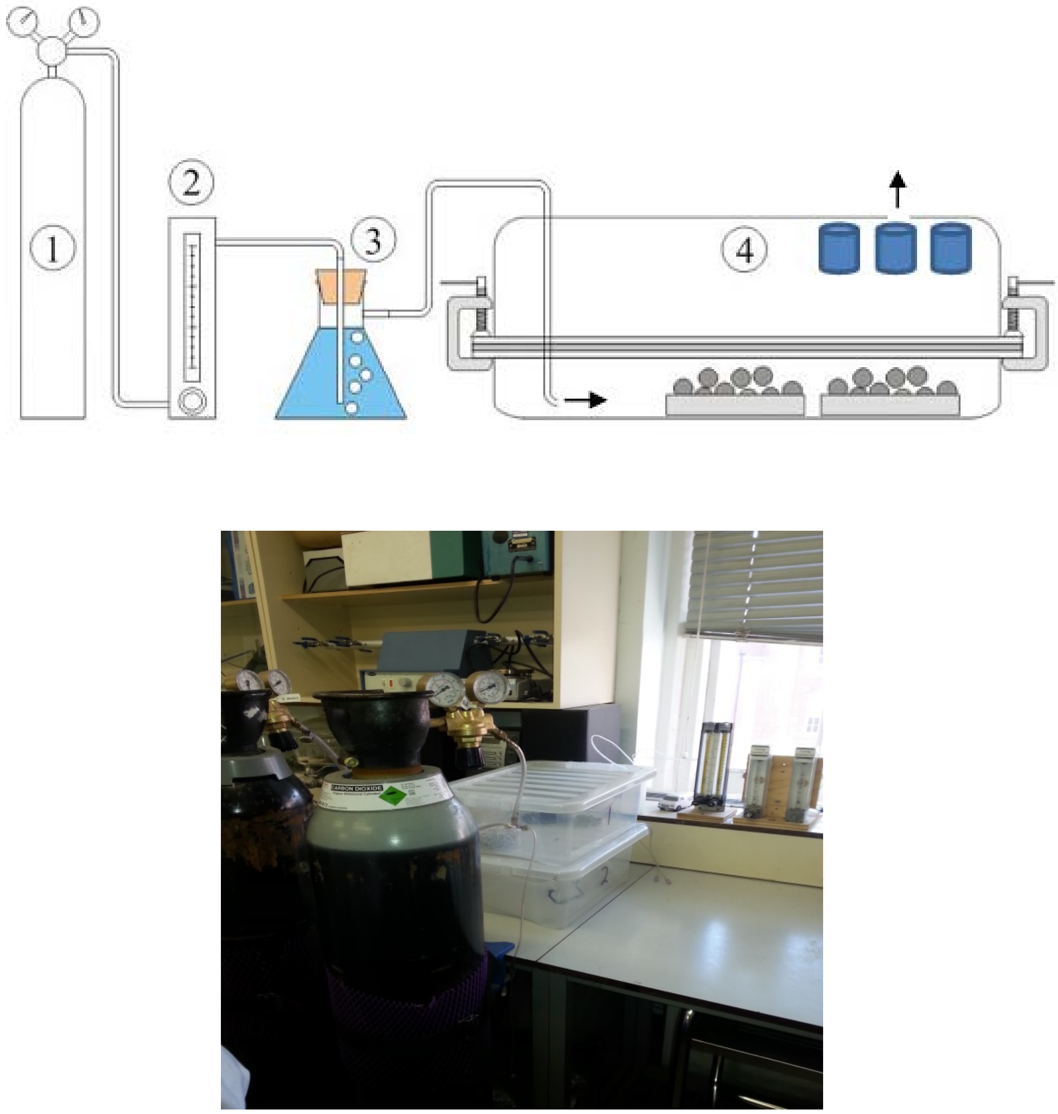


Figure 4.4: Schematic diagram and image of product curing

4.2.2.5 Bulk Density

After the curing period, the cylinders were weighted to an accuracy of 0.1% and their bulk density was estimated according to the active standard BS EN 12390-7:2000, following the equation below:

$$D = \frac{m}{V} \tag{4.1}$$

Where:

D: is the density of the specimen in kilograms per cubic meter (kg/m^3)
m: is the mass of the specimen in kilograms (kg)
V: is the volume of the specimen in cubic meters (m^3)

4.2.2.6 Compressive Strength

The method to determine the compressive strength of the cylinders was based on the active standard BS EN 12390-3:2002, following the equation below:

$$f_c = \frac{F}{\pi r^2} \tag{4.2}$$

Where:

fc: is the compressive strength, in megapascals (MPa)
F: is the fracture load, in newtons (N)
πr^2: is the cross section of the cylinder in mm^2

The cylinders were crushed and the fracture load was measured with a hand-held force meter (Mecmesin MFG250).

4.2.2.7 Water Absorption

The water absorption of the de-moulded cylinders was estimated according to the active standard BS EN 1097-6:2000.

The cylinders were oven dried at 378 K for 24 hours and their dry weight was recorded (M2). A pyknometer was overfilled by adding water and the cover was placed on top without trapping air in the vessel. Half of the contained water was removed and the dried cylinders were placed inside. The vessel was refilled with water, tapped to remove entrapped air and left sealed for 24 hours. The following day the specimens were taken out, placed on a dry cloth and weighted (M1).

The water absorption (as a percentage of the dry mass) after immersion for 24 hours was estimated according to the following equation:

$$WA_{24} = \frac{100 * (M1 - M2)}{M2} \tag{4.3}$$

Where:

M1: is the mass of the dried specimen (gr)
M2: is the mass of the oven-dried specimen (gr)

4.2.2.8 CO_2 Uptake

The CO_2 uptake of the treated materials (expressed as % CO_2 uptake by weight) was directly measured by Total Organic Carbon analysis as described in the previous chapter.

4.2.2.9 Materials Characterisation

The input materials were analysed by quantitative X-ray florescence to determine their chemical composition and the mineral composition of the de-moulded cylinders was studied by qualitative/ semi-quantitative X-ray diffraction. The experiments repeated three times and the error bars represent the standard error of the mean.

4.2.2.10 Variability and experimental error

Each experiment was repeated three times and the variability of results was estimated by using standard deviation and standard error of the mean. The latter represented the error bars in the following graphs.

4.3 Results

4.3.1 Elemental Analysis

The chemical composition of the input materials is shown in Table 4.1.

Table 4.1: Major oxides composition (% w/w)

	MgO	SiO_2	SO_3	Fe_2O_3	Cl	CaO	Al_2O_3	LOI
G002	97.96	0.19	0.31	0.08	0.23	0.99	0.19	0.1
G018	99.23	0	0.1	0.02	0.58	0	0	0.1
G255	82.31	12.8	0	0.49	0	3.61	0.61	0.1
$Ca(OH)_2$	0.25	0.3	0	0.06	0	99.2	0.08	0.1

The input grades of magnesium hydroxide contained 82%-98% of magnesium oxide. The most impure grade (G255) comprising 12.8% of silica and concentration of calcium oxide at 3.6%. Calcium hydroxide composed almost exclusively of calcium oxide (99.2%).

4.3.2 Carbonation under Ambient Conditions

Samples of $Mg(OH)_2$ and $Ca(OH)_2$ were carbonated for 1 hour under ambient temperature and pressure using the apparatus shown in Figure 4.1. An image of the same apparatus is shown in Figure 4.5. For both hydroxides, one low, two intermediate and one high water-to-solid (w/s) ratio were chosen (0.2, 1, 10, and 100), in order to examine the reaction efficacy at different water concentrations. The recorded CO_2 uptakes of magnesium and calcium hydroxide at the selected w/s ratios are shown in Figures 4.6 and 4.7.

The CO_2 uptake of all the three grades of magnesium hydroxide was significantly lower than calcium hydroxide across all the tested w/s ratios. The highest CO_2 uptake obtained for $Ca(OH)_2$ was 25% at 0.2 ratio, while the uptake of $Mg(OH)_2$ at the same w/s ratio was 3% for the grade with the coarsest particles (Grade255). The yields of the other grades were less than 0.5%.

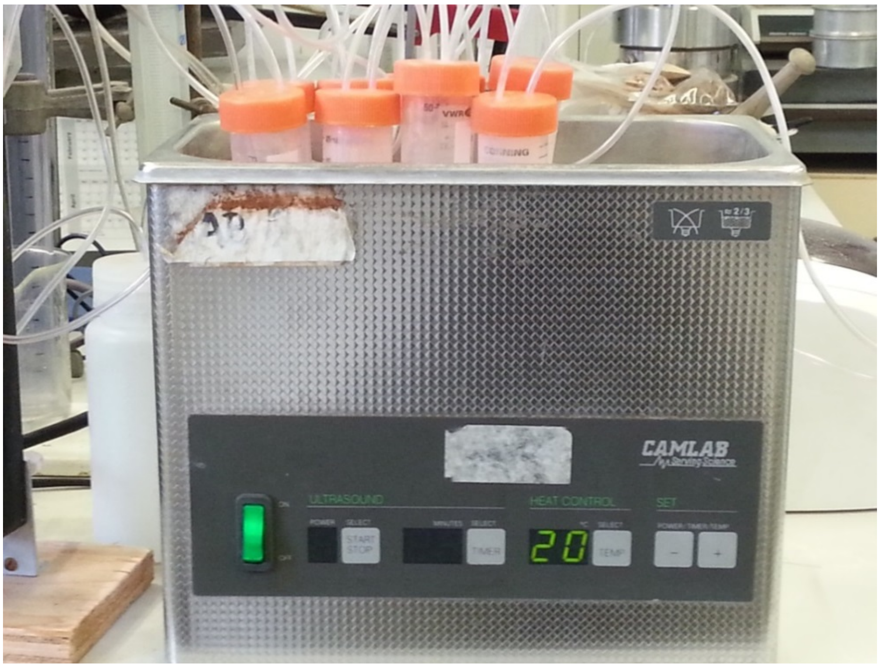


Figure 4.5: Image of ultrasonic bath

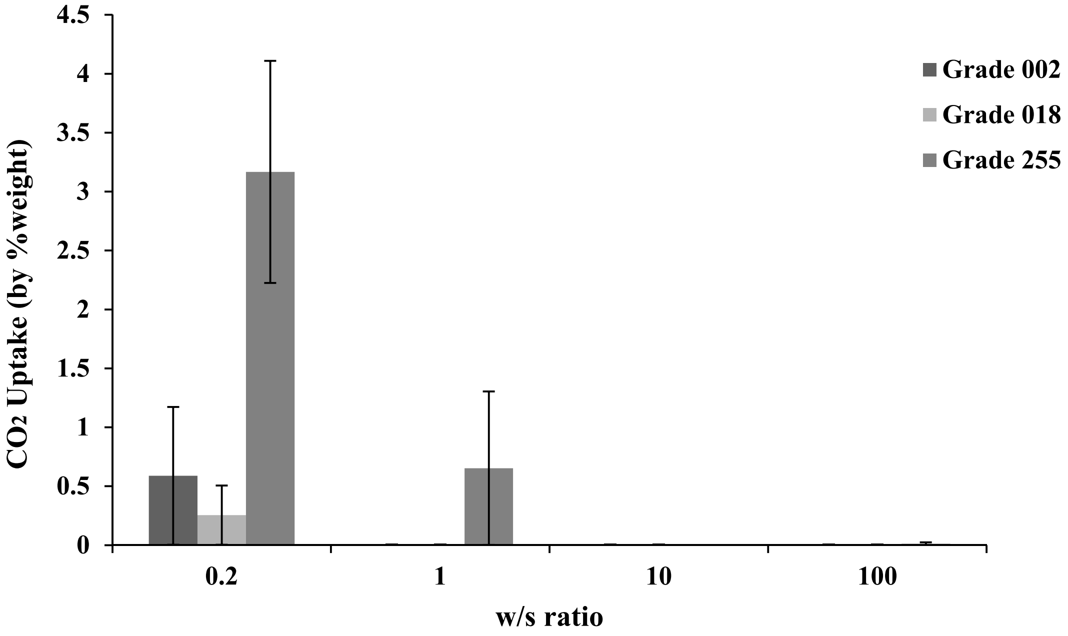


Figure 4.6: CO_2 uptake for $Mg(OH)_2$ under ambient carbonation

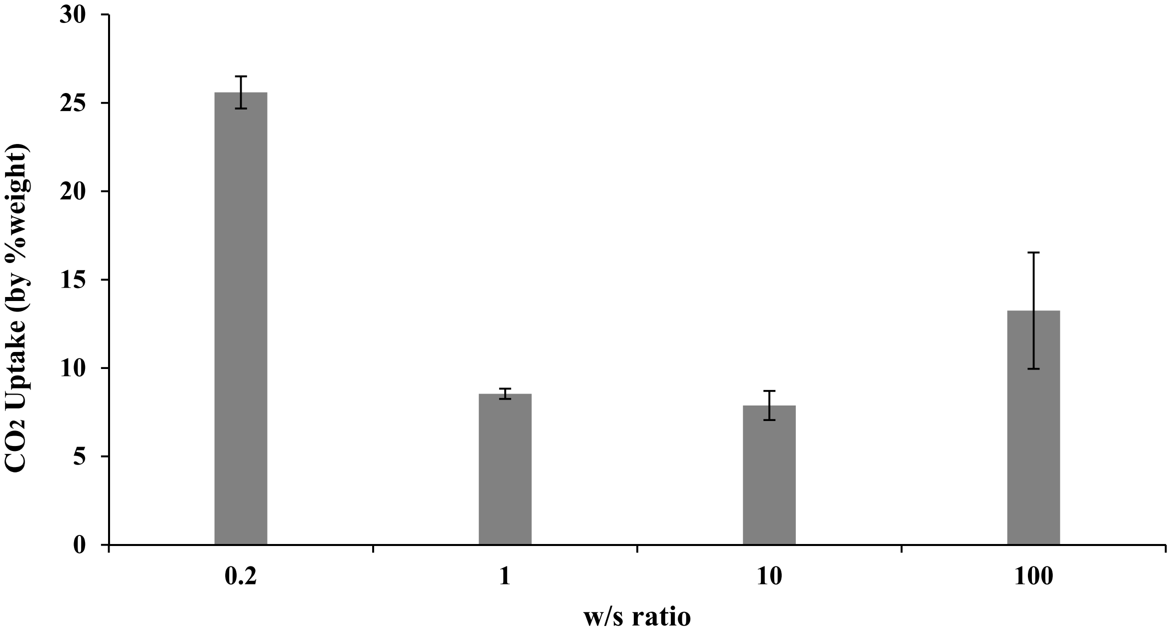


Figure 4.7: CO_2 uptake for $Ca(OH)_2$ under ambient carbonation

4.3.3 Carbonation with Ultrasound

The experiments of the previous section were repeated under the presence of an ultrasonic field (35 kHz). Again, the recorded CO_2 uptake of magnesium hydroxide was considerably lower compared to calcium hydroxide.

The grade with the middle size particles (Grade 018) gave the highest CO_2 uptake (3.5%) at w/s=100. The grade with the least coarse particles (Grade 002) gave 2.5% uptake at w/s=0.4, while the Grade 255 was more reactive, similarly to the Grade 018, at high w/s ratio (100). On the other hand, the reactivity of $Ca(OH)_2$ was high at low w/s ratios (between 0.2-0.6) and the largest measured CO_2 uptake was 29% at 0.4 w/s ratio.

The results for both materials are shown in Figures 4.8 and 4.9. Figure 4.9 is characteristic of the change of CO_2 uptake across different w/s ratios. At dry conditions (0.2-0.6) the uptake reached a peak and then decreased gradually until w/s =10 where it started to rise again. This trend is attributed to the amount of water in each w/s ratio region and is explained in more detail in the discussion section.

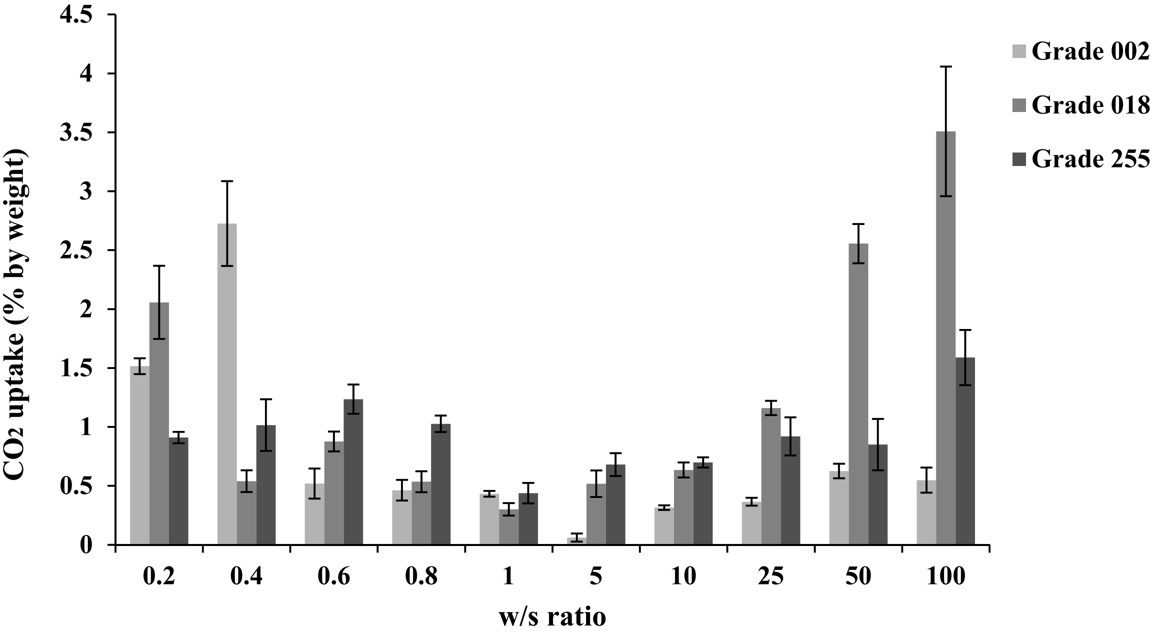


Figure 4.8: CO_2 uptake for $Mg(OH)_2$ under carbonation with ultrasound

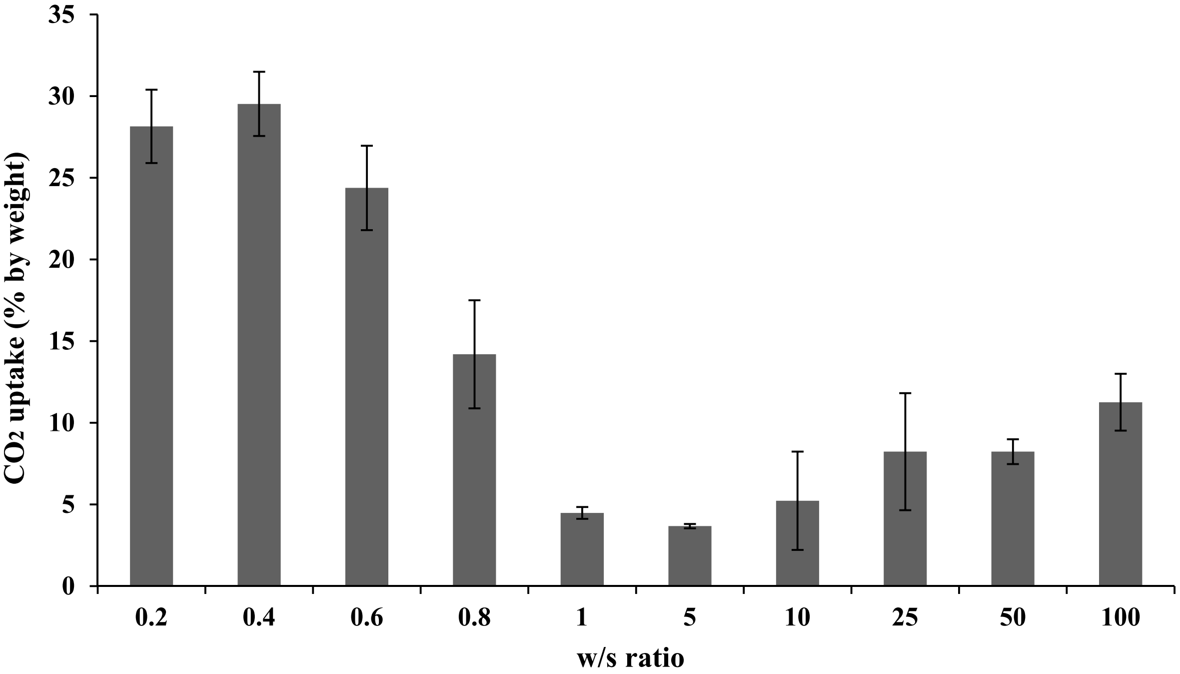


Figure 4.9: CO_2 uptake for $Ca(OH)_2$ under carbonation with ultrasound

4.3.4 Pressurised Carbonation

The 1 hour treatment of $Mg(OH)_2$ under ambient temperature and pressure proved insufficient for achieving high CO_2 uptake. Also, low yields were recorded after carbonation with ultrasound. For this reason, experiments inside a pressurised chamber were conducted and the reaction time increased to 24 hours. The selected w/s ratios ranged from 0.2 to 10.

The elevated conditions resulted in higher uptake for both $Mg(OH)_2$ and $Ca(OH)_2$. The former showed the highest reactivity (25% uptake) at w/s ratio=0.4 while the latter gave 45% uptake at the same ratio. The results for magnesium and calcium hydroxides are shown in Figures 4.10 and 4.11 respectively.

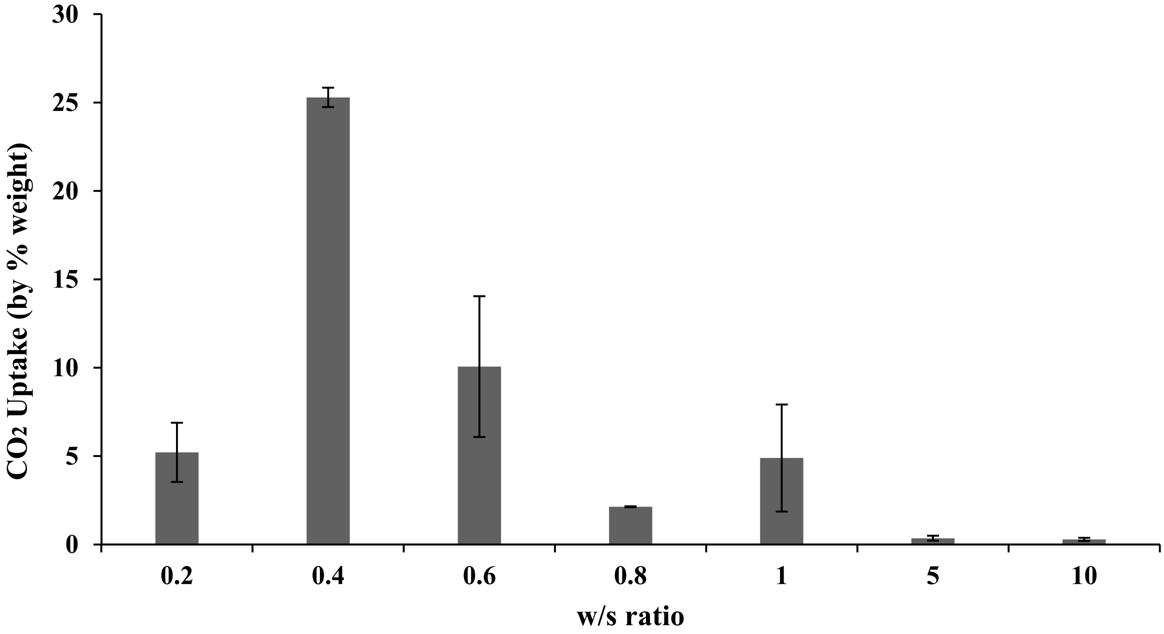


Figure 4.10: CO_2 uptake for $Mg(OH)_2$ under pressurised carbonation

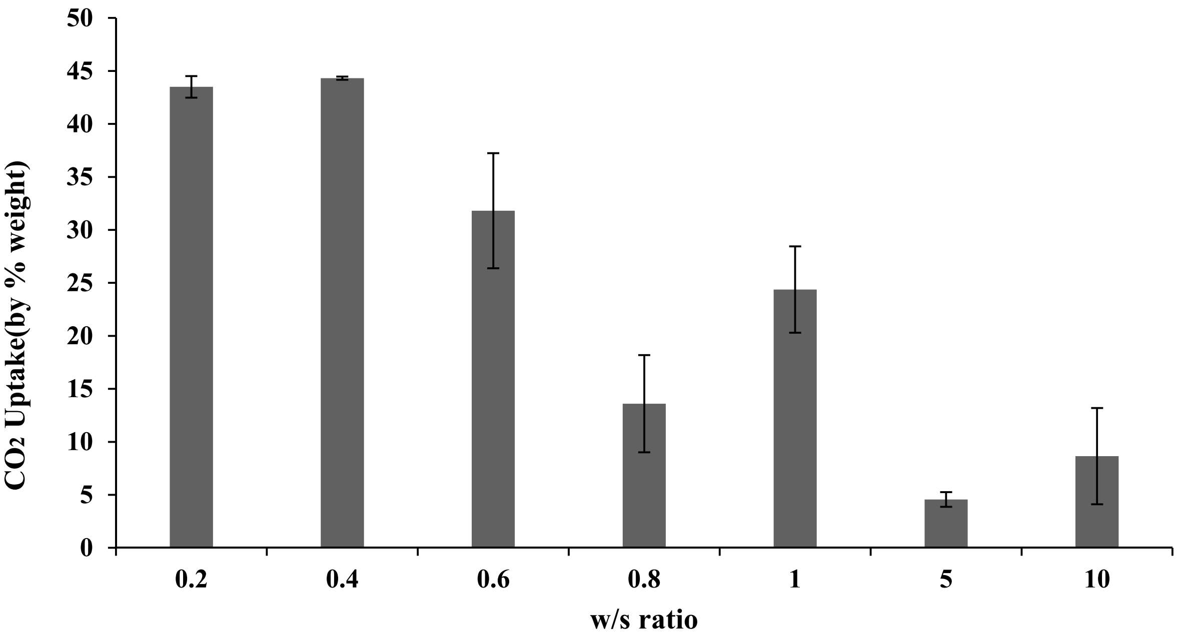


Figure 4.11: CO_2 uptake for $Ca(OH)_2$ under pressurised carbonation

Figure 4.12: Apparatus for pressurised carbonation

4.3.5 Water Vapour Carbonation

The final technique was carbonation with steam and the CO_2 uptake was measured after 6 hours of treatment. The results are shown in Figure 4.13. The yields recorded were lower compared to the previous carbonation methods, due to the great saturation of the samples, which inhibited the diffusion of CO_2 into the system.

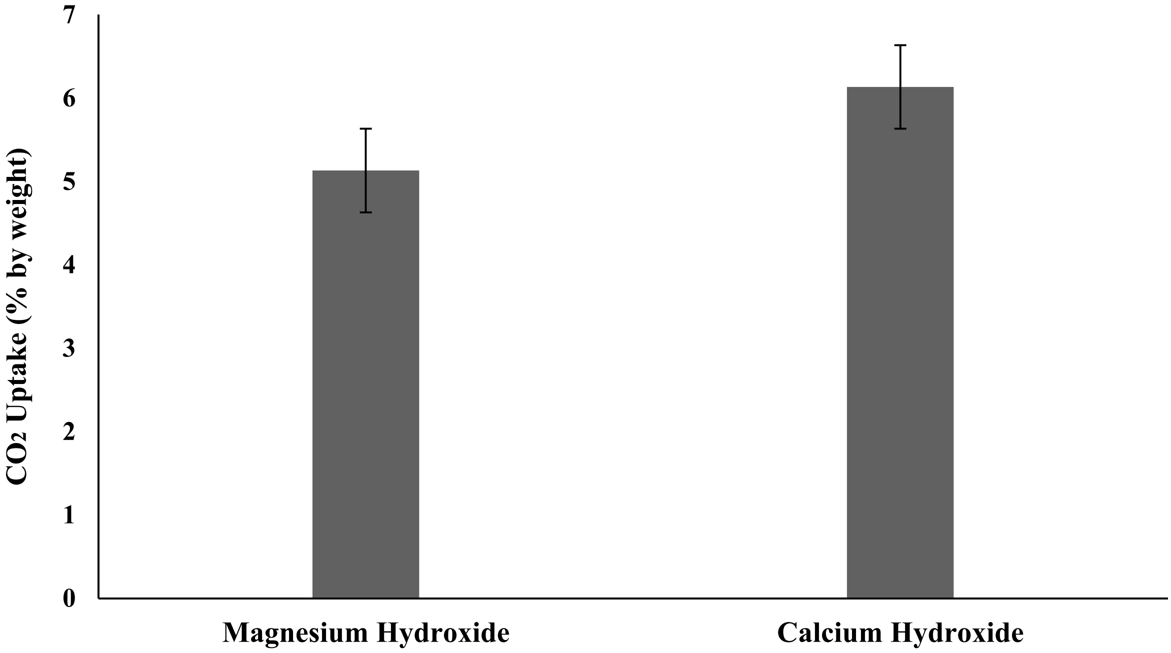


Figure 4.13: CO_2 uptakes of $Mg(OH)_2$ and $Ca(OH)_2$ in water vapour

4.3.6 Product Development

The possibility of producing monolithic products from $Mg(OH)_2$/$Ca(OH)_2$ mixtures was examined by mixing wetted powders of both hydroxides at different concentrations and compacted into 40 mm diameter moulds (40 mm height) as shown in Figure 4.14. The selected concentrations represented moulds of pure $MgOH_2$, pure $CaOH_2$ as well as three standard mixtures of both hydroxides to examine the change of CO2 uptake with the continuous addition of calcium into the mixes.

Five mixes were prepared:

- Mix 1= 100% $Mg(OH)_2$
- Mix 2= 75% $Mg(OH)_2$ + 25% $Ca(OH)_2$
- Mix 3= 50% $Mg(OH)_2$ + 50% $Ca(OH)_2$
- Mix 4= 25% $Mg(OH)_2$+ 75% $Ca(OH)_2$
- Mix 5= 100% $Ca(OH)_2$

Figure 4.14: Image of cured cylinders

The de-moulded cylinders were cured in dry CO_2 for 7 and 28 days and their CO_2 uptake was measured. The curing conditions were: 293 K and 0.1 MPa. The CO_2 uptakes after 7 and 28 days of curing are shown in Figures 4.15 and 4.16.

After 7 days the highest CO_2 uptake was achieved by the 100% Ca mix at 35% and the lowest by the 100% Mg at 11%. However, after 28 days the achieved CO_2 uptake of the 100% Mg mixture increased by up to three times (30%) and it was close to the uptake measured for the 100% Ca (35%).

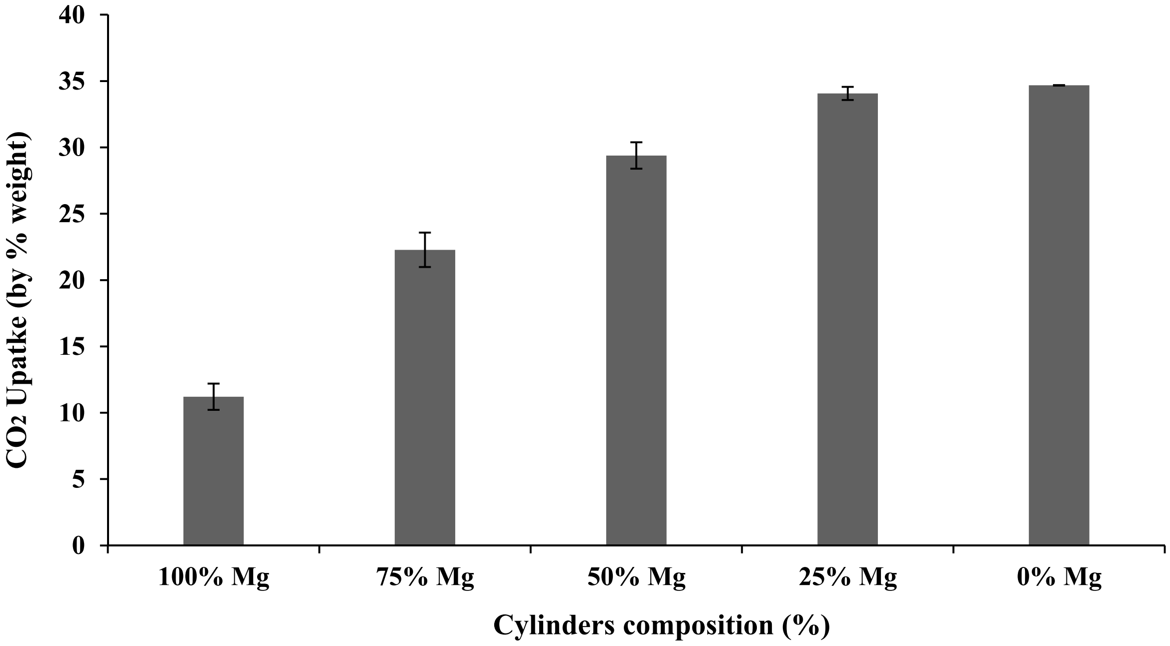


Figure 4.15: CO_2 uptake of cylinders after 7 days of curing

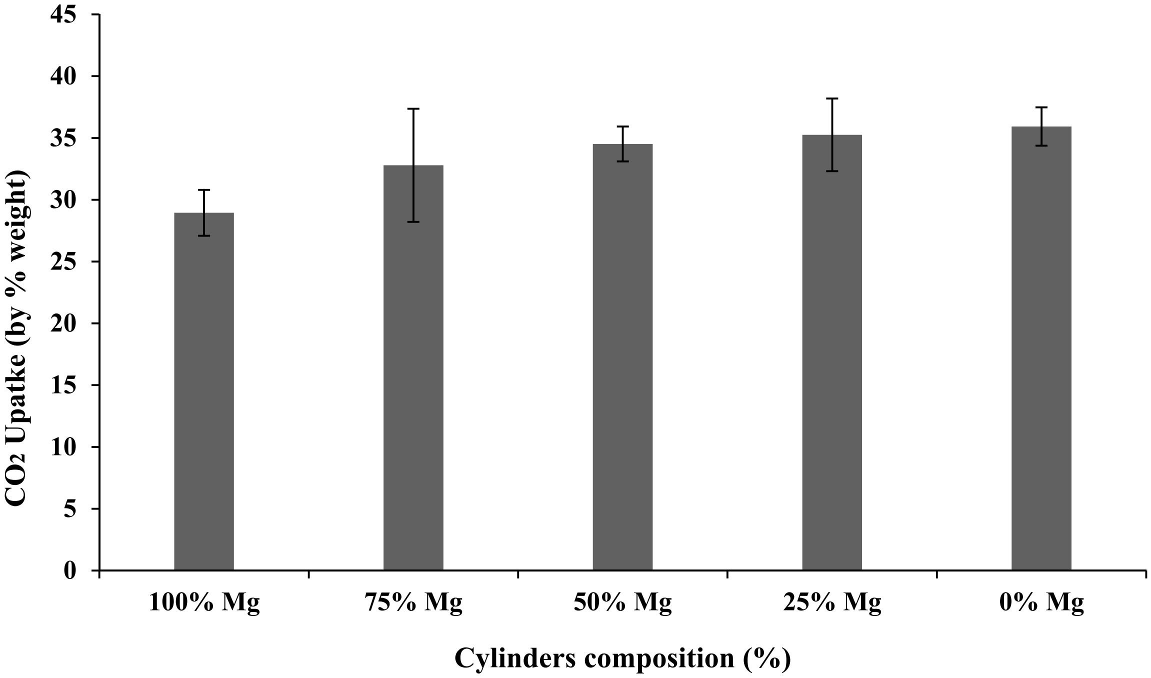


Figure 4.16: CO_2 uptake of cylinders after 28 days of curing

4.3.7 Mineral Phase Analysis

The mineralogy of the cylinders after curing in CO_2 was studied by X-Ray Diffraction (XRD) and the key mineral phases identified are presented in Table 4.2. Hydromagnesite, a hydrated magnesium carbonate mineral, was found in the 100% Mg and 75% Mg mixes, while nesquehonite was found in the 100% Mg mixes after 28 days of curing only. Magnesite was not identified in any of the examined specimens.

Table 4.2: Key mineral phases identified by XRD

Phase	MIX 1			MIX 2			MIX 3			MIX 4			MIX 5		
	0	7	28	0	7	28	0	7	28	0	7	28	0	7	28
Portlandite [$Ca(OH)_2$]				✓			✓	✓	✓	✓	✓	✓	✓	✓	
Calcite [$CaCO_3$]					✓	✓		✓	✓		✓	✓		✓	✓
Brucite [$Mg(OH)_2$]	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓			
Hydromagnesite [$Mg_5(CO_3)_4(OH)_2.4H_2O$]		✓	✓		✓	✓									
Nesquehonite [$MgCO_3.3H_2O$]			✓												

MIX 1 = 100% Mg
MIX 2 = 75% Mg+ 25% Ca
MIX 3 = 50% Mg + 50% Ca
MIX 4 = 25% Mg+ 75% Ca
MIX 5 = 100% Ca

4.3.8 Compressive Strength

The compressive strengths of the formed cylinders were measured and the results are shown in Figures 4.17 and 4.18. The 100% Mg mixes showed the highest compressive strength after 7 and 28 days (up to 4.2 MPa) of curing. The lowest strengths (up to 1.2 MPa) were recorded for the mixes of pure calcium hydroxide.

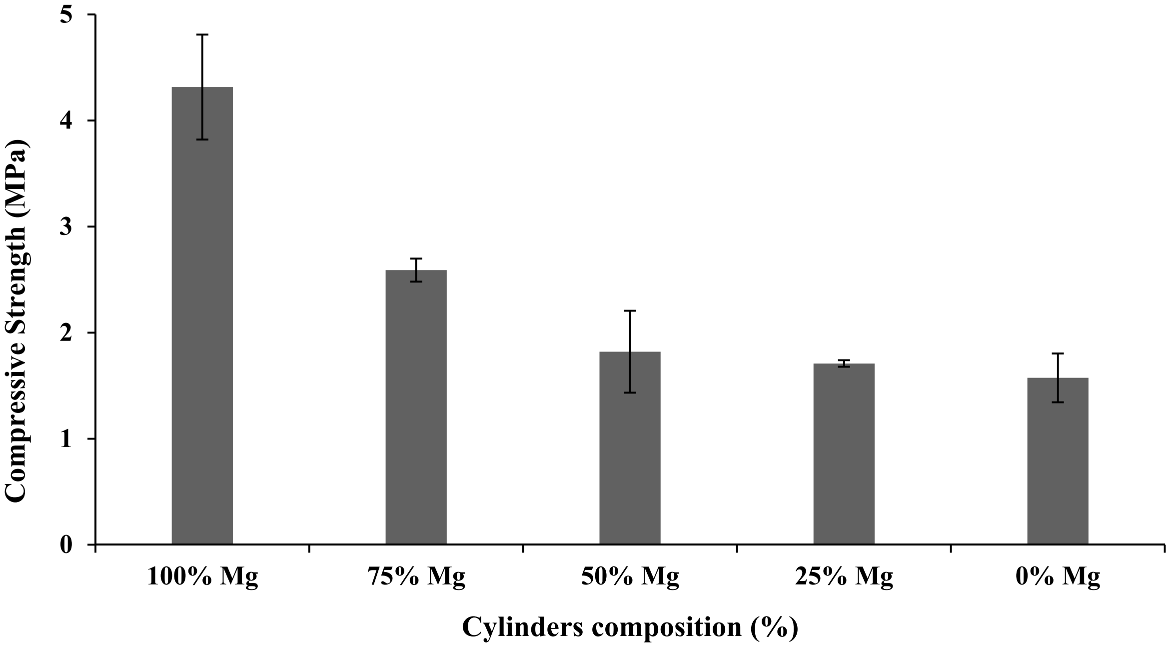


Figure 4.17: Compressive strength after 7 days of curing

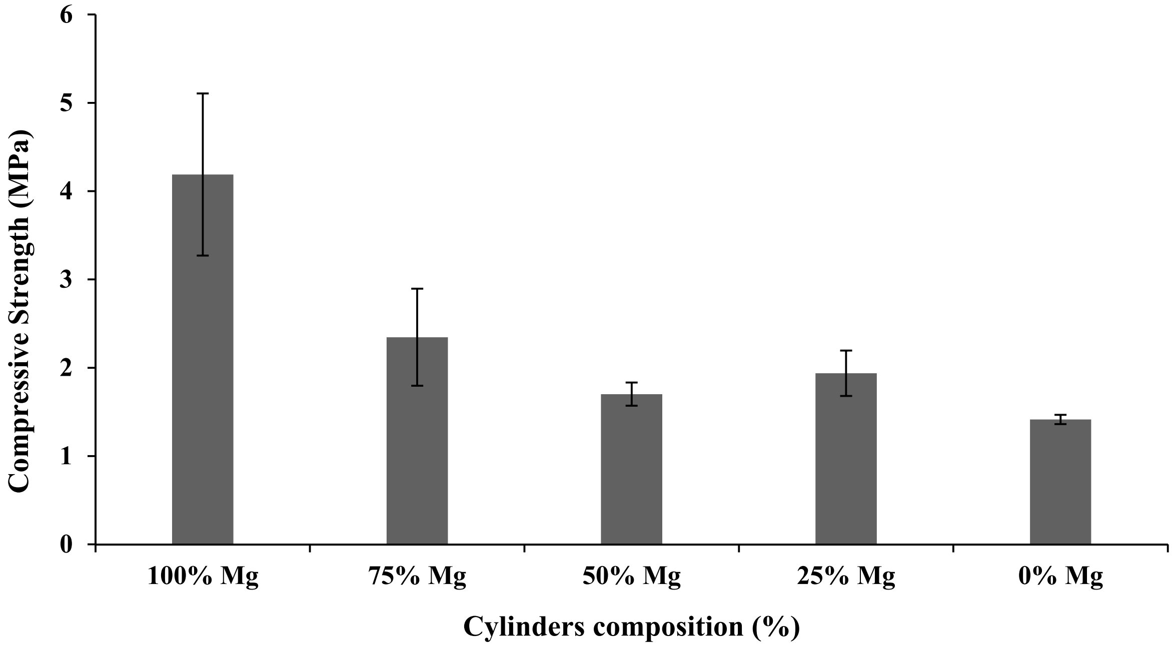


Figure 4.18: Compressive strength after 28 days of curing

4.3.9 Bulk Density

The bulk densities of the mixes are shown in Figures 4.19 and 4.20. After 7 days the highest density was given by the 100% Mg mix (1480 kg/m^3) and the lowest by the 100% Ca (922 kg/m^3). Similar results obtained after 28 days, when again the cylinders composed of pure magnesium gave the highest density at 1500 kg/m^3 and those of pure calcium the lowest at 1000 kg/m^3.

4.3.10 Water Absorption

Water absorption (as a percentage of the dry mass) after immersion for 24 hours of the tested cylinders is presented in Figures 4.21 and 4.22. The results suggested that the 100% Mg mixes had the lowest absorption (21.85%) and the 100% Ca the highest (52%-57%) after both curing periods.

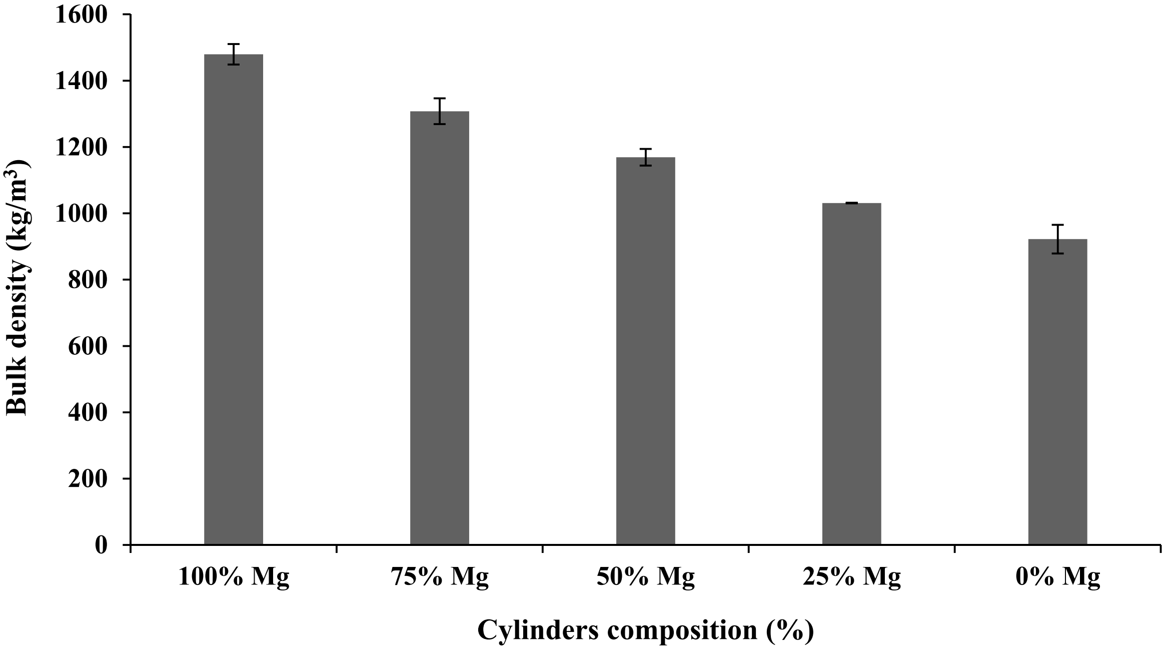


Figure 4.19: Bulk density after 7 days of curing

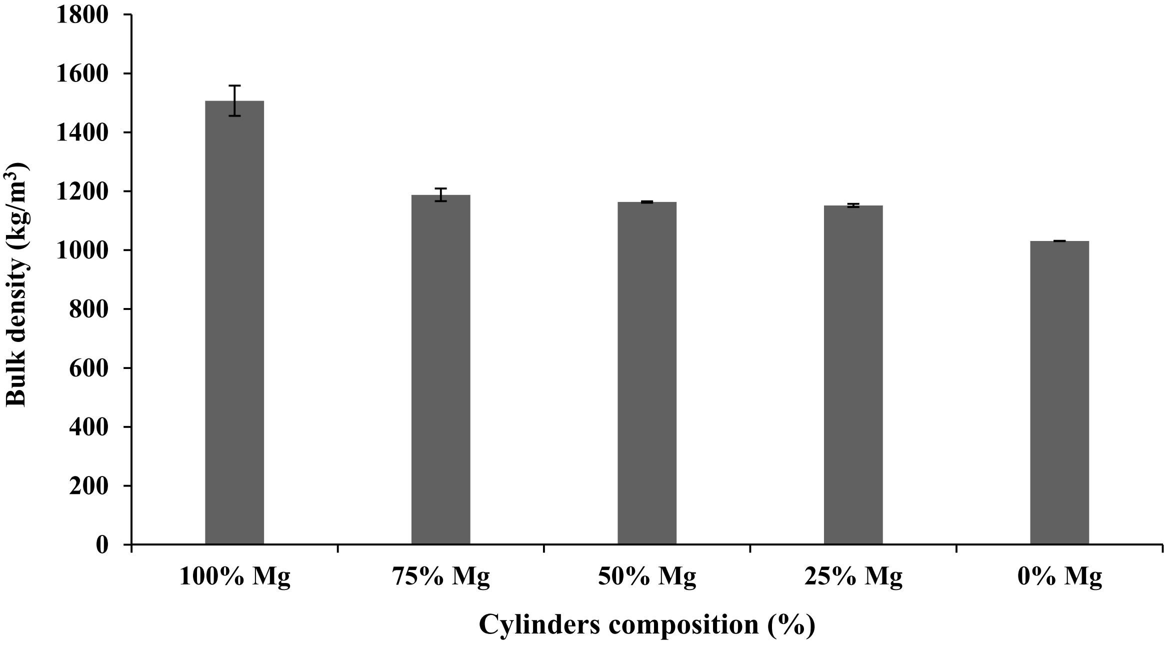


Figure 4.20: Bulk density after 28 days of curing

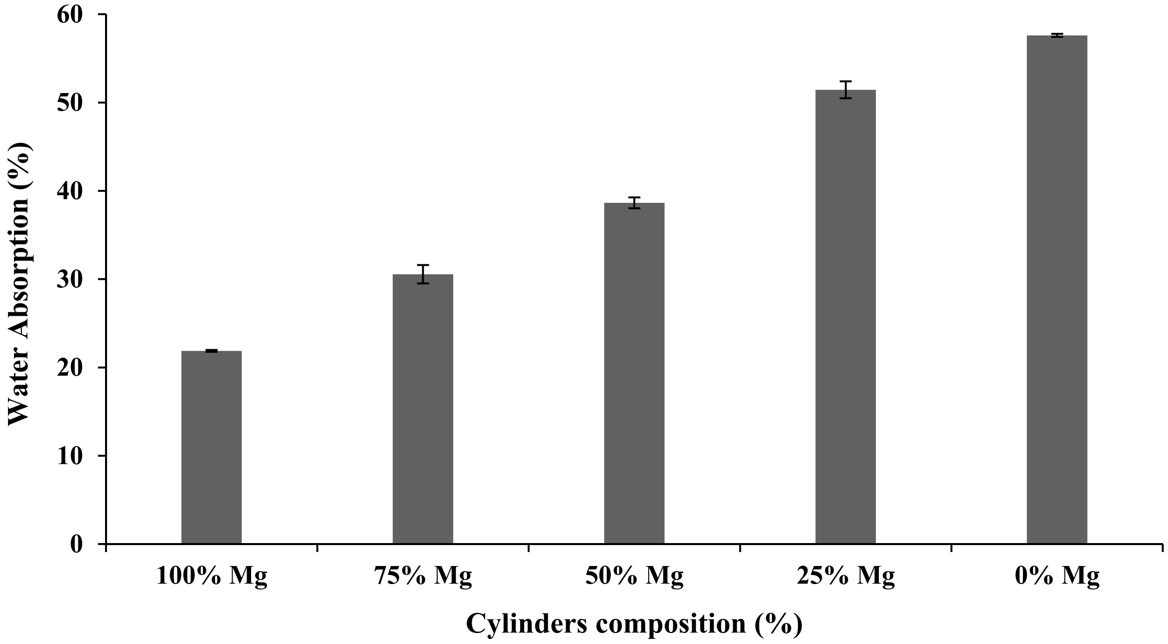


Figure 4.21: Water absorption (% w/w) after 7 days of curing

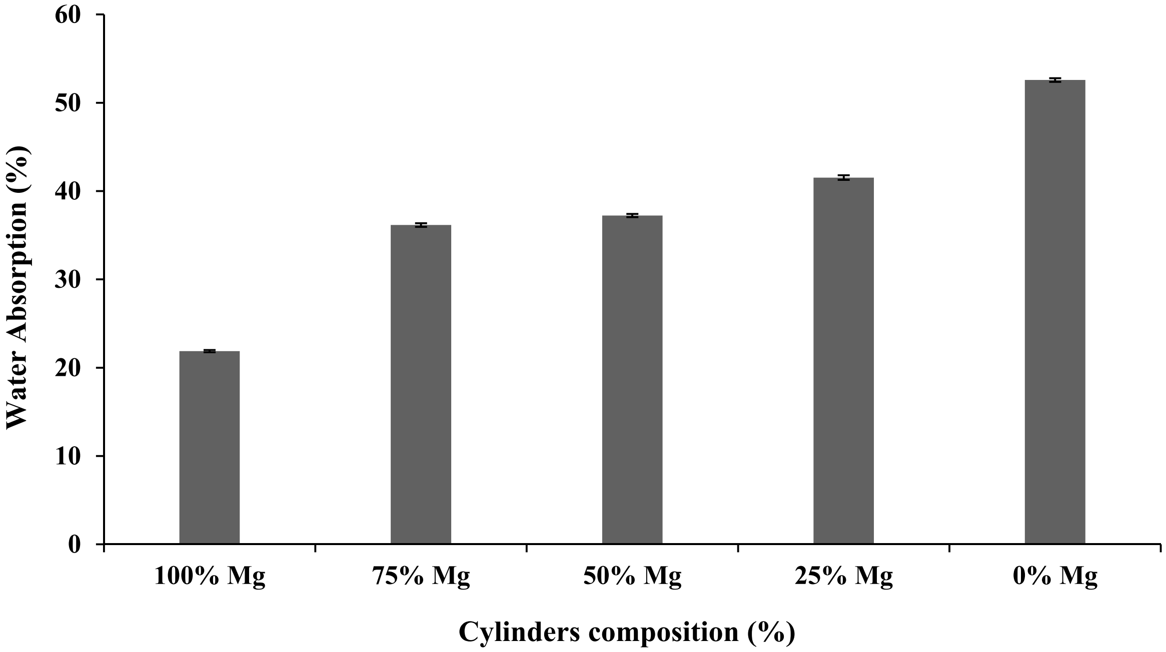


Figure 4.22: Water absorption (% w/w) after 28 days of curing

4.4 Discussion

4.4.1 Reactivity of Magnesium Hydroxide

4.4.1.1 Carbonation under Ambient Conditions

The CO_2 uptake of samples under ambient carbonation (Figures 4.6 and 4.7) showed that the reactivity of $Ca(OH)_2$ was considerably higher than the reactivity of $Mg(OH)_2$ for all the tested w/s ratios after 1 hour of treatment.

The samples of calcium hydroxide achieved a maximum uptake of 25% at a low water solid ratio (0.2), but also exhibited signs of increasing uptake at high ratio (100). At the intermediate ratios (w/s= 1 and 10) the reaction yield remained low (under 10%).

On the other hand, magnesium hydroxide showed only a small amount of CO_2 uptake (3%), and only at low ratio. The highest uptake was given by the grade with the coarsest particles (Grade 255). At intermediate and high w/s ratios the yields were very close to 0 and it seems that the diffused CO_2 did not pass into the bulk sample due to the lack of mechanical stirring or mixing.

The reactivity of $Mg(OH)_2$ at ambient temperature and pressure and rapid reaction time is low as a result of thermodynamic constraints that inhibit the reaction (Fagerlund et al., 2010). Effective conversion of magnesium hydroxide into magnesium carbonate requires elevated temperatures and pressures in the regions of 673-773 K and 2.85-8.2 MPa respectively (Fagerlund et al., 2011, Fricker and Park, 2013, Schaef et al., 2011). However, the handling/processing of minerals at elevated reaction conditions raises the associated costs considerably.

4.4.1.2 Carbonation with Ultrasound

Although ultrasound promoted the carbon uptake of both magnesium hydroxide and calcium hydroxide, the overall conversion of $Mg(OH)_2$ remained low.

$Ca(OH)_2$ combined with up to 30% by weight of carbon dioxide at the optimum w/s ratio of 0.4 (Figure 4.9). It is known from previous studies that accelerated carbonation is promoted under dry conditions (Asavapisit et al., 1997, Klemm and Berger, 1972). As the saturation of pores increased, the CO_2 uptake steadily decreased to a minimum, at w/s= 5. The diffusion of CO_2 was suppressed by the presence of water which caused pore-blocking (Li et al., 2006). However, the CO_2 uptake was then observed to rise again as the w/s ratio continued to increase. This characteristic change of yield across the different water contents has been observed repeatedly in the past, and has been attributed to the increased volume of water providing a large total capacity for carbon dioxide dissolution and hydration/ionisation.

The recorded yield for magnesium hydroxide was notably lower, than the yield for calcium hydroxide (Figure 4.8). The results showed that the 18 µm grade powder was the most reactive. This may be due to the combined effects of the larger surface area of the finer grade powder (Grade 002) facilitating the reaction and a grain size that is also not so fine as to inhibit gas diffusion. Reactivity was observed to be greater at w/s ratio greater than 10 and the maximum uptake achieved was 3.5%.

4.4.1.3 Carbonation under Pressure

During carbonation under pressure, the slightly elevated pressure (0.2 MPa) and the longer reaction time (24 hours) increased the reactivity of magnesium hydroxide significantly and the maximum CO_2 uptake was at 25.5%, at w/s ratio= 0.4 (Figure 4.10). As explained before, the carbon dioxide uptake was highly dependent upon the moisture content, and it was suppressed when the w/s ratio increased above 0.4. Similarly to $Mg(OH)_2$, the CO_2 uptake of calcium hydroxide increased with a maximum value at 44% at w/s=0.4 (Figure 4.11), compared to a maximum of 30%, achieved previously under ambient conditions.

Although the conversion rate of $Mg(OH)_2$ into $MgCO_3$ at elevated pressure increased, the long treatment time (24 hours) is a deterrent for the economically viable processing/handling of large amounts of minerals at large scale (Gunning et al., 2014).

4.4.1.4 Water Vapour Carbonation

Accelerated carbonation with steam did not enhance the reactivity of the input materials. The CO_2 uptake was lower than the uptake recorded during the previous carbonation techniques (Figure 4.13). This is likely due to the saturation of powders with water in the reaction tube, inhibiting the diffusion of carbon dioxide.

The effective carbonation of magnesium hydroxide is important, as it is the intermediate compound during the conversion of magnesium oxide into magnesium carbonate. MgO is the basic component of the magnesium-rich minerals olivine and serpentine, which are considered the largest available feed-stocks suitable for mineral carbonation. However, the results of this study showed that at moderate conditions the reactivity of $Mg(OH)_2$ is low. This is the main reason why the current average cost of mineral carbonation is estimated at USD100-120 per tonne of CO_2 (Araizi et al., 2013). A previous study suggested that the economically viable development of mineral carbonation at large scale, requires overall costs between USD20 and USD30 per tonne of CO_2 (Lackner, 2002).

4.4.2 Product development

4.4.2.1 CO_2 Uptake

The analysis of Figure 4.15 indicated that the yields were proportional to the concentration of calcium hydroxide in the mixes. The cylinders composed of pure $Ca(OH)_2$, gave the highest CO_2 uptake at 35%, closely followed by the 25% Mg cylinders, which took up 34% of CO_2. The carbon uptake for the 100% Mg mix was three times lower (11%), however, the CO_2 uptake given by the 75% Mg specimen was double, while the CO_2 uptake of the 50% Mg mix was 30%.

The yields after 28 days of curing suggested that the pure magnesium hydroxide cylinders bound more carbon dioxide compared to 7 days of curing (almost 30%). Also, the addition of calcium hydroxide in the mixes increased the CO_2 uptakes slightly (32% in the 75% Mg mix), while the 50% Mg, 25% Mg and 100% Ca mixtures did not seem to absorb a higher amount of CO_2.

4.4.2.2 X-Ray Diffraction

The key mineral phases identified in the cured cylinders were summarised in Table 4.2. The un-carbonated materials were found to be almost totally composed of either calcium hydroxide (portlandite) or magnesium hydroxide (brucite), as expected.

After 7 days of curing, the materials still contained these unreacted mineral phases, but showed the appearance of reaction products, including hydromagnesite (identified in the 100% Mg and 75% Mg mixes) and calcite (identified in the 75% Mg, 50% Mg, 25% Mg and 100% Ca cylinders). Hydromagnesite is a hydrated magnesium carbonate mineral with the formula $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$. It usually occurs in ultramafic rocks and serpentine or hydrothermally altered dolomite and marble (Minerology, 2005).

Hydromagnesite is a polymorph of magnesium carbonate with added-value as it can be used for commercial purposes. The most common industrial use of hydromagnesite is as a mixture of huntite as a flame retardant or fire retardant additive for polymers (Hollingbery and Hull, 2010, Hollingbery and Hull, 2012, Haurie et al., 2007, Haurie et al., 2006). Other commercial uses of this mineral is as an additive in paper filling or flame retardant in electrical and electronic parts (Montes-Hernandez et al., 2012).

After 28 days of curing, the concentration of calcite in the materials increased as can be observed by the relevant diffractograms. Whilst the 100% Mg cylinder retained a significant proportion of unreacted brucite, nesquehonite another hydrated magnesium carbonate mineral with the formula $MgCO_3.3H_2O$ was present in addition to hydromagnesite. The results suggested the complete absence of magnesite in the analysed specimens.

Magnesite is the most thermodynamically stable mineral form of $MgCO_3$ and the industrial uses of this mineral are similar to hydromagnesite. However, the precipitation of magnesite at low temperatures and pressures is restricted by the selective precipitation of hydrated products, mainly nesquehonite (Hänchen et al., 2008, Zhao et al., 2009, Kloprogge et al., 2003, Zhang et al., 2006). The key mineral phases identified in the 75% Mg mixes were calcite, hydromagnesite and un-reacted brucite, while the other two mixes (50% Mg and 25% Mg) composed primarily of calcite, un-reacted portlandite and brucite. Finally, the XRD analysis of the 100% Ca mix showed almost total conversion of portlandite into calcite.

4.4.2.3 Physical Properties

The analysis of Figures 4.17-4.20 suggested that the differences in compressive strength and bulk density of the mixes with the same composition were small after 7 and 28 days of curing.

The cylinders composed of pure magnesium hydroxide showed the highest strengths with an average value at 4.3 MPa. The addition of calcium hydroxide in the 75% Mg mix resulted in lower compressive strength (2.6 MPa), while strength continued to decrease with the increase of the concentration of $Ca(OH)_2$ in the mixtures. The lowest value was given by the 100% Ca cylinders at 1.5 MPa.

Similarly to compressive strength, the bulk density of the 100% Mg mixes was the highest (1500 kg/m^3 for 28 days of curing) and the density decreased with the addition of $Ca(OH)_2$ in the mixtures. Again, the lowest values were given by the 100% Ca cylinders at 920-1030 kg/m^3. The average measured compressive strengths, bulk densities and water absorptions are summarised in Table 4.3.

Table 4.3: Physical properties of the cured cylinders

MIX	Strength after 7 days (MPa)	Strength after 28 days (MPa)	Density after 7 days (kg/m^3)	Density after 28 days (kg/m^3)	Water absorption (%) after 7 days	Water absorption (%) after 28 days
100% Mg	4.3	4.3	1480	1500	21.85	21.85
75% Mg	2.6	2.6	1300	1300	36.0	30.5
50% Mg	1.8	1.8	1170	1160	38.5	37.0
25% Mg	1.70	1.9	1030	1150	51.5	41.5
0% Mg	1.55	1.40	920	1030	57.5	52.5

According to the British Concrete Society the compressive strength of normal concrete is between 20 and 40 MPa and its bulk density between 2250 and 2400 kg/m^3. In the case of lightweight concrete, the typical values are lower at 17-20 MPa for the strength and minimum 1200kg/m^3 for the bulk density (Bozkurt and Yazicioglu, 2010). Despite of the lower strength and density compared to normal and lightweight cement found in this study, the preliminary results are encouraging and future research should focus on the mixing of pure $Mg(OH)_2$ with additives/binders for increasing the hardness and density of the formed specimens.

Instead of using traditional binders such as ordinary Portland cement (Barnard et al., 2006) it would be reasonable to utilise alkaline waste residues, which are known to have a significant reaction with CO_2. Candidate residues comprising cement kiln dust, wood ash and paper ash as all of them have been successfully used for the production of sustainable lightweight aggregates (LWA) with improved physical properties (Gunning et al., 2009).

The water absorption of cylinders after immersion for 24 hours was significantly higher than the range for normal concrete of 1%-5% (Smith and Collis, 2001). The lowest values were recorded for the pure magnesium mixtures (21.85%) and the highest for the cylinders composed of pure calcium (52.5%-57.5%). Water absorption is an important physical property of concrete, as materials with high water absorption may result in increased susceptibility to freeze-thaw weathering (C.I.R.I.A, 2001).

4.5 Conclusions

The main aims of this chapter were to increase the reactivity of $Mg(OH)_2$ by using various carbonation techniques and to explore the possibility of producing monolithic products with added-value from magnesium/calcium based materials.

The achieved carbon dioxide uptakes for magnesium hydroxide after ambient, ultrasonic and water vapour carbonation were low compared to $Ca(OH)_2$. The findings were in accordance with previous studies, suggesting low conversion rate of this mineral into magnesium carbonate at low temperature, pressure and reaction time as a result of thermodynamic constraints.

On the other hand, carbonation in a pressurised system (0.2 MPa) and longer treatment time (24 hours) increased the reaction yield and the achieved CO_2 uptake was 25% at 0.4 ratio. However, the processing/handling of large amounts of minerals over a prolonged reaction time or at elevated temperature and pressure results in increased associated costs.

The results of a product development study suggested that after 7 days of curing the CO_2 uptake of the 100% Mg cylinders was lower compared to the cylinders composed of 100% Ca. However, the addition of calcium hydroxide in the 75% Mg mix increased the achieved carbon dioxide uptake by up to two times. The recorded CO_2 uptake of the 100% Mg mixtures after 28 days of curing increased considerably and the values obtained were similar to those of the 100% Ca mixes.

XRD analysis revealed the presence of hydromagnesite, a desirable hydrated polymorph of $MgCO_3$, in the 100% Mg and 75% Mg mixtures. Magnesite was not found in the carbonated products, as expected, as it is known from previous studies that under ambient temperature and pressure the precipitation of this mineral is inhibited by the selective precipitation of low-value hydrated mineral forms of magnesium carbonate, mainly nesquehonite. The latter was identified in the pure $Mg(OH)_2$ cylinders after 28 days of curing only.

The non-standard cylinders were subject to a testing of compressive strength, bulk density and water absorption (after 24 hours immersion) and the initial results were promising regarding the 100% Mg mixtures. Although the measured physical properties were inferior compared to normal and lightweight concrete, future research focusing on the application of alkaline waste residues as additives/binders, could lead the way to the formation of structures close to lightweight concrete.

In this chapter the topic of mineral carbonation was covered by carbonating samples of magnesium hydroxide. The next chapter explores the topic of waste carbonation technology by testing alkaline waste residues under ambient temperature and pressure and at various water concentrations.

5 ACCELERATED CARBONATION OF WASTE RESIDUES

5.1 Introduction

In chapter 2, the examination of seven alkaline industrial waste residues showed that they have potential to sequester up to 1 GTonne of CO_2 every year at relatively moderate reaction conditions and competitive costs. The main aim of this chapter was to validate the literature findings by carbonating samples of these residues and select the most reactive ones, for conducting further carbonation experiments with the aid of physical and chemical accelerators.

Air pollution control residues, bauxite residues, cement bypass dust, coal fly ash, MSWI bottom ash, and steel-making slags were carbonated under ambient temperature and pressure for 1 hour and at various w/s ratios. The achieved CO_2 uptakes were measured and compared with the theoretical maximum values derived from the Steinour formula.

Also, wollastonite, a mineral rich in calcium, was also carbonated under the same experimental conditions. The reference material used in this study was ordinary Portland cement type 1 (CEM 1) due to its wide availability and well-known carbonation mechanism.

The different reactivity of the input materials was explained by their initial concentration in calcium oxide and the mineral phases in which CaO was present. For this reason, elemental analysis was performed by using quantitative X-ray fluorescence and mineral phase analysis by qualitative/ semi-quantitative X-ray diffraction.

5.2 Materials and Methods

5.2.1 Materials

The input materials included alkaline industrial waste residues that are known to sequester high amounts of CO_2 at moderate reaction conditions and competitive costs (Araizi et al., 2013, Renforth et al., 2011, Kirchofer et al., 2013).

Air pollution control (APCr) obtained from Slough Heat and Power, bauxite residues (BR) from Ziltec Australia, cement bypass dust (CBD) from CEMEX Rugby Plant, coal fly ash class C (CFA) from Nova Scotia Canada, MSWI bottom ash (BA) from Ballast Phoenix and steel-making slag (SS) from Harsco Sweden. Also, ordinary Portland cement type 1 (CEM 1) with 42.5 N acquired by CEMEX and used as the reference substance. The latter was remained non-hydraulic into the system.

Finally, a commercial grade of wollastonite (WOL) (Nyad 325) was acquired by IMCD UK Limited. Wollastonite, a calcium/silica-based natural silicate, is a candidate feed-stock suitable for mineral carbonation and it has been widely studied in the past (Huijgen et al., 2006, Daval et al., 2009, Gerdemann et al., 2007).

5.2.2 Methods

5.2.2.1 Materials Preparation

The materials were received as finely grained powders (particles size less than 120 μm) and before treatment 500 grams of each were dried in an oven at 378 K for 24 hours. After oven drying, the samples were cooled in a desiccator for approximately 30 min and then mixed with water at the desired w/s ratios.

5.2.2.2 Experimental Set Up

The experiments were conducted in the apparatus described previously in chapter 4 (section 4.1). The selected w/s ratios varied from 0.2 to 100 and represented dry (0.2-0.6), intermediate (0.8-10), and wet conditions (25-100). The materials were carbonated for 1 hour under ambient temperature and pressure, 100% CO_2 and 0.2 L/min flow-rate.

5.2.2.3 Carbon Uptake Measurement

The CO_2 uptake of the reaction products (expressed as % CO_2 weight/total weight of the carbonated products) was measured by an IL 550 TOC-TN/DSC1300 analyser, and it was determined by the difference between the CO_2% concentration before and after carbonation.

5.2.2.4 Materials Characterisation

The un-reacted materials were analysed by using quantitative X-ray fluorescence and qualitative/ semi-quantitative X-ray diffraction in order to determine their elemental and mineral composition.

5.2.2.5 Variability and experimental error

Each experiment was repeated three times and the variability of results was estimated by using standard deviation and standard error of the mean. The latter represented the error bars in the following graphs. Cement was used as the reference material.

5.3 Results

5.3.1 Chemical Characterisation

The input materials were predominantly composed of calcia, silica, iron oxide (III) and aluminium oxide (see Table 5.1). The APCr, CBD, and CFA contained sulphate at 9%, 12% and 21% respectively. Trace amounts of P_2O_5, ZnO and TiO_2 and other metal oxides were also present.

Table 5.1: Major oxides composition (% w/w)

	Al_2O_3	CaO	Fe_2O_3	Cl	K_2O	MgO	MnO	P_2O_5	SiO_2	SO_3	TiO_2	ZnO	LOI
APCr	0.77	65.2	0.83	9.79	2.31	1.19	0.17	0.2	2.48	12.0	1.95	2.51	0.6
BR	19.3	1.64	11.7	0	4.30	2.96	0.14	0.2	56.8	1.34	1.32	0.02	0.3
CBD	2.84	68.1	2.61	3.02	4.79	0.89	0.08	0.1	7.69	9.28	0.21	0.02	0.37
CFA	4.6	44.0	5.18	0.14	0.86	0.55	0.16	0	9.79	20.8	0.2	0.01	13.7
BA	4.06	5.52	4.99	0.96	1.86	0.89	0.37	0.2	25.2	0.4	0.46	0	55.1
SS	5.61	50.8	5.09	0	0.12	13.4	1.71	0	16.3	0.35	0.82	0.07	0.73
WOL	0.22	64.7	1.83	0	0	0	0.335	0	32.9	0	0	0	0.01
CEM 1	3.78	70.0	3.16	0	0.62	1.30	0	0.25	16.5	3.81	0.322	0	0.2

1: steel slags contained 5% Chromium (Cr)

5.3.2 Mineral Composition

The mineralogy of the non-carbonated materials was analysed by XRD. The key mineral phases identified are presented in Table 5.2. APCr and cement dusts were rich in calcium-based mineral phases, mainly anhydrite, calcite, lime and portlandite. Bauxite residues contained high concentration of quartz, gibbsite and hematite. The predominant mineral phases of CFA were anhydrite, calcite, quartz and hematite, while the untreated bottom ash was rich in silica found in the minerals Akermanite, christobalite and quartz. The five mineral phases of cement were: calcite, hatruite, larnite, brownmillerite and gypsym. Finally, steel slag was the waste with the most complex mineralogy as it composed of several minerals.

Table 5.2: Key mineral phases of the un-treated materials identified by XRD

Phases	Formula	CEM 1	APCr	BR	CBD	CFA	B.A	S.S	WOL
Akermanite	$Ca_2Mg(Si_2O_7)$						●	●	
Albite	$NaAlSi_3O_8$						●		
Aluminium Phosphate	$Al(PO_4)$		●						
Anhydrite	$CaSO_4$		●		●	●			
Bassanite	$Ca(SO_4)(H_2O)0.5$		●						
Brownmillerite	$Ca_2(Al,Fe)_2O_5$	●							
Brucite	$Mg(OH)_2$							●	
Calcite	$CaCO_3$	●	●		●	●		●	
Calcium Chloride Hydroxide	$CaClOH$		●						
Calcium Iron Titanium Oxide	$CaFe_3(TiO_3)_4$		●						
Chromite	$(Fe, Mg)Cr_2O_4$							●	
Cristobalite	SiO_2		●				●		
Gehlenite	$Ca_2Al[AlSiO_7]$				●				
Gibbsite	$Al(OH)_3$			●					
Glaucophane	$Na_2(Mg_3\ Al_2\ Fe_2)Si_8O_{22}(OH)_2$						●		
Goethite	$FeO(OH)$			●					
Gypsum	$CaSO_4 \cdot 2H_2O$	●							
Halite	$NaCl$		●						
Hatruite	$Ca_3(SiO_4)O$	●							
Hematite	Fe_2O_3			●					
Larnite	Ca_2SiO_4	●			●				
Lime	CaO		●		●	●			
Magnesium Oxide Hydroxide	$Mg_5O(OH)_8$		●						
Manganolangbeinite	$K_2Mn_2+2(SO_4)_3$							●	
Merwinite	$Ca_3Mg(SiO_4)_2$							●	
Periclase	MgO					●		●	
Portlandite	$Ca(OH)_2$		●		●			●	
Pyrophanite	$Mn(TiO_3)$							●	
Quartz	SiO_2			●	●	●	●	●	
Rutile	TiO_2		●						
Sylvite	KCl		●		●	●			
Titanite	$CaTiSiO_5$							●	
Wollastonite	$CaSiO_3$								●

5.3.3 Carbon Dioxide Uptake Measurement

The actual CO_2 uptake is a function of the initial and final CO_2% and it is defined by the equation 5.1 (Baciocchi et al., 2009a).

$$CO_{2UPTAKE}\% = \frac{CO_{2FINAL}\% - CO_{2INITIAL}\%}{100 - CO_{2FINAL}\%} x100 \tag{5.1}$$

The CO_2 uptakes of the carbonated materials after 1 hour of treatment are shown in Figures 5.1-5.7. Table 5.3 includes all the measured CO_2 uptakes at the tested w/s ratios as well as the variability of experimental data (error bars).

The results suggested that APCr, CBD, CEM 1 and steel-making slag were the most reactive residues amongst the input materials. The lowest CO_2 reactivity was given by bauxite residues (CO_2 uptake=0) and wollastonite.

The highest CO_2 uptake was recorded for the samples with low water content, indicating that carbonation was favoured at dry conditions. At intermediate w/s ratios the reactivity of all the input materials remained low however, as the w/s increased the recorded CO_2 uptake started to rise again.

In Figure 5.1 the yield for APCr is presented. The highest reactivity observed at low water content (0.2-0.6). At intermediate w/s ratios the yield decreased considerably until w/s=25 where it started to rise again.

Similarly to APCr, the reactivity of CBD was dependent upon the water content and favoured at dry conditions (Figure 5.2).

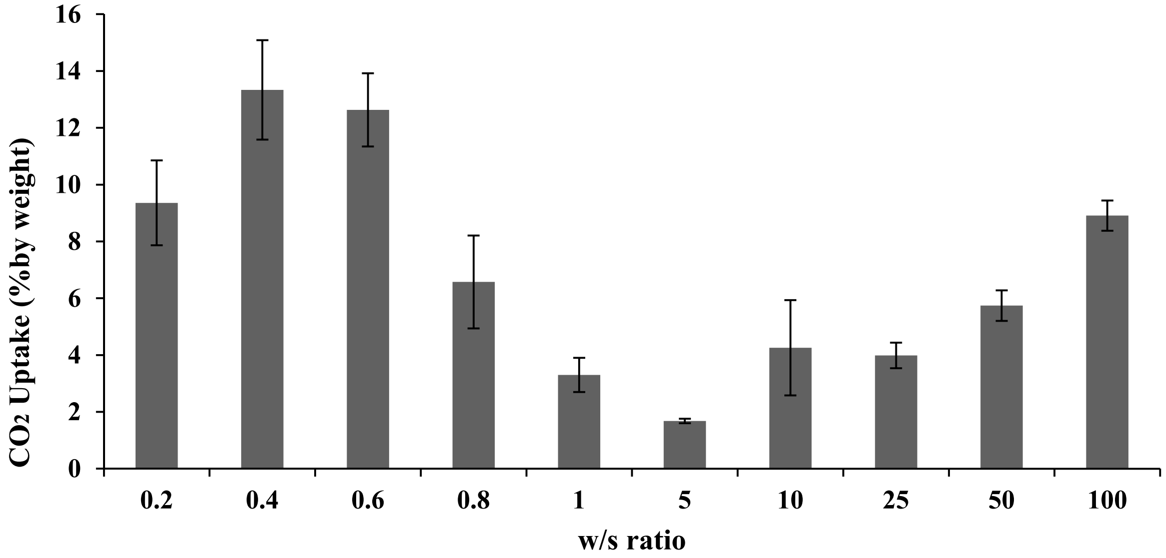


Figure 5.1: CO_2 uptake for APCr at various w/s ratios

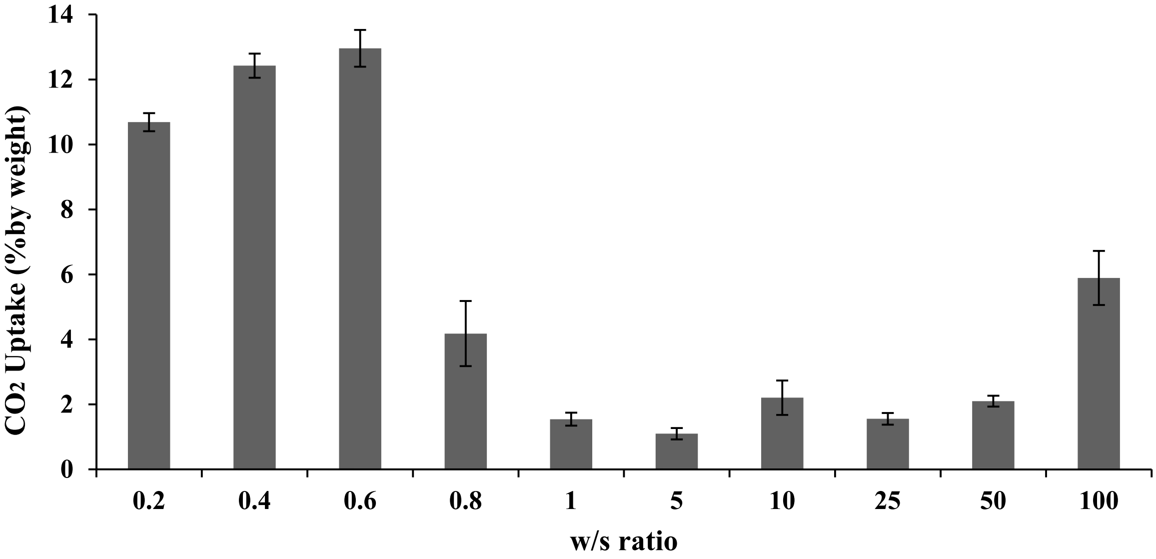


Figure 5.2: CO$_2$ uptake for CBD at various w/s ratios

The yield for the reference material is shown in Figure 5.3. The results suggested that the carbonation of CEM 1 occurred at low w/s ratio only (0.2-0.4). For w/s ratio greater than 0.4 the CO$_2$ uptake remained under 2% and only at w/s=100 started to increase. Figure 5.5 showed that carbonation of coal fly ashes took place only at five w/s ratios (0.2, 0.4, 25, 50 and 100).

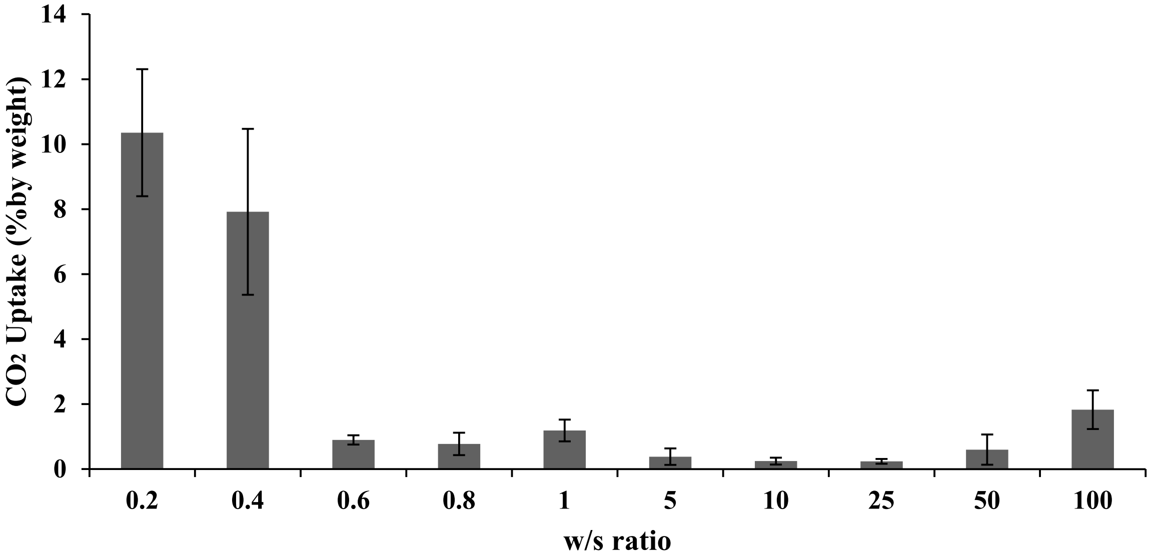


Figure 5.3: CO$_2$ uptake for CEM 1 at various w/s ratios

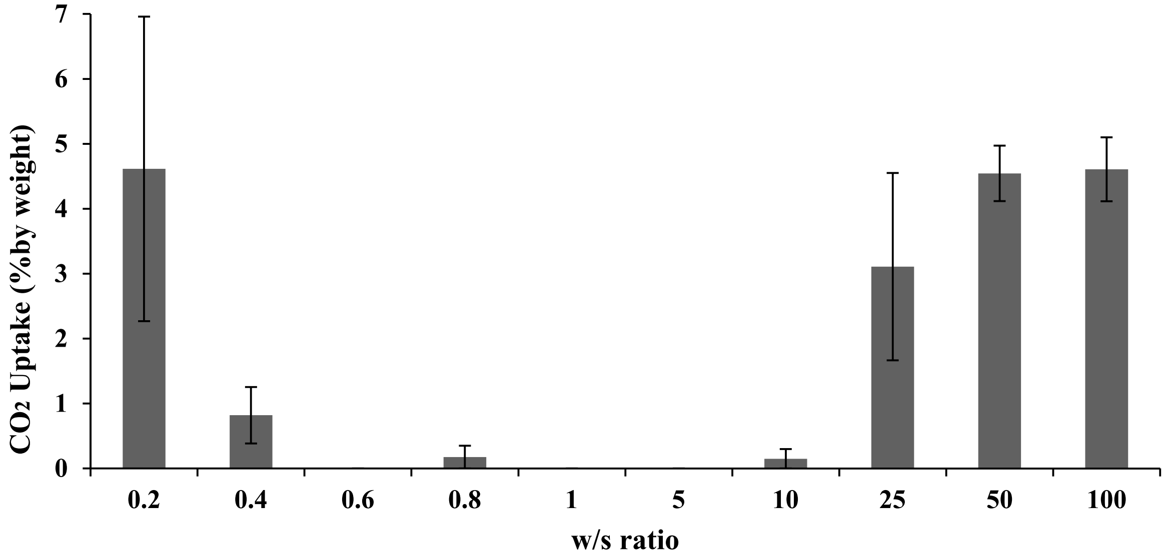


Figure 5.4: CO_2 uptake for CFA at various w/s ratios

The CO_2 uptake for MSWI bottom ash did not exceed 2.5% (Figure 5.5). The highest value (2.5%) achieved at low water content (w/s=0.4). At intermediate w/s ratios (1, 5 and 10) the TOC analysis showed that no carbonation occurred.

The results for steel-making slag showed that the effective carbonation of this residue is favoured at w/s=0.2 only.

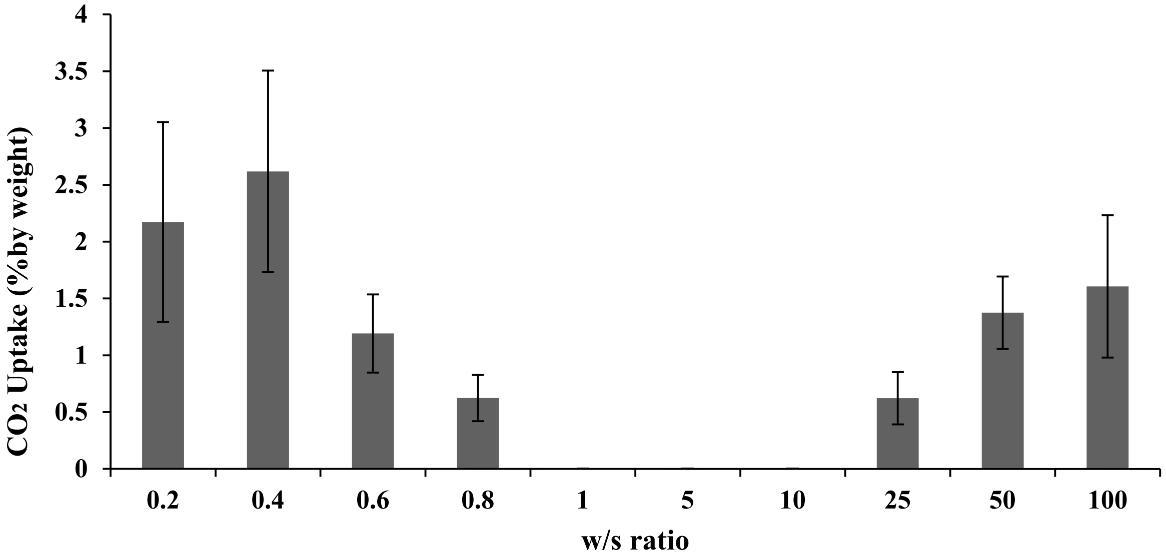


Figure 5.5: CO_2 uptake for bottom ashes at various w/s ratios

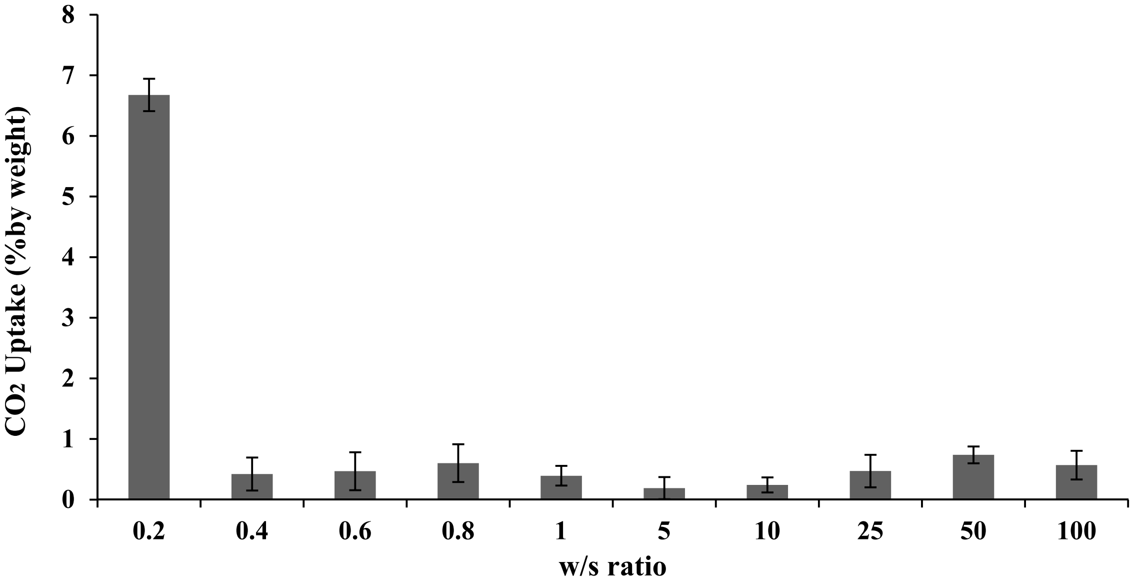


Figure 5.6: CO_2 uptake for steel slag at various w/s ratios

Finally, the yield for wollastonite is shown in Figure 5.7. The reactivity of this mineral under ambient temperature and pressure was low and the highest CO_2 uptake achieved at 1%, at w/s=0.2 and w/s=100.

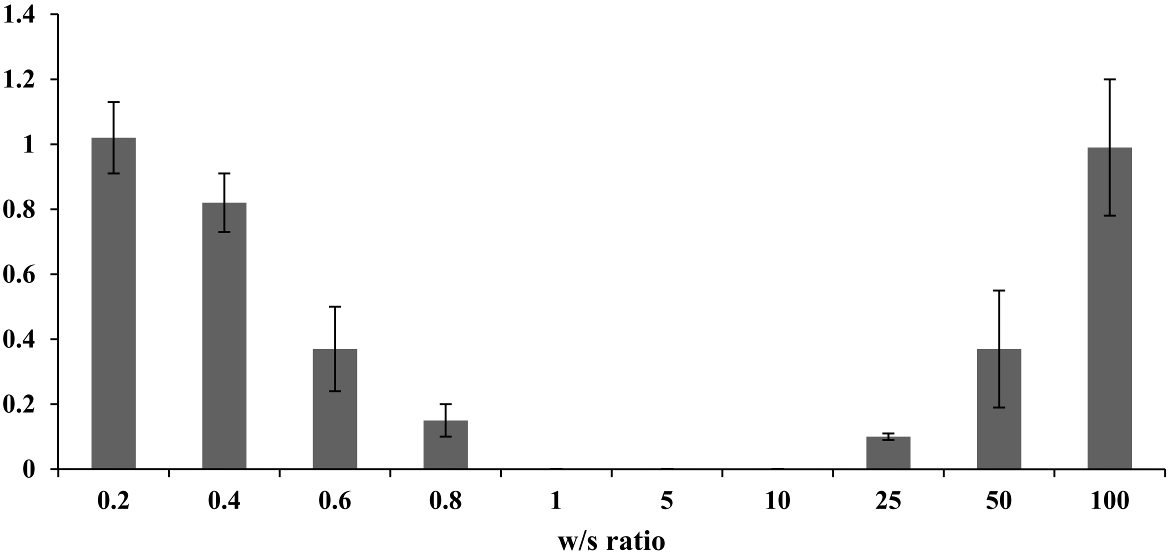


Figure 5.7: CO_2 uptake for wollastonite at various w/s ratios

All the CO_2 uptakes are summarised in Table 5.3. The average values, respective w/s ratios and the variability of experimental data are also presented.

Table 5.3: CO_2 uptakes after 1 hour of carbonation at ambient conditions

	Carbon dioxide uptake (expressed as % CO_2 weight/total weight of the carbonated products)									
w/s	**0.2**	**0.4**	**0.6**	**0.8**	**1**	**5**	**10**	**25**	**50**	**100**
APCr	9.3±1.4	13.3±1.7	12.6±1.2	6.5±1.6	3.3±0.6	1.6±0.0	4.2±1.6	3.9±0.4	5.7±0.5	8.9±0.5
BR	0	0	0	0	0	0	0	0	0	0
CBD	10.6±0.2	12.4±0.3	12.9±0.5	4.1±1.0	1.5±0.1	1.1±0.1	2.2±0.5	1.5±0.1	2.1±0.1	5.8±0.8
CEM	10.3±1.9	7.9±2.5	0.9±0.1	0.7±0.3	1.1±0.3	0.3±0.2	0.2±0.1	0.2±0.0	0.6±0.4	1.8±0.5
CFA	4.6±2.3	0.8±0.4	0	0.1±0.1	0	0	0.1±0.1	3.1±1.4	4.5±0.4	4.6±0.4
BA	2.1±0.8	2.6±0.8	1.2±0.3	0.6±0.2	0	0	0	0.6±0.2	1.3±0.3	1.6±0.6
SS	6.6±0.2	0.4±0.2	0.4±0.3	0.6±0.3	0.4±0.1	0.1±0.1	0.2±0.1	0.4±0.2	0.7±0.1	0.5±0.2
WOL	1.0±0.1	0.8±0.1	0.3±0.1	0.1±0.0	0	0	0	0.1±0.1	0.3±018	1.0±0.2

5.3.4 Theoretical CO_2 Uptake

The theoretical maximum CO_2 uptake of a candidate residue can be estimated by the Steinour formula (Fernandez Bertos et al., 2004).

This model is solely based on the elemental composition and it is a function of calcium oxide, sulphur trioxide, sodium oxide and potassium oxide, according to equation 5.2.

$$CO_2\% = 0.785\left(CaO - 0.7SO_3\right) + 1.09Na_2O + 0.93K_2O \tag{5.2}$$

A comparison between the actual and predicted CO_2 uptakes is illustrated in Figure 5.8. The actual values (black columns) were considerably lower than the theoretical ones (grey column). The theoretical predictions are mainly proportional to chemical composition, mainly calcium oxide, while in fact the actual CO_2 depends on several carbonation variables. More details are given in the discussion section.

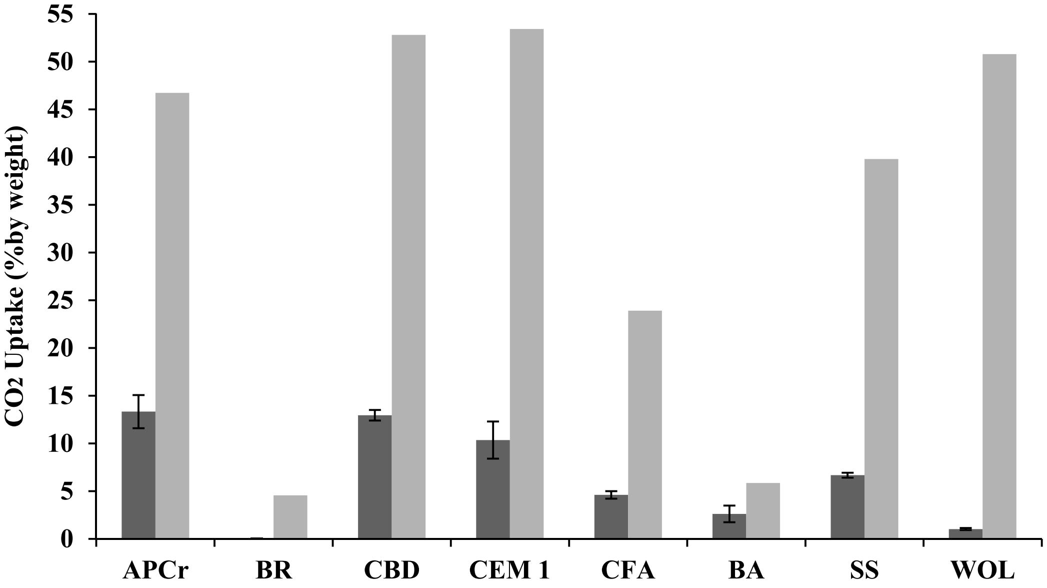


Figure 5.8: Theoretical against actual CO_2 uptakes

5.4 Discussion

5.4.1 Elemental Analysis and Mineral Composition

Chemistry and mineralogy are two important materials parameters influencing accelerated carbonation of wastes, as they both determine the reactivity of a candidate residue to CO_2. More details about the different CO_2 reactivity of the input materials of this study are given in section 5.4.

The elemental analysis of APCr showed that the untreated ashes contained 65% of calcium oxide present mainly as anhydrite ($CaSO_4$), calcite ($CaCO_3$), lime (CaO) and portlandite ($Ca(OH)_2$), 12% of sulphur trioxide as anhydrite and bassanite ($Ca(SO_4)(H_2O)0.5$), and 9.7% of chlorine bound to the minerals halite (NaCl) and sylvite (KCl). For the rest traced elements, silica (2.5%) was present as cristobalite, potassium (2.3%) as sylvite, and titanium dioxide as rutile (TiO_2). Finally, the chemical analysis revealed small amounts of aluminium/phosphorus, iron (III) and magnesium oxides, present as aluminium phosphate $Al(PO_4)$, calcium iron titanium oxide $CaFe_3(TiO_3)_4$ and magnesium oxide hydroxide $Mg_5O(OH)_8$ respectively. The mineral phase of the element Zn (2.5%) could not be identified by X-ray diffraction.

Bauxite residues were primarily composed of 57% silica present as the mineral quartz (SiO_2). The mineral phase of aluminium oxide (20%) was gibbsite $Al(OH)_3$, while the identified iron (11.7%) was found in hematite (Fe_2O_3) and goethite ($FeO(OH)$). Finally, the XRD analysis of this residue revealed peaks of magnesium oxide hydroxide, the mineral that the measured MgO (3%) was present.

Elemental analysis of CEM 1 showed that the main elements were CaO (70%), SiO_2 (16.5%), SO_3 (3.8%), Al_2O_3 (3.8%) and Fe_2O_3 (3.15%). The key mineral phases of the un-treated cement included calcite, hatruite ($Ca_3(SiO_4)O$), larnite and brownmillerite $Ca_2(Al,Fe)_2O_5$. Sulphate co-existed with calcium oxide in the mineral gypsym ($CaSO_42H_2O$).

Cement dusts are produced during cement manufacture and for this reason they usually contain high amounts of calcium (Huntzinger and Eatmon, 2009). The elemental analysis of CBD showed that the un-treated dusts contained 68% of calcium oxide bound to calcite, anhydrite, gehlenite ($Ca_2Al_2SiO_7$), larnite (Ca_2SiO_4), lime and portlandite. Gehlenite was also the mineral phase of alumina (2.85%), while anhydrite was the mineral phase of the element sulphur which accounted for 10% of the initial composition. Silica (7.7%) was found as larnite and quartz, and finally potassium oxide and chlorine co-existed in the mineral sylvite.

Coal fly ashes were primarily composed of calcium oxide (44%), sulphate (21%), silica (9.7%), and iron (III) oxide (5.2%). The respective minerals phases of these oxides were anhydrite, calcite and lime for CaO, anhydrite for SO_4^{-2}, quartz for SiO_2 and hematite for F_2O_3. The XRD analysis revealed the presence of periclase (MgO) as the mineral phase of the measured magnesium oxide (0.55%) and sylvite as the mineral phase of both potassium oxide and chlorine. The elemental analysis showed that the concentration of alumina was 4.6% however; the latter could not be identified by X-ray diffraction.

The elemental analysis of MSWI bottom ash gave a very high loss of ignition (56%). This is probably due to the chemical nature of bottom ashes as often the incineration of municipal wastes produces waste-streams full of organic and hydrated matter, and carbonated materials. The untreated BA was rich in silica (25%), which was found in the minerals akermanite ($Ca_2Mg(Si_2O_7)$), christobalite and quartz. Akermanite was also the mineral phase of calcium oxide (5.5%) and MgO (0.55%). Alumina was present as albite ($NaAlSi_3O_8$), and glaucophane $Na_2(Mg_3\ Al_2\ Fe_2)Si_8O_{22}(OH)_2$. In glaucophane was also bound the oxide F_2O_3 (5%).

The XRF analysis suggested that the predominant oxides contained in steel-making slag were calcium (51%), alumina (5.6%), iron (III) (5%), magnesium (13.5%) silica (16%) and chromium (III) (5%). The chemical analysis also revealed the presence of various other heavy metal oxides, while the mineral analysis revealed the presence of several mineral phases, confirming the complex mineralogy of this waste residue. Calcium oxide was bound to calcite and portlandite, magnesium oxide to brucite ($Mg(OH)_2$) and periclase, and silica to quartz. The three elements were also co-existed in the minerals akermanite and merwinite ($Ca_3Mg(SiO_4)_2$). Chromium and iron were present in chromite $(Fe,Mg)Cr_2O_4$, titanium dioxide in titanite ($CaTiSiO_5$), and potassium/magnesium in manganolangbeinite ($K_2Mn_2+2(SO_4)_3$).

Finally, wollastonite was composed of calcia and silica at 64.7% and 33% respectively. The analysis by XRD showed peaks of the mineral wollastonite ($CaSiO_3$) only. However, the mineral phase of the contained iron (III) (1.85%) could not be identified.

5.4.2 Experimental CO_2 uptake

The yields at different w/s ratios were similar for all the residues, with the highest yield observed at low w/s ratios (between 0.2 and 0.6) showing the advantage of carbonation under dryer conditions (Fernández Bertos et al., 2004). At intermediate w/s ratios (between 0.8 and 10) the yield decreased considerably due to the presence of water, inhibiting the diffusion of CO_2 by pore-blocking (Li et al., 2007). However, a further increase in w/s ratio (between 25 and 100) resulted in higher yield, as the increased volume of water provided a reservoir with a larger total capacity for carbon dioxide solution and ionisation/hydration.

APCr was the most reactive waste residue with maximum CO_2 uptake at 13.3% at w/s=0.4. The carbonation of APCr was favoured at dry conditions (w/s ratio between 0.2-0.6), but also exhibited signs of increasing uptake at high w/s ratios (50-100). At intermediate w/s ratios (0.8-10) the achieved CO_2 uptake was under 5% (see Figure 5.1).

Air pollution control residues, also known as fly ash, are a waste-stream arising from the incineration of municipal wastes. It is mixture of fly ash, lime and pure carbon and it is known to react effectively with CO_2 (Li et al., 2007). Previous workers estimated the maximum CO_2 uptake of these ashes at 12% (Lam et al., 2010) and the results of this study validated this finding.

The accelerated carbonation of APCr leads to the formation of products with value-added. For example, the technology of Carbon8 Systems involves the production of sustainable materials such as “green” aggregates and concrete blocks from the carbonation of APCr ashes via a carbon negative process (Gunning et al., 2013).

The second most reactive material was CBD with CO_2 uptake of 12.9% at w/s=0.6. Similarly to APCr, the reactivity of cement dusts was high at low water content and it started to decrease when the w/s ratio was larger than 0.8. After w/s=1 the achieved CO_2 uptake was low and only at w/s=100 started to increase again (5.9%).

The accelerated carbonation of cement dusts is favoured under ambient temperature and pressure especially for samples with low concentration of water. Previous literature findings suggested that under these conditions the recorded CO_2 uptake was found to be in the region of 11.5% (Huntzinger et al., 2009), and the recorded yield shown in Figure 5.2 verified these findings.

The effective carbonation of the reference material (CEM 1) occurred at low w/s ratios only (0.2 and 0.4) with maximum CO_2 uptake at 10.35% and at w/s=0.2 (see Figure 5.3). The addition of water in the less dry samples inhibited the diffusion of carbon dioxide into the system and the recorded CO_2 uptakes were under 2%. Even at w/s ratio=100 where the majority of the tested materials showed increased yield, the reactivity of the samples of CEM 1 remained low (1.8%). Ordinary Portland cement is known to have a high reactivity to CO_2 as it typically contains large concentration of calcium oxide (70% in this study), which usually indicates successful carbonation (Johnson, 2000).

Steel-making slag was the last material showing increased yield after 1 hour of treatment with maximum CO_2 uptake at 6.67% and at w/s=0.2. The latter was the only w/s ratio where effective carbonation took place, as at higher ratios the CO_2 uptake obtained was less than 1% (Figure 5.6).

Previous findings suggested that steel slags could sequester vast amounts of carbon dioxide. Maximum CO_2 uptakes obtained for steel slag were found to range between 22.7% and 30% however, the reactions occurred at elevated temperatures and pressures, 1.7 MPa and 308 K respectively (Baciocchi et al., 2010, Eloneva et al., 2010, Eloneva et al., 2008).

The valorisation of steel-making slags is a process of particular interest as it forms high value valorised/carbonated products such as aggregates and fillers for concrete blocks and asphalt. Recmix is actively investigating the successful utilisation of steel making slags for profit-making purposes (Recmix, 2014).

Bauxite residues, also known as red mud, are the waste-streams formed after the Bayer process when alumina is extracted from bauxite ores. The valorisation or treatment prior to disposal of this residue is of particular interest as the transport, disposal or re-use of red mud is difficult due to its high alkalinity and elevated sodium concentration (Johnston et al., 2010). In addition, the quantity of stock-piled red mud is estimated at 2.7 Gtonnes worldwide, increasing by 120 Mtonnes every year (Power et al., 2011). However, the TOC analysis showed that BA was the least reactive of the input materials with 0% CO_2 uptake regardless of the concentration of water in the carbonated samples.

Although, a previous study suggested that 1 kg of bauxite could sequester up to 53 g of CO_2 at p=0.35 MPa and t=3.5 hours (Yadav et al., 2010) it seems that the reactivity to CO_2 of this waste under ambient conditions is negligible. However, the processing of large amounts of feed-stock even at slightly elevated reaction conditions can involve significant costs.

The CO_2 binding capacity of coal fly ashes found in literature varies as the reactivity of these ashes depends on composition and reaction conditions. For example, the CO_2 uptake after accelerated carbonation of CFA composed of 4% CaO was estimated at 2.6%, whereas in a mixture of brown coal fly ash and brine was less than 1% (Montes-Hernandez et al., 2009). Less than 1% was also the CO_2 uptake obtained after the carbonation of CFA containing 7% CaO under ambient temperature and pressure (Jo et al., 2012). However, significant CO_2 uptakes (up to 26.5%) were recorded during accelerated carbonation of high CaO- and MgO-containing brown coal fly ash derived from Latrobe Valley in Australia with acetic acid leachate (Sun et al., 2012).

The results shown in Figure 5.4 indicated that the carbonation of coal fly ash was favoured at extremely dry (w/s ratio=0.2) or wet conditions (w/s ratio 50 and 100). The highest CO_2 uptake was estimated at 4.6% at w/s ratio=0.2 and 100. However, the variability of the experimental data at low water content was large.

The reactivity of the MSWI bottom ashes was low and the maximum CO_2 uptake estimated at 2.6% and at w/s=0.4. At dry conditions (w/s between 0.2 and 0.6) the reaction proceeded more effectively compared to intermediate ratios (0.8-10) where the yield remained very low. At higher ratios (greater than 25) the CO_2 uptake started to rise again (see Figure 5.5).

MSWI BA is the bottom waste stream coming from the incineration of municipal wastes and it is composed of aluminium silicates and various heavy-metal substances (Fernandez Bertos et al., 2004). The valorisation of bottom ashes leads to products with added-value, that could be used in road pavement construction, glass and ceramics, and in agriculture and waste water treatment (Lam et al., 2010, Li et al., 2006).

Finally, the recorded yield for wollastonite was presented in Figure 5.7. The results suggested that the maximum CO_2 uptake of this mineral reached 1.0% at w/s=0.2 and w/s=100. The reactivity of the other samples was extremely low (carbon uptake close to 0%) and the findings were in accordance with previous studies, showing that the effective carbonation of wollastonite requires elevated temperatures (= 428 K) and pressures (=11.5 MPa) (Gerdemann et al., 2007).

5.4.3 Theoretical CO_2 Uptake

The recorded CO_2 uptakes of the input materials after 1 hour of accelerated carbonation were compared with the theoretical values derived from the Steinour formula in Figure 5.8. In all cases, the predicted maximum CO_2 uptakes were higher than the achieved. The reason is that this theoretical model is based entirely on the chemical composition of a candidate residue, mainly on the concentration of calcium oxide, however, the actual CO_2 uptake is also determined by several variables including the mineral phases in which calcium is present, temperature, pressure, reaction time, water content etc. (Gunning, 2010). These variables were discussed in Chapter 2. The theoretical and experimental maximum uptakes as well as their % difference are presented in Table 5.4.

Table 5.4: Difference between actual and theoretical CO_2 uptakes

Material	Ratio	Actual maximum CO_2 uptake	Theoretical maximum CO_2 uptake
APCr	0.4	13.3±1.74	46.7
BR	n/a	0	4.5
CBD	0.6	12.9±0.56	52.8
CEM 1	0.2	10.3±1.95	53.4
CFA	0.2	4.6±2.34	23.9
BA	0.4	2.6±0.88	5.8
SS	0.2	6.6±0.26	39.8
WOL	0.2	1.0±0.11	50.8

1: The comparison was based on the average actual uptakes

5.4.4 Reactivity

The different reactivity to CO_2 of the input materials could be explained by their initial concentration in calcium oxide and the mineral phases in which calcium was present. Reactive calcium-based mineral phases such as calcite, portlandite, lime and larnite are known to promote accelerated carbonation and the precipitation of $CaCO_3$, while other calcium-based phases such as anhydrite, akermanite and glaucophane have no actual effect upon the final CO_2 uptake (Gunning et al., 2010b).

The chemical analysis of the four most reactive residues showed that all of them contained high concentrations of calcium oxide (between 51% and 70%). Also, X-ray diffraction revealed the presence of calcite and portlandite in the un-reacted APCr, CBD and steel slags. Lime, another calcium-based reactive phase, was present in APCr and CBD.

On the other hand, bauxite residues would not carbonate at any w/s ratio, due to their very low calcium content of the un-treated residues (1.6%), and a high composition of silica and alumina. Moreover, the XRD analysis showed the absence of reactive calcium-based phases which promote the reaction.

The elemental analysis of bottom ashes, similarly to red mud, showed low concentration of calcium oxide (5.5%), while the un-reacted diffractogram revealed the presence of akermanite and glaucophane as the mineral phases in which calcium oxide was present.

The importance of the mineral phases that calcium should be bound in order to achieve increased CO_2 uptake was eminent during the treatment of coal fly ash. Although the CFAs contained 44% of calcium oxide, the highest CO_2 uptake obtained did not exceed 4.6%. The XRD analysis showed that CaO was predominantly present in the mineral anhydrite ($CaSO_4$), which is known to have a neutral effect during accelerated carbonation (Gunning et al., 2010a).

5.5 Conclusions

In this chapter, six alkaline waste residues, cement (as the reference material) and wollastonite were carbonated for 1 hour under ambient temperature and pressure and at 10 different water-to solid ratios varying from 0.2 to 100. The CO_2 uptakes were measured by total organic carbon analysis and compared with the theoretical values derived from the Steinour formula.

The yields at different w/s ratios showed that the accelerated carbonation was favoured at dry conditions (w/s=0.2-0.6). At intermediate w/s ratios (between 0.8 and 10) the yield decreased considerably due to the presence of water, inhibiting the diffusion of CO_2 by pore-blocking. However, a further rise in w/s ratio (25 to 100) resulted in higher CO_2 uptake, as the increased volume of water provided a reservoir with a larger total capacity for carbon dioxide solution and ionisation/hydration.

On every occasion, the actual CO_2 uptakes were considerably lower than the predicted ones, as the theoretical predictions are based exclusively on the initial chemical composition, mainly the concentration of CaO, of a candidate residue, while in fact the final CO_2 uptake is dependent upon several carbonation variables including mineralogy, temperature, pressure, reaction time, relative humidity as well as water content etc.

The results suggested that the air pollution control residues, cement bypass dust, cement and steel-making slag showed the highest reactivity to CO_2 due to their high initial concentration in calcium oxide and the presence of reactive calcium-based mineral phases such as calcite, lime and portlandite.

On the other hand, the reactivity of bauxite residues and MSWI bottom ashes was low, as a result of the low concentration of CaO in the untreated residues. Coal fly ashes although containing 44% of CaO did not show remarkable reactivity to CO_2 as the XRD analysis showed that CaO was bound to the mineral anhydrite, which is known to have a neutral effect upon CO_2 uptake.

Finally, the CO_2 uptake for wollastonite was approximately 1.0%, showing that the accelerated carbonation of minerals under low temperature and pressure is weak. The low reactivity of wollastonite and of magnesium hydroxide presented in the previous chapter suggested that little amounts of CO_2 can be sequestrated via mineral carbonation at moderate reaction conditions.

In the following chapter the most reactive materials identified in Chapter 5 (APCr, CBD, CEM 1 and steel slag) were carbonated in the presence of an ultrasonic field to assess the effect of sonication upon their CO_2 uptake, mineralogy and morphology.

6 CARBONATION OF WASTES AIDED BY ULTRASOUND

6.1 Introduction

As described before, the basic principal of ultrasonic irradiation is cavitation, where energy is transmitted between a solid and a sonication device through an aqueous medium. Although the literature offers knowledge about the beneficial effects of sonication on $CaCO_3$ precipitation, there are limited previous studies regarding the effects of this technique during the carbonation of alkaline waste residues.

In this chapter, the effect of sonication upon the CO_2 uptake of air pollution control (APCr), cement bypass dust (CBD), ordinary Portland cement (CEM 1) and steel slag-residues was investigated and the recorded yields were compared with the yields achieved without ultrasound. On many occasions, sonication requires high energy demands and thus, an ultrasonic bath (instead of probe) was used in this study.

The sonication experiments were carried out under ambient temperature and pressure, and at 10 different water-to-solid ratios. The selected ratios were divided into three categories: low (0.2-0.6), intermediate (0.8-10) and high (25-100) to study how cavitation proceeds in samples with different concentrations of water.

The variables examined throughout the experiments included the optimum water content, treatment time and ultrasonic frequency. The mineral composition of the un-treated and sonicated/non-sonicated waste materials were analysed by qualitative/semi-quantitative X-Ray diffraction.

In addition, scanning electron microscopy was conducted to elucidate differences in mineral carbonate precipitates. Finally, the particles size of the sonicated samples was measured by wet laser diffraction analysis and compared with the particles size of the un-treated ones.

6.2 Materials and Methods

6.2.1 Materials

The input materials comprising air pollution control (APCr) (Slough Heat and Power), cement bypass dust (CBD) (CEMEX Rugby Plant), steel-making slag (SS) (Harsco Sweden) and ordinary Portland cement type 1 (CEM 1), 42.5 N acquired by CEMEX. The selection of these four materials was based on the findings of the previous chapter suggesting high reactivity to CO_2.

6.2.2 Methods

6.2.2.1 Materials Preparation

The materials received as finely grained powders (particles size less than 120 μm) and before treatment 500 grams of each were dried in an oven at 378 K for 24 hours. After oven drying, the samples were cooled in a desiccator for approximately 30 min and then mixed with water at the desired w/s ratios.

6.2.2.2 Materials Characterisation

The wastes were subject to a standard materials characterisation. This comprised an evaluation of the particles size distribution by using wet laser diffraction analysis (Malvern Mastersizer MS2000), and phase characterisation by X-ray diffraction (Bruker D8 Advance).

6.2.2.3 Experimental Set-Up

The experimental apparatus was described previously in chapter 4 and 5. The ultrasonic field at 35 kHz frequency was generated by an ultrasonic bath (Camlab, 150-300 W). A second bath (Globaltronics GmbH&Co. KG, 50W) operating at half or full wave setting was also used for the sonication of the reference material at a higher frequency (46 kHz), in order to assess whether sonication increased the achieved CO_2 uptake. The experiments were conducted at T=293 K, p=0.1 MPa, C_{CO2}=100% and flow-rate= 0.2 L/min.

6.2.2.4 Products Characterisation

After treatment, the CO_2 uptake of the reaction products (expressed as % CO_2 weight/total weight of the carbonated products) was measured by an IL 550 TOC-TN/DSC1300 analyser, the particles size were re-measured, and any change in mineralogy was identified by using XRD. Samples were also prepared for an examination of morphology by using a JEOL JSM-5310LV, where particle surfaces were analysed by secondary electron detection.

6.2.2.5 Variability and experimental error

Each experiment was repeated three times and the variability of results was estimated by using standard deviation and standard error of the mean. The latter represented the error bars in the following graphs. Cement was used as the reference material.

6.3 Results

6.3.1 Apparatus Testing

Prior to sonication of the waste residues, the ultrasonic bath was tested for equal distribution of CO_2 into the system and the attenuation of sound of waves passing through plastic and Pyrex containers. The equal distribution of CO_2 was examined by carbonating the reference material in each individual tube three times at w/s ratio=0.4 for 1 hour and measuring the CO_2 uptake of the samples. The results showed that the recorded CO_2 uptakes were not dependant on the tube position in the apparatus and thus, it was assumed that the gas was equally distributed throughout the apparatus.

The attenuation of sound waves was tested by sonicating cement at three different w/s ratios (0.4, 1 and 100) for 1 hour inside plastic and Pyrex containers. The results showed that the average CO_2 uptake of CEM 1 inside the plastic tubes was higher compared to Pyrex (see Figures 6.2-6.4).

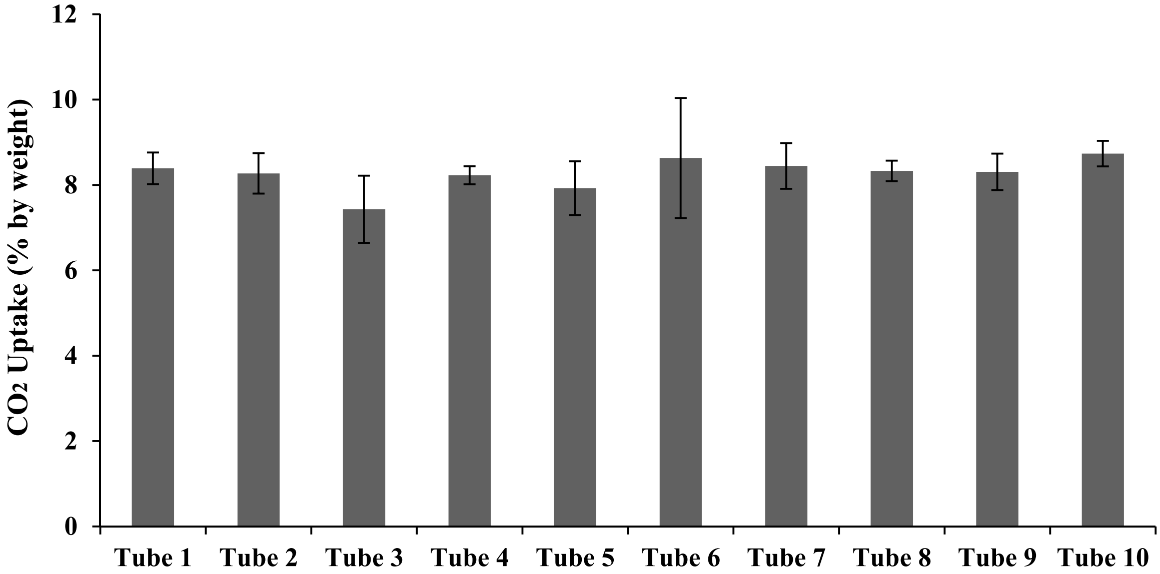


Figure 6.1: Testing of equal CO_2 distribution into the system

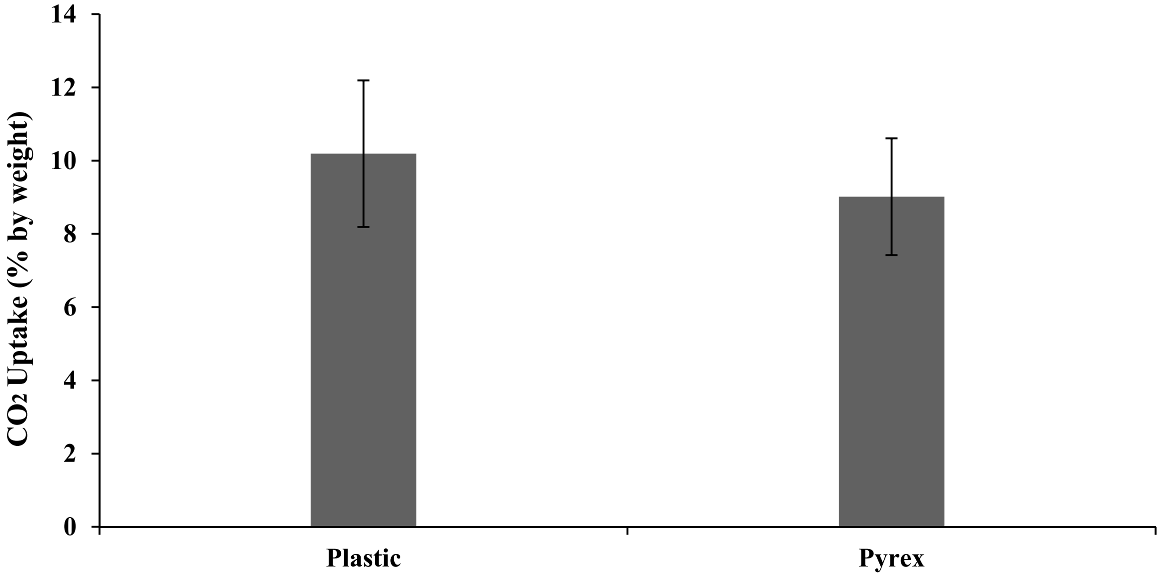


Figure 6.2: The attenuation of sound waves at w/s=0.4

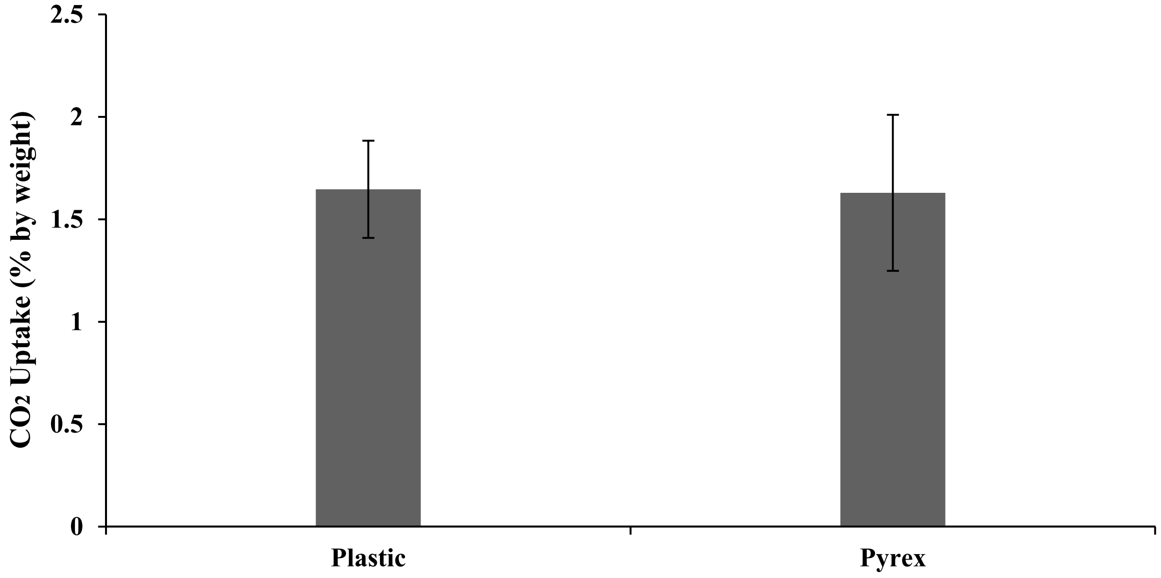


Figure 6.3: The attenuation of sound waves at w/s=1

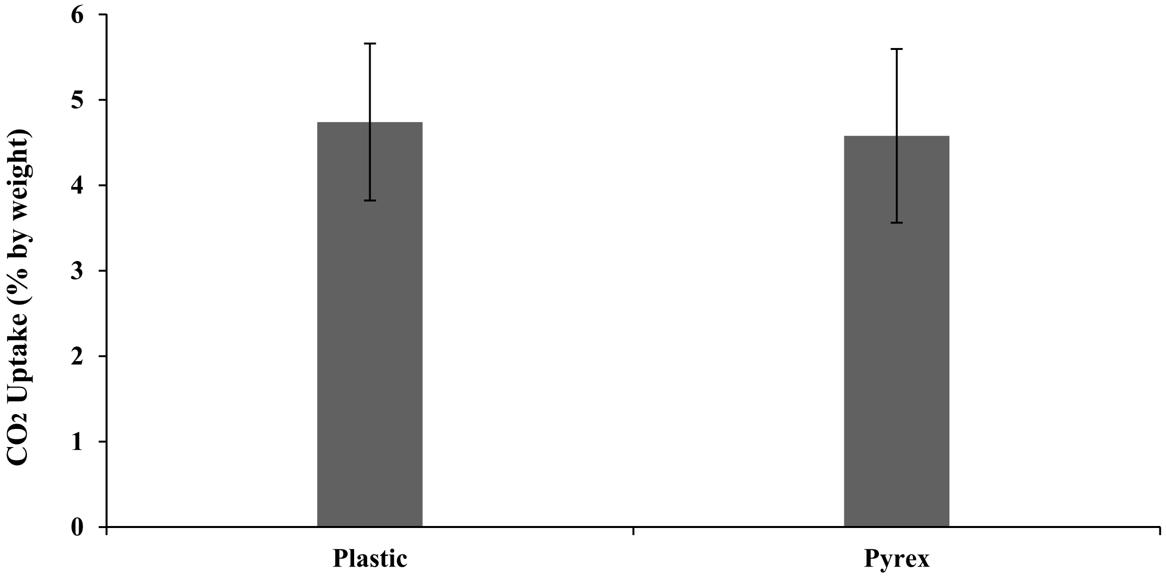


Figure 6.4: The of attenuation of sound waves at w/s=100

6.3.2 Sonication at 35 kHz

Initially, the input materials were sonicated for 1 hour at 35 kHz and 10 different water-to-solid ratios (0.2, 0.4, 0.6, 0.8, 1, 5, 10, 25, 50 and 100) and the CO_2 uptake of the products was measured. The results suggested that sonication increased the average CO_2 uptake of the products by 4%-28% for dry and by 62%-400% for wet samples. The recorded yields for non-sonicated and sonicated samples are shown in

Figures 6.5-6.8. The black columns represent the samples without ultrasound, while the grey columns the samples with ultrasound.

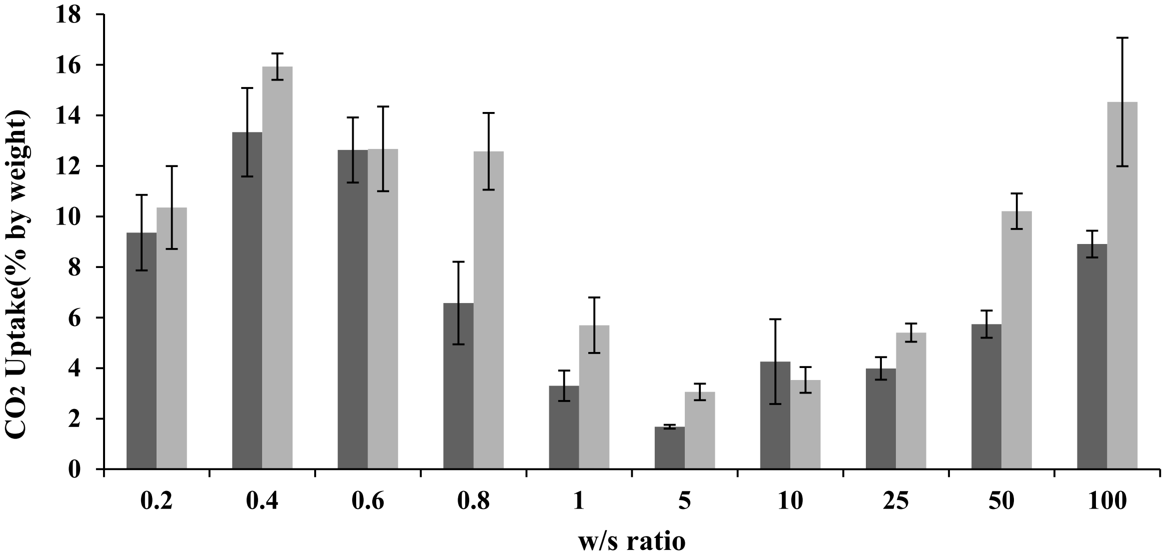


Figure 6.5: CO_2 uptake for APCr after 1 hour of sonication at various w/s ratios

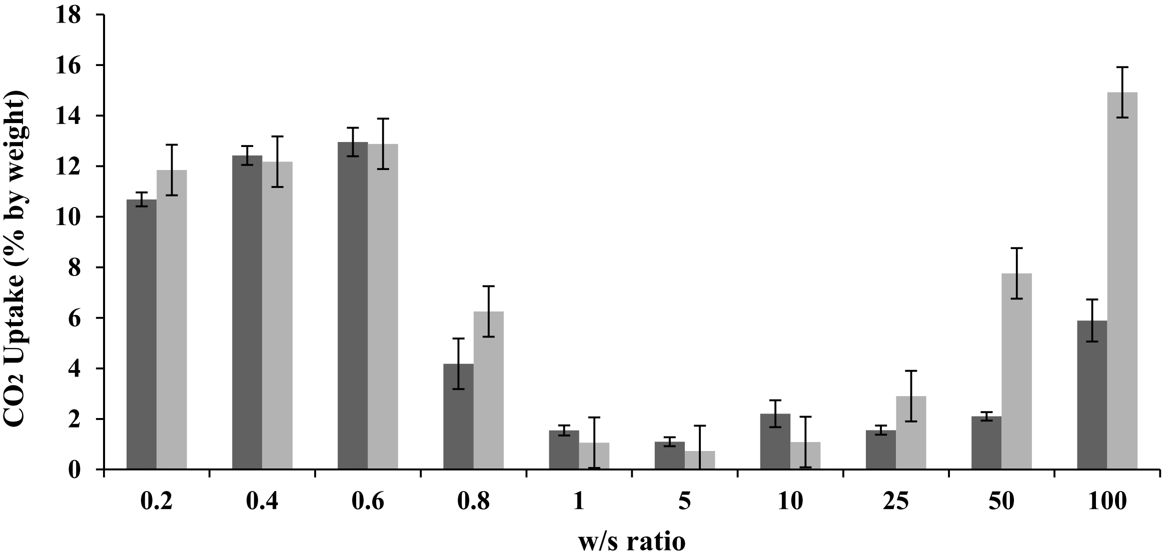


Figure 6.6: CO_2 uptake for CBD after 1 hour of sonication at various w/s ratios

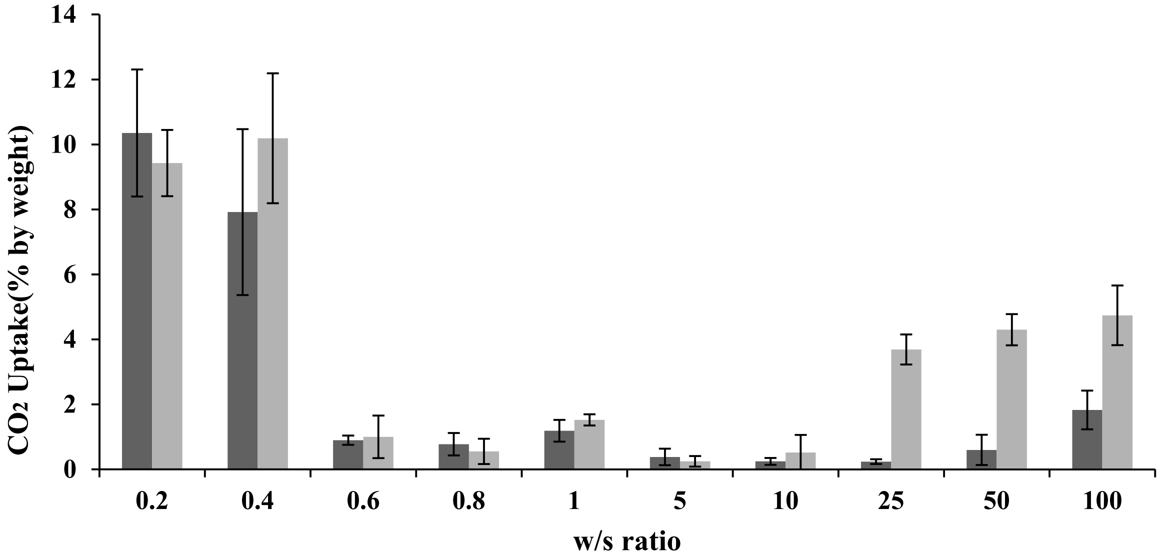


Figure 6.7: CO_2 uptake for CEM 1 after 1 hour of sonication at various w/s ratios

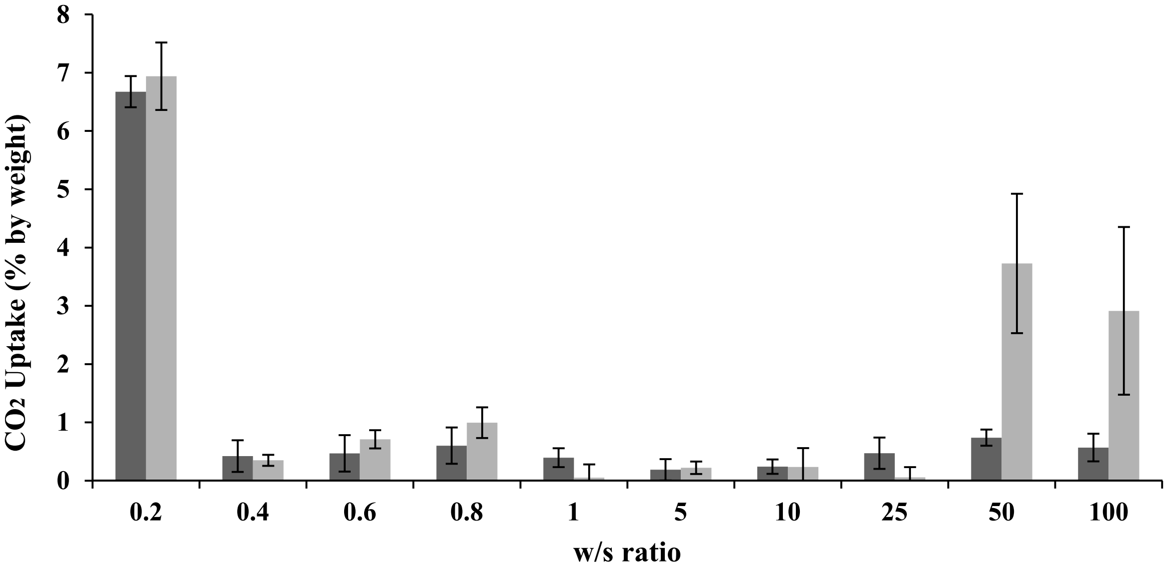


Figure 6.8: CO_2 uptake for steel slag after 1 hour of sonication at various w/s ratios

6.3.3 Effect of Sonication Time at 35 kHz

The results of the previous section showed that ultrasound increased the CO_2 uptakes at low and high water concentration. For air pollution control the optimum w/s ratios found to be 0.4 and 100, for cement bypass dust 0.6 and 100, for cement 0.4 and 100, and finally for steel-making slag 0.2 and 50.

Using the optimum w/s ratios mentioned above, the waste residues were sonicated up to 8 hours and the achieved CO_2 at nine different time intervals are presented in Figures 6.9-6.16. The chosen time intervals were: 30 min, 1 hour, 2 hours, 3 hours, 4 hours, 5 hours, 6 hours, 7 hours and 8 hours.

The results suggested that a substantial percentage of CO_2 uptake after 1 hour of sonication was achieved compared to 8 hours of treatment. This percentage was higher for the dry samples and ranged from 67%-99%, while for the wet samples the percentage ranged from 27%-87%.

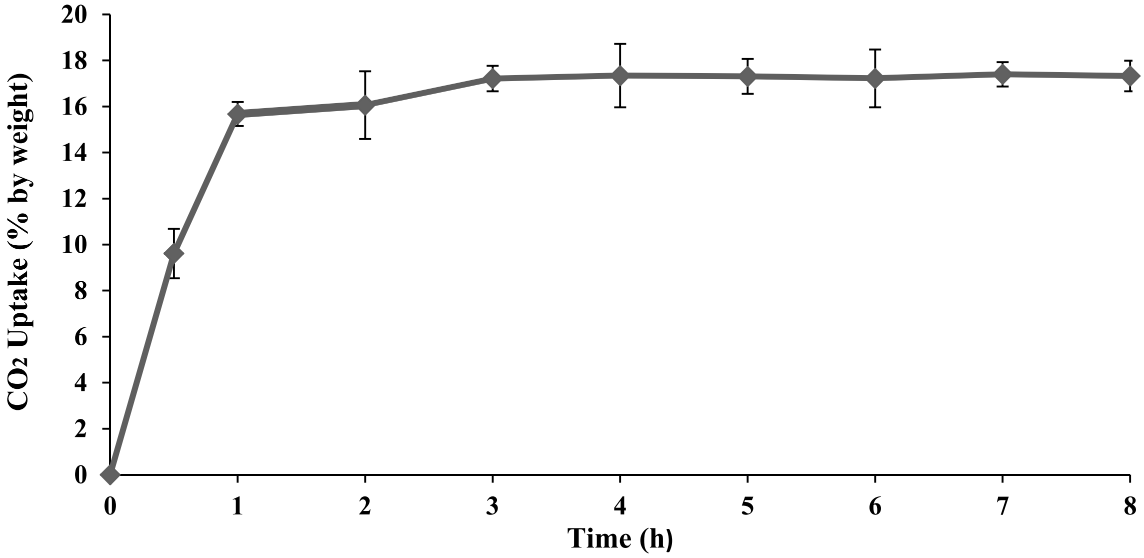


Figure 6.9: CO_2 uptake for APCr after 8 hours of sonication at w/s=0.4

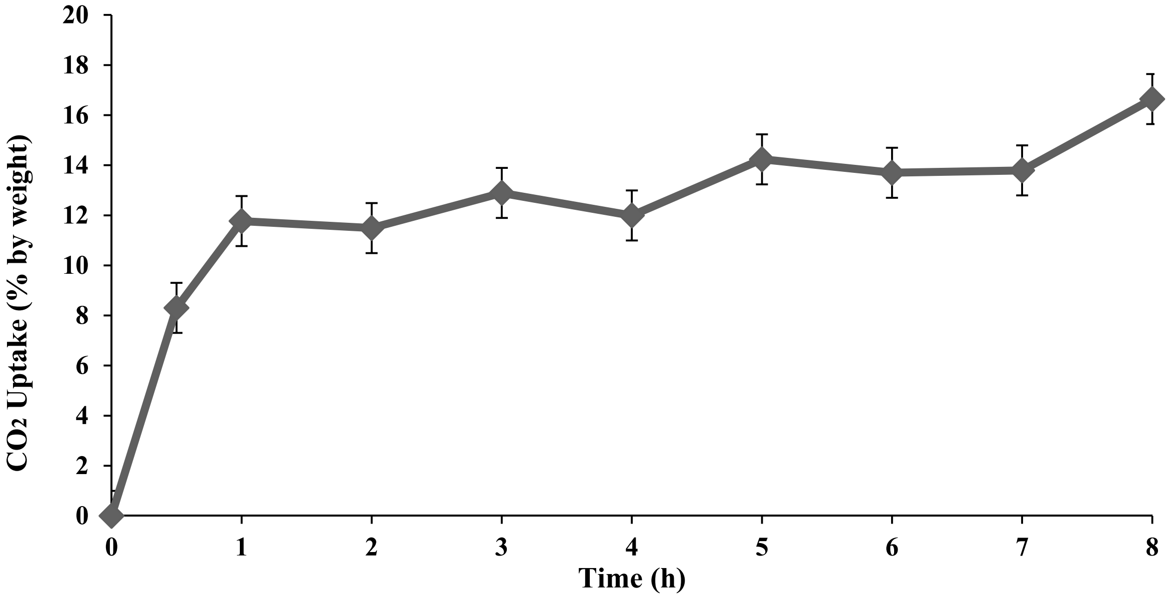


Figure 6.10: CO_2 uptake for CBD after 8 hours of sonication at w/s=0.6

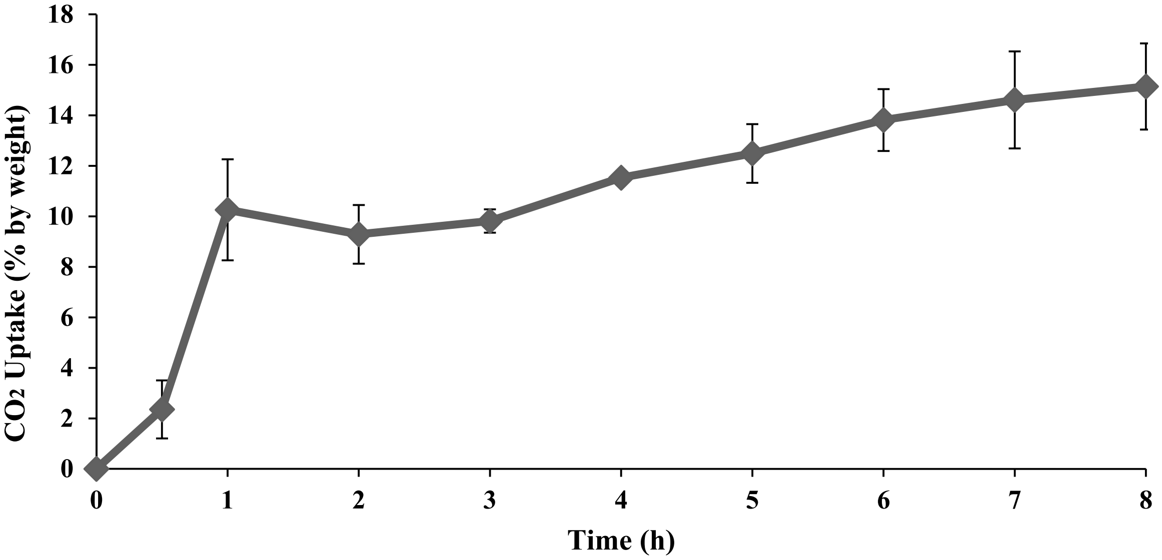


Figure 6.11: CO_2 uptake for CEM 1 after 8 hours of sonication at w/s=0.4

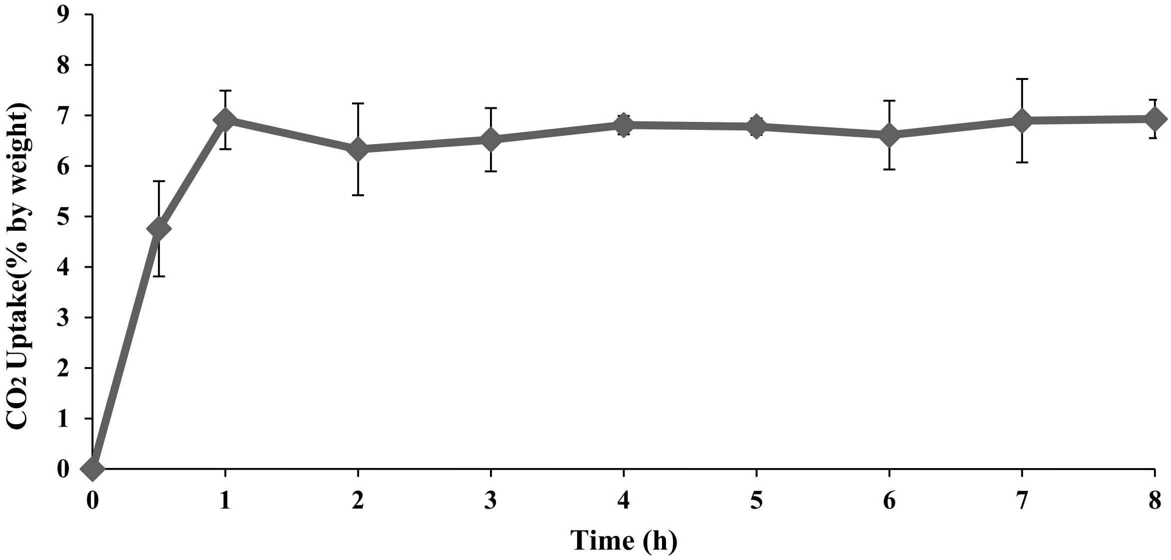


Figure 6.12: CO_2 uptake for steel slag after 8 hours of sonication at w/s=0.2

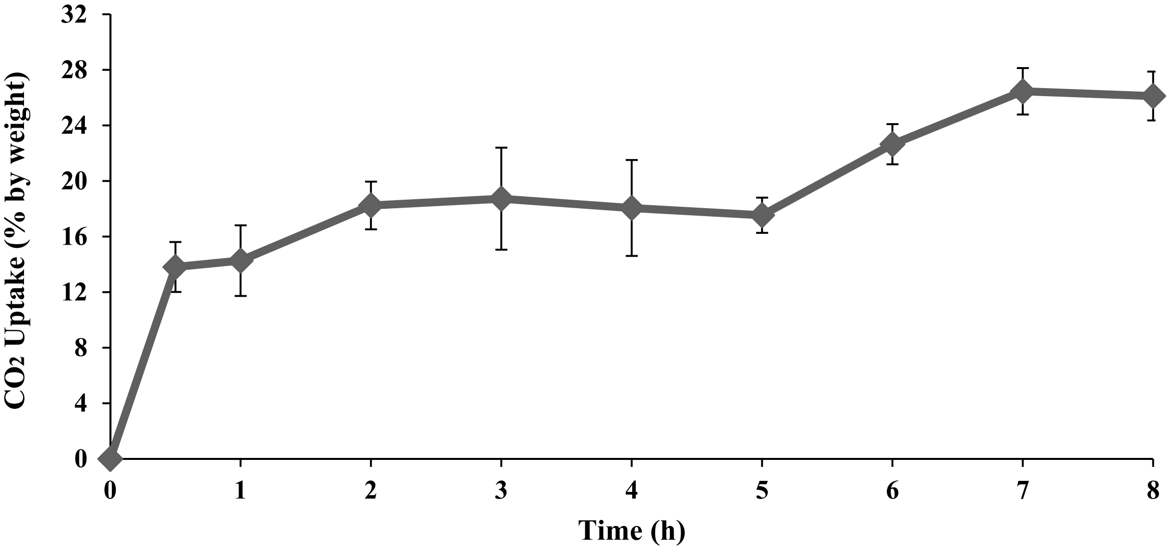


Figure 6.13: CO_2 uptake for APCr after 8 hours of sonication at w/s=100

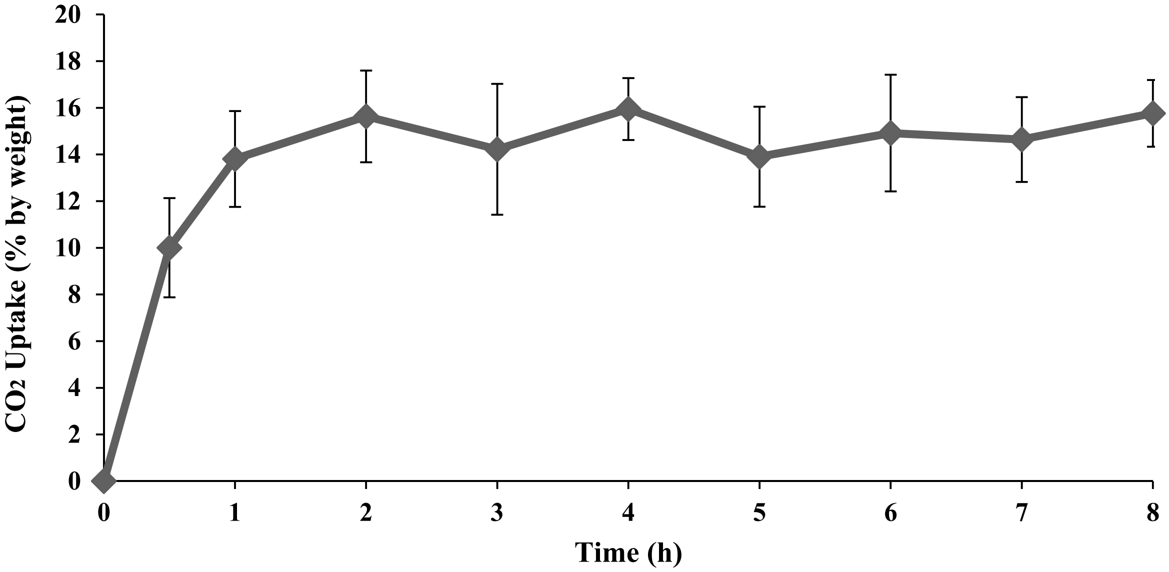


Figure 6.14: CO_2 uptake for CBD after 8 hours of sonication at w/s=100

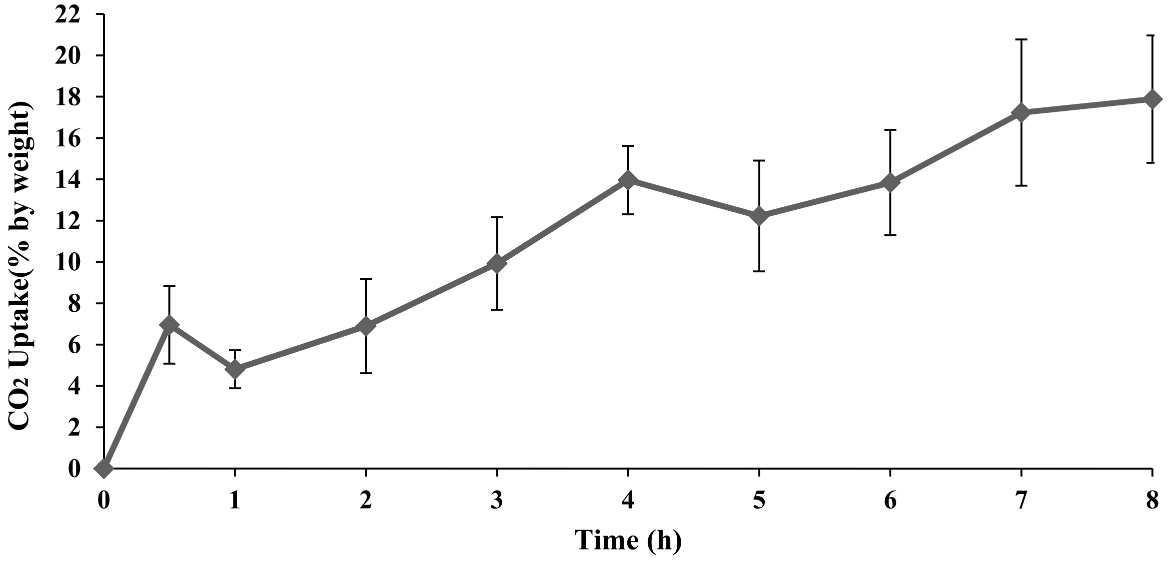


Figure 6.15: CO_2 uptake for CEM 1 after 8 hours of sonication at w/s=100

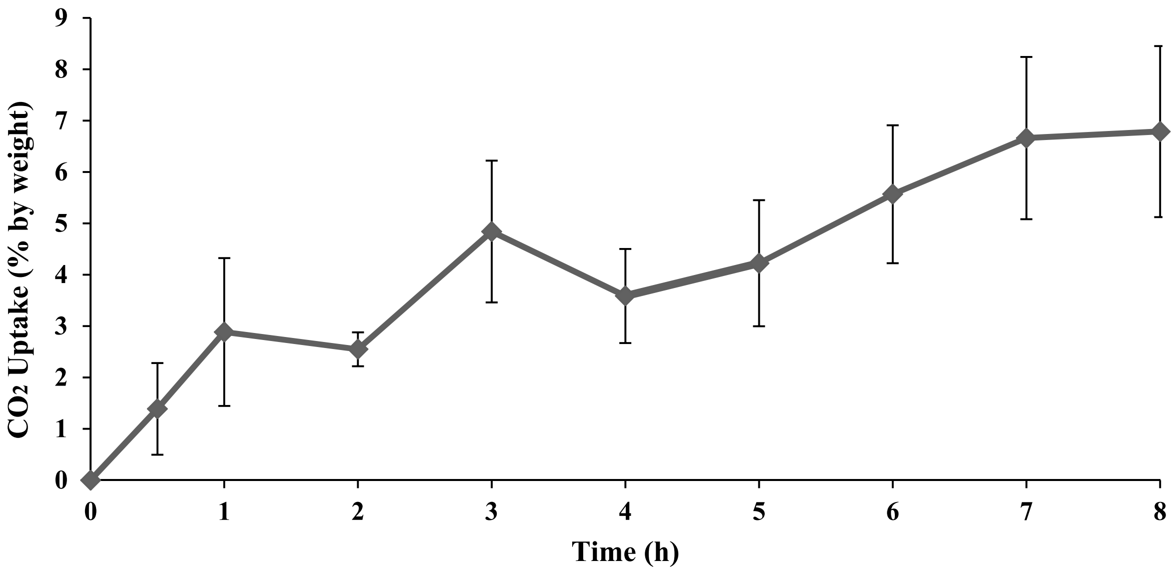


Figure 6.16: CO_2 uptake for steel slag after 8 hours of sonication at w/s=50

6.3.4 Sonication at 46 kHz

The reference material (CEM 1) was carbonated in an ultrasonic field at higher frequency (46 kHz) at half and full wave operation for 1 hour and at three different w/s ratios (0.4, 10 and 100). The recorded CO_2 uptakes were compared with the uptakes during sonication at 35 kHz.

The results showed that the exposure of the reference material to a higher frequency did not increase the achieved CO_2 uptake and thus, no further experiments were conducted at this frequency.

The recorded CO_2 uptakes at different frequencies are presented in Figure 6.17. Black columns represent the samples sonicated at 35 kHz, the pale grey columns the samples at 46 kHz half wave and the grey the samples at 46 kHz full wave.

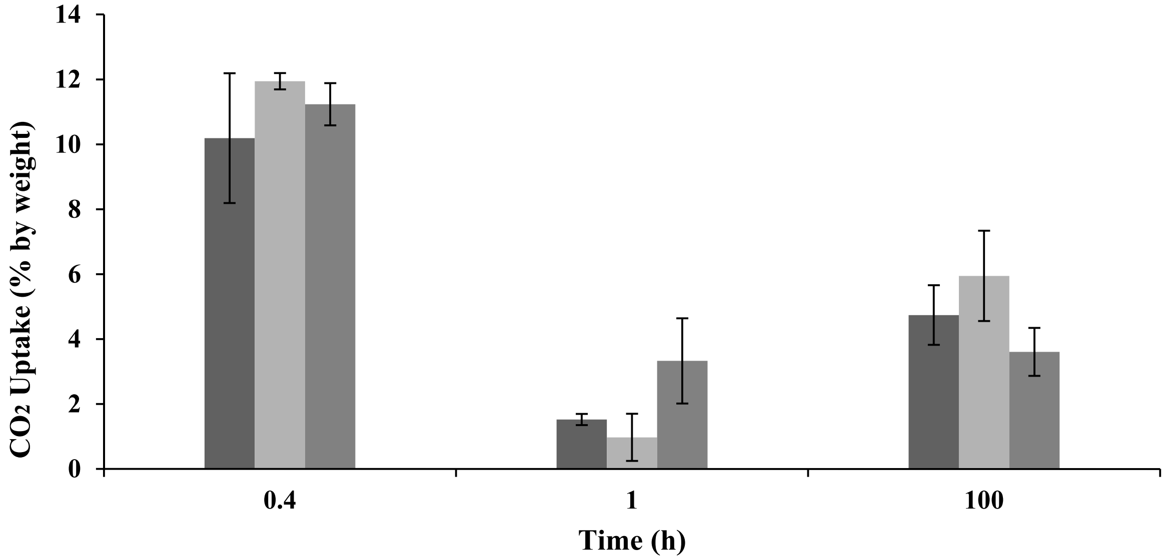


Figure 6.17: Recorded yield for CEM 1 at 35 kHz and 46 kHz-half/ full wave

6.3.5 Analysis by X-Ray Diffraction

Qualitative/semi-quantitative XRD analysis was carried out on the un-treated and treated materials. The results indicated (see Table 6.1) that both non-ultrasonic and ultrasonic treatment fully carbonated several minerals and increased the calcite concentration in the products. However, the analysis did not demonstrate any major differences between the mineralogy of non-sonicated and sonicated samples.

6.3.6 Particles Size Distribution

The particles size (d (0.5) µm) of the input materials before and after sonication was measured by wet laser diffraction analysis. The results suggested that ultrasound reduced the particles size of APCr, CBD and CEM 1, while the particles size of steel-making slags showed little change. In Figure 6.18 the particles size of the un-treated samples are represented by the black columns and the sonicated ones by the grey.

Table 6.1: Key mineral phases identified by XRD

		CEM				APCr				CBD				S.S			
Phases	**Formula**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
Akermanite	$Ca_2Mg(Si_2O_7)$													●	●	●	●
Aluminium Phosphate	Al(PO4)					○	○	○	○								
Anhydrite	CaSO4					●	●	●	●	●	●	●	●				
Bassanite	$Ca(SO_4)(H_2O)0.5$					●	●	●	●								
Brownmillerite	$Ca_2(Al,Fe)_2O_5$	●	●	●	●												
Brucite	$Mg(OH)_2$													●	●	●	●
Calcite	$CaCO_3$	++	+++	++	+++	++	++	++	++++	+	+++	+	+++	++	++	++	++
Calcium Chloride Hydroxide	CaClOH					●	●	●	○								
Calcium Iron Titanium Oxide	$CaFe_3(TiO_{3)4}$					○	○	○	○								
Chromite	$(Fe, Mg)Cr_2O_4$													●	●	●	●
Cristobalite	SiO_2					●	○	○	○								
Gehlenite	n/a									-	-	-	-				
Gypsym	CaSO4·2H2O	●	●	●	●												
Halite	NaCl					●	●	●	●								
Hatruite	$Ca_3(SiO_4)O$	-	--	-	--												
Larnite	Ca_2SiO_4	●	●	●	●					●	●	●	●				
Lime	CaO					○	○	○	○	--	○	--	○				
Magnesium Oxide Hydroxide	$Mg_5O(OH)_8$					○	○	○	○								
Manganolangbeinite	$K_2Mn_2+2(SO_4)_3$													●	●	●	●
Merwinite	$Ca_3Mg(SiO_4)_2$													●	●	●	●
Periclase	MgO													●	●	●	●
Portlandite	$Ca(OH)_2$					--	--	--	○	-	---	-	---	--	--	--	--
Pyrophanite	$Mn(TiO_3)$													●	●	●	●
Quartz	SiO_2									●	●	●	●	●	●	●	●
Rutile	TiO_2					●	●	●	●								
Sylvite	KCl					●	●	○	○	●	--	●	--				
Titanite	$CaTiSiO_5$													●	○	●	●
Vaterite	$Ca(CO_3)$					▪	▪	▪	▪								

1: Non-sonicated samples at low ratio
2: Sonicated samples at low ratio
3: Non-sonicated samples at high ratio
4: Sonicated samples at high ratio

● Present in untreated/treated material
○ Absent in treated material
+ Increase after carbonation
- Decrease after carbonation
▪ New mineral phase

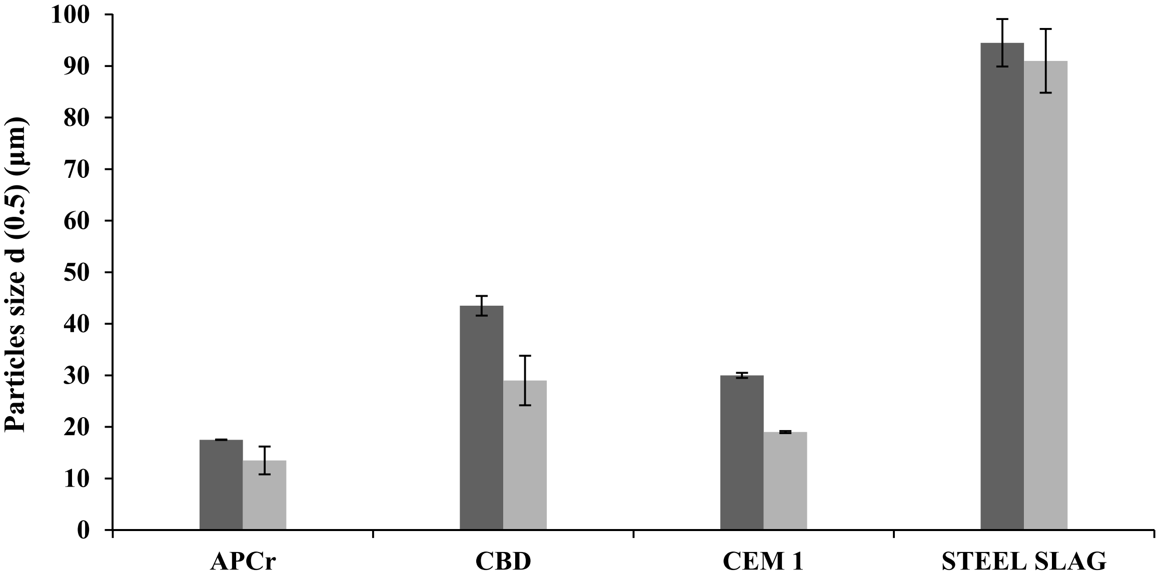
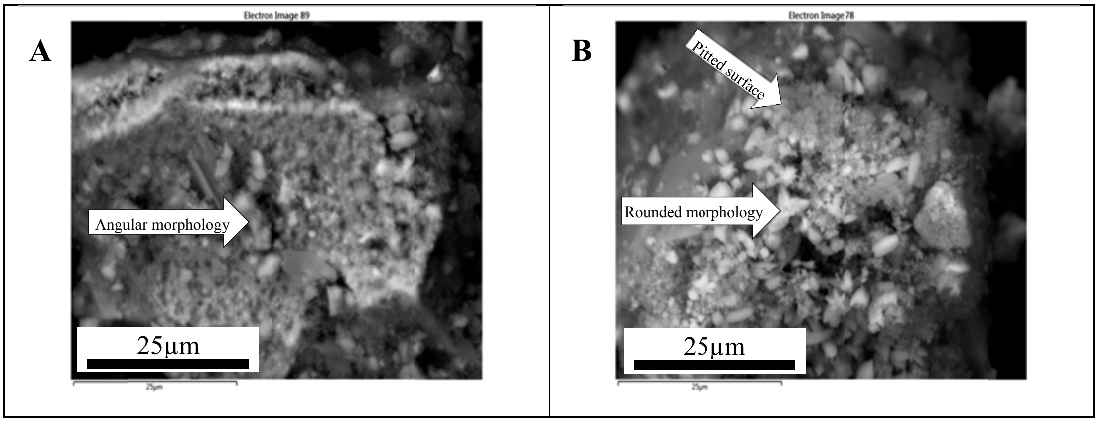


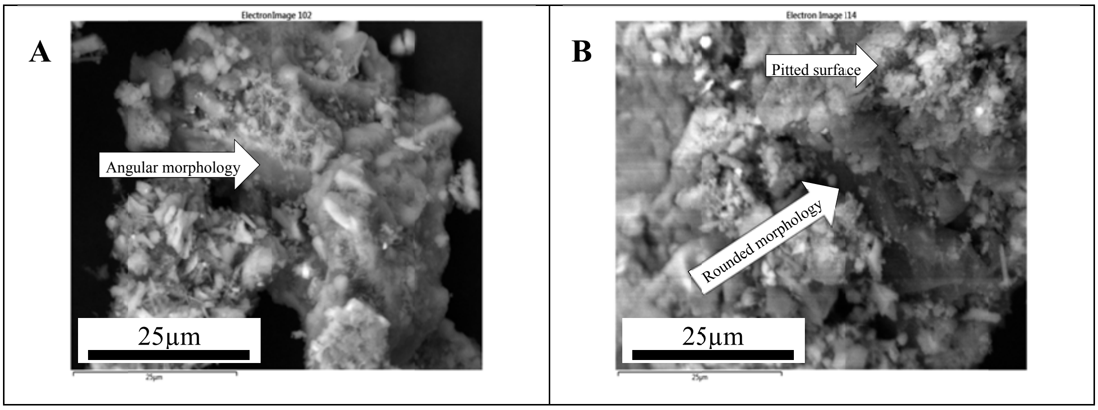
Figure 6.18: Particles size d(0.5) for un-treated and sonicated samples

6.3.7 Scanning Electron Microscopy

SEM secondary electron imaging of particle surfaces was used to identify morphological changes between non-sonicated and sonicated samples (Figure 6.19). The images showed that ultrasound did not alter the morphology of the particles significantly. The only noted change was that the non-sonicated materials characterised by a more angular appearance, while the sonicated ones exhibited a more rounded morphology with pitted surfaces.



CEM 1



Steel slags

Figure 6.19: SEM imaging for A: non-sonicated and B: sonicated materials

6.4 Discussion

6.4.1 Apparatus Testing

The equal distribution of CO_2 into the apparatus was tested by measuring the recorded CO_2 uptake of each plastic container (see Figure 6.1). The average CO_2 uptake (% by weight) was found at 8.25%, the standard deviation at 0.98 and the standard error at 0.18. Any difference in the CO_2 uptake was independent of the tube position in the bath and thus, it was assumed that the carbon dioxide was equally distributed through the apparatus.

Attenuation of sound waves occurs when sound travels through a solid medium, and its intensity reduces with distance. Previous studies suggested that the extent of ultrasonic attenuation is mainly dependent upon the physical properties of the solid medium and the frequency in which the waves are generated (Mason and McSkimin, 1947, Vitelli, 2010, Louisnard, 2010).

In this study, the available types of testing tubes comprising plastic and Pyrex, and in order to select the most appropriate material for ultrasound the reference material was carbonated at three w/s ratios and the yield was recorded. The achieved carbon uptakes shown in Figures 6.2-6.4 indicated that the average CO_2 uptake during sonication by using plastic containers was higher than Pyrex at all the selected w/s ratios.

6.4.2 Effect of Sonication on CO_2 Uptake

The results presented in Figures 6.5-6.8 suggested that the "strength" of particles cavitation was proportional to the concentration of water in the samples. The selected w/s ratios represented three types of samples: The dry samples where the w/s ratio was between 0.2 and 0.6, the intermediate samples where the ratio was between 0.8 and 10 and finally, the wet samples where the ratio was between 25 and 100.

The effect of ultrasound on the CO_2 uptake of samples under the 'dry' conditions was weak, as generally too little water was available to facilitate cavitation. Modest average increases in yield were recorded for CEM 1 (an increase of 28.6%), for APCr (19.4%) and steel slag (4%), whereas no change was observed for CBD.

At intermediate w/s ratios the CO_2 uptake of the input materials was low regardless of the type of treatment. However, at w/s ratio=0.8 effective sonication of APCr and CBD occurred. The results shown in Figures 6.2 and 6.3 indicated that ultrasound increased the average CO_2 uptake of APCr by 90% and of CBD by 50%.

At the high w/s ratios (25-100) examined, the conditions for sonication were much improved as more CO_2 was available to the aqueous medium (Rao et al., 2007). The average CO_2 uptake for steel slag increased by over 400% followed by CEM 1 and CBD (at 159% and 153%, respectively). The increase in yield with APCr was lower at 63%. Table 6.2 gives the results for sonicated and non-sonicated samples. The % increase (based on the average CO_2 uptake) and its respective w/s ratio is also presented.

Table 6.2: CO_2 uptake increase (%) after ultrasonic carbonation

Material	Ratio	Uptake (%)	Uptake (%) with ultrasound	% increase[1]
APCr	0.4	13.3±1.7	15.9±0.5	19.4
APCr	100	8.9±0.5	14.5±2.5	63.1
CBD	0.6	12.9±0.5	12.9±0.1	0
CBD	100	5.9±0.8	14.9±2.0	153
CEM 1	0.4	7.9±2.5	10.1±2.0	28.6
CEM 1	100	1.8±0.5	4.7±0.9	159
Steel slag	0.2	6.6±0.2	6.91±0.5	3.9
Steel slag	50	0.7±0.1	3.7±1.1	400

1: Values were based on average uptakes

The exposure of the reference material to a higher ultrasonic frequency showed that the CO_2 uptake did not increase (Figure 6.17). Is should be noted though, that the effect of amplitude was not considered in this study as both ultrasonic baths had a nominal amplitude value of 1 W/cm^2. The amplitude of the ultrasound waves is known to influence the precipitation rate of calcium carbonate and crystals size was of carbonates (Kojima et al., 2010).

6.4.3 Effect of Sonication Time on CO_2 Uptake

Accelerated carbonation is known to proceed rapidly under ideal conditions and the reaction can be completed within hours or even minutes (Maries, 2008). The shapes of the curves in Figures 6.9-6.12 gave the same conclusion, indicating that sonication proceeded rapidly at dry conditions. After 1 hour, the average recorded CO_2 uptakes represented 67%-99% of the respective values after 8 hours of treatment.

On the other hand, the analysis of Figures 6.13-6.16 showed that excess in water during sonication inhibited the rapid diffusion of CO_2 into the system resulting in a slower reaction. The only exception was the cement bypass dusts, where after 1 hour the average achieved uptake was 87.5% of the uptake obtained after 8 hours of sonication. For APCr, CEM 1 and steel slag the same percentage ranged from 27%-54.8%.

Table 6.3: Theoretical and actual carbonation yields

Material	Ratio	Theoretical Uptake	Actual Uptake after 1hour	Actual Uptake after 8hours
APCr	0.4	46.7	15.9±0.5	17.3±1.1
APCr	100	46.7	14.5±2.5	26.1±3.0
CBD	0.6	52.8	12.9±0.1	16.6±0.3
CBD	100	52.8	14.9±2.0	15.7±1.4
CEM 1	0.4	53.4	10.1±2.0	15.1±1.7
CEM 1	100	53.4	4.7±0.9	17.8±3.0
Steel slag	0.2	39.7	6.91±0.5	6.93±0.3
Steel slag	50	39.7	3.7±1.1	6.7±1.6

1: Values were based on average uptakes

The yields after 8 hours of treatment with ultrasound were also compared with the theoretical values derived from the Steinour formula. In line with the findings of the previous chapter, the CO_2 uptake predicted by the theoretical model for each residue was significantly higher than the experimental CO_2 uptake obtained after carbonation with ultrasound. The results after 1 hour and 8 hour of sonication as well as the predictions derived from the Steinour formula were summarised in Table 6.3.

6.4.4 Mineral Phases Analysis

Qualitative/semi-quantitative XRD analysis was conducted for the un-treated, non-sonicated and sonicated samples. The analysis showed that ultrasound enhanced the precipitation of calcite in the reaction products and fully carbonated several mineral phases found in the un-treated materials. The differences between the mineralogy of sonicated and non-sonicated samples were relatively small.

Calcite is one of the three polymorphs of calcium carbonate. Vaterite and aragonite are the other two. At ambient conditions the most thermodynamically stable polymorph is calcite which consists of rhombohedra crystals, while aragonite crystals are found in orthorhombic formation. Aragonite is favoured at elevated temperatures and pressures and is converted naturally to calcite after thousands of years. Vaterite, is the least thermodynamically stable polymorph of $CaCO_3$ with hexagonal crystals and is transformed rapidly in either calcite or aragonite (Price et al., 2010).

In this study aragonite was not identified in any of the treated wastes. Vaterite was found in the carbonated samples of APCr. Also, the XRD analysis of these ashes indicated that sonication at high w/s ratio fully carbonated aluminium phosphate, calcium iron titanium oxide, cristobalite, magnesium oxide hydroxide, sylvite and calcium chloride hydroxide. In addition, the precipitation of calcite after carbonation with ultrasound in the high w/s ratio samples increased, due to the complete conversion of lime and portlandite into $CaCO_3$. In the "dry" samples the precipitation of calcite was lower as the analysis revealed the presence of un-reacted portlandite. Portlandite was also found in the non-sonicated samples, which were also showed peaks of calcium chloride hydroxide, christobalite and sylvite (at high w/s ratio only). Finally, no change was noted for the minerals anhydrite, bassanite, halite and rutile.

Sonication of CBD found to increase the precipitation of calcite in the carbonated products, as lime and portlandite reacted to $CaCO_3$. On the other hand, the precipitation of calcite in the non-sonicated samples was lower since the reactivity of lime and portlandite was lesser. The mineral sylvite was fully carbonated after sonication, while the concentration of gelhenite seemed to decrease after both types of treatments. The concentration of the minerals anhydrite, larnite and quartz remained unchanged.

The predominant mineral phases of cement were brownmillerite, calcite, hatruite gypsym and larnite. The diffractograms of both sonicated and non-sonicated samples revealed the presence of all these minerals after treatment. However, the concentration of calcite in the sonicated samples slightly increased due to the higher conversion of hatruite into $CaCO_3$.

Steel slag is the main by-product of the steel production process, comprising calcium, iron, aluminium, magnesium, manganese and other heavy metals and due to its high alkalinity intensive pre-treatment prior to disposal or valorisation is required (Santos et al., 2013b). The complex mineralogy of this waste was validated by the number of mineral phases found by X-ray diffraction. The analysis suggested that the concentration of akermanite, brucite, chromite, manganolangbeinite, merwinite, periclase, pyrophanite, quartz and titanite (for high w/s ratio samples) remained unchanged after both types of treatment. The only recorded mineralogical alteration was the moderate conversion of portlandite into calcite and the complete carbonation of titanite after sonication at low w/s ratio.

6.4.5 Particles Size Distribution

The particles size of the waste residues before and after sonication was measured by wet laser diffraction analysis (Figure 6.18). It was found that the d(0.5) of the sonicated particles decreased in accordance with findings of previous studies (Kojima et al., 2010, Lu et al., 2002, Rao et al., 2007, Santos et al., 2010). The results suggested that the average d(0.5) of cement particles reduced by 35.5%, closely followed by the particles of cement dust (33.5%) and APCr (24%). Steel-making slag was the only waste showing little change in particles size as after ultrasound the d(0.5) reduced only by 3%.

Scanning electron microscopy (see Figure 6.19) did not reveal any big differences between sonicated and non-sonicated samples. The only noted morphological change was that the non-sonicated materials were characterised by a more rounded appearance and lower relief, whereas the sonicated particles exhibited a more angular appearance with high relief. The latter appeared to exhibit a pitted and eroded surface, which was evident in cement and steel slag. The pitting may be ascribed to fracturing of particles from the surface as a result of resonance induced by ultrasound. ‘Eroded’ morphologies of particles exposed to ultrasound has previously been observed in a study conducted upon steel slags (Santos et al., 2010).

6.5 Conclusions

In this study, the effect of sonication on CO_2 uptake and mineralogy of APCr, CBD, CEM 1 and steel-making slags at ambient temperature and pressure was examined.

Ultrasound did not increase the CO_2 uptake of the tested materials at low w/s ratios (0.2-0.6). In these 'dry' conditions the cavitation of the solid particles was unlikely to occur, as the film of water surrounding particle surfaces was generally too 'thin'. Despite this, the average CO_2 uptake appeared to increase slightly between 4% and 28%. At high w/s ratios (50-100) a significant increased yield was recorded (62%-400%), as the conditions were much more suited for sonication. As might be expected, ultrasound decreased the particle size of the newly formed carbonated products.

The CO_2 uptakes achieved after 8 hours of sonication were compared with the theoretical values derived from the Steinour formula. In every occasion, the actual CO_2 uptakes were considerably lower than the predicted ones. However, the recorded CO_2 uptakes after 1 hour of sonication indicated that a large percentage of CO_2 was bound into the products compared to 8 hours of treatment. For low w/s ratios this percentage ranged from 67%-99%, showing that carbonation occurred rapidly, while for "wet" samples (except for cement bypass dusts) the same percentage was 27%-54.8% as the high water content resulted in a slower reaction.

Analysis by X-ray diffraction showed that ultrasonic-induced carbonation enhanced the formation of calcite and promoted the carbonation of several mineral phases found in the un-treated samples. The only input material that showed little change in its mineral composition before and after treatment was steel slag, due to its complex mineralogy and diverse chemical composition.

Finally, SEM imaging showed that the non-sonicated samples was characterised by a more rounded appearance and lower relief, while sonicated materials exhibited a more angular appearance with high relief and eroded morphology.

In the following chapter the same materials were carbonated with the aid of organic or in-organic chemical substances to examine whether the carbonation yield could be increased.

7 CHEMICAL ACCELERATORS

7.1 Introduction

The final experimental chapter investigates the effect of four candidate catalysts on the CO_2 uptake of waste residues during waste carbonation. There are limited previous studies regarding the chemical catalysis of accelerated carbonation, since the application of many proposed organic and in-organic chemical substances was rejected, due to their high cost and toxicity or the formation of un-desired by-products.

In this study, aqueous solutions of acetic acid, ethanol, sodium hypochlorite and sodium nitrite, four relatively non-expensive and non-toxic compounds, were mixed with APCr, CBD, CEM 1 and steel-making slags at the optimum low and high w/s ratios established in the previous chapter and the CO_2 uptake of the carbonated products was measured by total organic carbon analysis.

The candidate catalysts were mixed with water at three different molarities (0.1M, 0.5M and 2.5M) representing solutions of different strength. Accelerated carbonation was conducted under ambient temperature and pressure and 1 hour reaction time. The same experiments were repeated under the presence of an ultrasonic field at 35 kHz frequency, in order to assess the combined effect of chemical acceleration and ultrasound upon the achieved yield.

The samples that showed the highest CO_2 uptake were analysed by X-Ray diffraction in order to identify any toxic products after carbonation. It is known that analysis by XRD can identify substances with concentration higher than 0.5%. Finally, health, safety and environmental issues associated with the process/handling of acetic acid, ethanol, sodium hypochlorite and sodium nitrite found in literature were discussed.

7.2 Materials and Methods

7.2.1 Materials

The input materials comprising the reactive waste residues identified in the previous chapters (APCr, CBD and steel-slag), while CEM 1 was used as the reference material.

For the purpose of this study acetic acid glacial (99.7%) ethanol (Absolute ethanol 99%), sodium hypochlorite (General Purpose Grade) and sodium nitrite (97%) were purchased from Fischer Scientific. Table 7.1 summarises the applied chemicals, their chemical formula and general applications found in literature.

Table 7.1: Chemical formula and general applications of the applied chemicals

Chemical	Formula	General Applications
Acetic acid	CH_3COOH	Acetic acid, also known as ethanoic acid, is a colourless organic compound with a distinctive sour smell and taste. It is considered an important chemical reagent and industrial chemical as it used for the production of cellulose acetate for photographic films (Han et al., 2008), the production of polyvinyl acetate used for wood glue and synthetic fibres and fabrics (Luyben and Tyréus, 1998), as well as a food regulator and condiment (Pérez-Martínez et al., 2010).
Ethanol	C_2H_5OH	Ethanol is a volatile, flammable and colourless compound and it is the principal ingredient found in alcoholic drinks. The biggest health issue regarding ethanol concerns the consumption of large amount of alcohol from humans that leads to intoxication and other serious diseases (Rubin et al., 1970). Recently, one of the most important commercial uses of ethanol includes the production

		of bioethanol which is used as a substitute of petrol for road transport vehicles (Alvira et al., 2010).
Sodium hypochlorite	NaClO	The catalytic reaction of chlorine with sodium hydroxide leads to the formation of sodium hypochlorite (Chatenet et al., 2002). A common commercial form of sodium hypochlorite is in aquatic solution (known as bleach), which is the most effective disinfectant and bleaching agent. Other uses of this compound involves the chlorination of swimming pools (Li and Blatchley, 2007) and the oxidation of CN^- of cyanide wastewater and natural water (Nonomura, 1987).
Sodium nitrite	$NaNO_2$	Sodium nitrite is an in-organic solid compound with a characteristic white to pale yellow colour and the most important use of this substance is as an inhibitor of microbial growth in fresh meat (Milkowski et al., 2010). Also, sodium nitrite is widely used as a reagent for the conversion of amines into diazo which is the key precursor to many dyes (Goddard-Borger and Stick, 2007) .

7.2.2 Methods

7.2.2.1 Chemicals Preparation

Each chemical was initially combined with water at the selected molarities (0.1M, 0.5M and 2.5M) and then, the solutions were mixed with the waste residues at the desired w/s ratios.

The solutions were prepared in a fume cabinet. Conical flasks of 250 ml volume were filled up to 1/3 with distilled water and with the aid of an electronic pipet (in the case of sodium nitrite a spatula was used) the required amount of each chemical was added through a funnel into the flask. Then the flask was filled up with distilled water and the mixes were agitated with manual stirring to become homogeneous.

The required volumes (in ml) in 1 L of water of acetic acid, ethanol and sodium hypochlorite were estimated by using the equation below:

$$V_x = \frac{M * MW}{\rho} \tag{7.1}$$

Where:

V_x= is the volume of chemical in ml
M: is the selected molarity in mol/L
MW: is the molecular weight in g/mol
ρ: is the density in g/ml

The only solid chemical substance was sodium nitrite and the mass required for each solution was estimated according to equation 7.2.

$$\mathrm{M}_x = M * MW \tag{7.2}$$

Where:

M_x= is the mass of sodium nitrite in gr
M: is the selected molarity in mol/L
MW: is the molecular weight of sodium nitrite in g/mol

The molecular weight (MW), density and volume/mass added in 1 L and 250 ml of water respectively, for each chemical are summarised in Table 7.2.

Table 7.2: Volume and mass of each chemical at 0.1M, 0.5M and 2.5M

Chemical	M (mol/L)	MW (g/mol)	ρ (g/ml)	V_x or M_x added in 1 L of water (ml or gr)	V_x or M_x added in 250 ml of water (ml or gr)
Acetic acid	0.1	60.05	1.05	5.72	1.43
Acetic acid	0.5	60.05	1.05	28.60	7.15
Acetic acid	2.5	60.05	1.05	142.9	35.7
Ethanol	0.1	46.05	0.79	5.83	1.46
Ethanol	0.5	46.05	0.79	29.20	7.30
Ethanol	2.5	46.05	0.79	145.9	36.5
Sodium Hypochlorite	0.1	74.44	1.11	6.70	1.67
Sodium Hypochlorite	0.5	74.44	1.11	33.55	8.40
Sodium Hypochlorite	2.5	74.44	1.11	167.6	41.9
Sodium Nitrite	0.1	68.99		6.90	1.70
Sodium Nitrite	0.5	68.99		34.50	8.62
Sodium Nitrite	2.5	68.99		172.5	43.1

7.2.2.2 Experimental Set-Up

The experimental apparatus was described in the previous chapters. The applied ultrasonic field (35 kHz) was generated by an ultrasonic bath (Camlab, 150-300 W). The reaction conditions were: T=293 K, p=0.1 MPa, C_{CO2}=100% and flow-rate=0.2 L/min.

7.2.2.3 Products Characterisation

After treatment, the CO_2 uptake of the reaction products (expressed as % CO_2 weight/total weight of the carbonated products) was measured by an IL 550 TOC-TN/DSC1300 analyser. The samples that showed the highest CO_2 uptake were analysed by X-Ray diffraction in order to examine whether any toxic products were formed after chemical acceleration.

7.2.2.4 Variability and experimental error

Each experiment was repeated three times and the variability of results was estimated by using standard deviation and standard error of the mean. The latter represented the error bars in the following graphs. Cement was used as the reference material.

7.3 Results

7.3.1 Carbonation under Dry Conditions

Initially, the input materials were carbonated at the optimum low w/s ratios found previously: APCr and CEM 1 at w/s=0.4, CBD at w/s=0.6 and steel-slag at w/s=0.2. The experiments were repeated under the presence of an ultrasonic field at 35 kHz to assess the combined effect of chemical acceleration and ultrasound on the CO_2 uptake of the reaction products. The CO_2 uptakes obtained for each residue are shown in graphs 7.1-7.4. The black columns represent the yields during chemical acceleration only, while the grey the yields during chemical acceleration with ultrasound.

The results suggested that the samples containing ethanol without sonication increased the CO_2 uptake of the APCr by 75% to 120%. Also, acetic acid without sonication increased the carbon uptake of cement dusts by 80%, while the same chemical at 0.5M and 2.5M increased the CO_2 uptake of steel slags by 50%-77%. In addition, the recorded yields indicated that the combined effect of chemical acceleration and sonication did not result in more effective carbonation. The only exception found in the samples of CEM 1 where acetic acid at 2.5M and sonication increased the achieved CO_2 uptake by 80%. Finally, it was found that during sonication of the ethanoic samples the contained ethanol was evaporated and the carbonation proceeded without chemical acceleration.

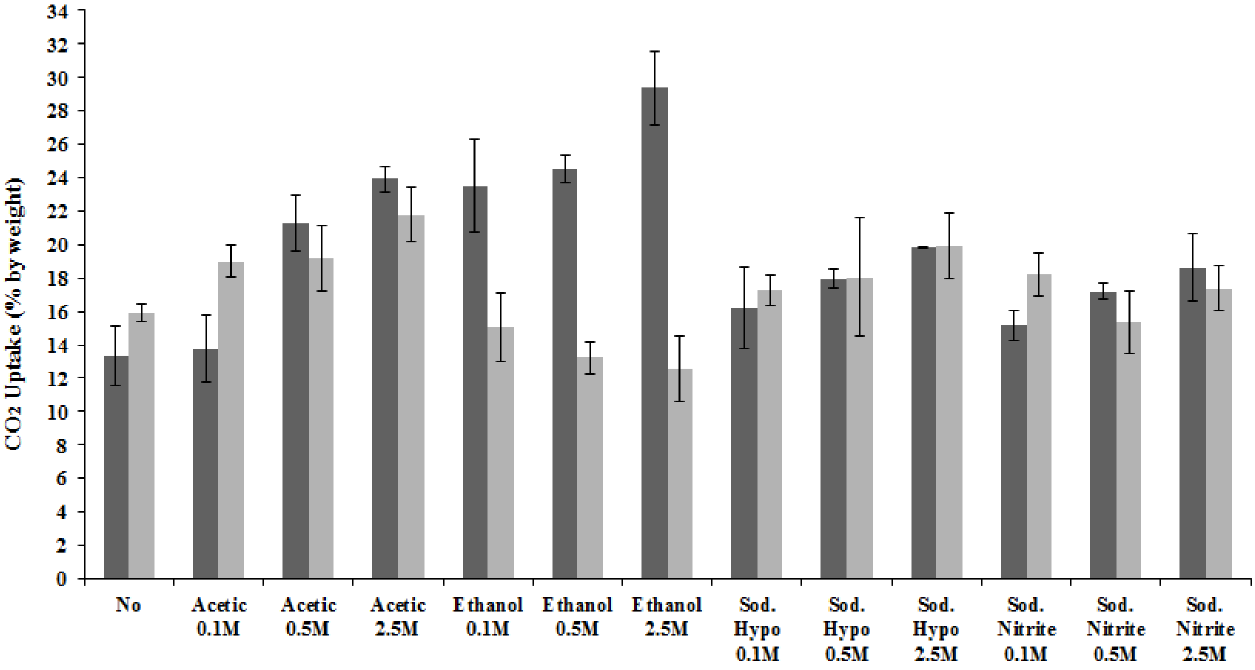


Figure 7.1: CO_2 uptake for APCr at w/s=0.4

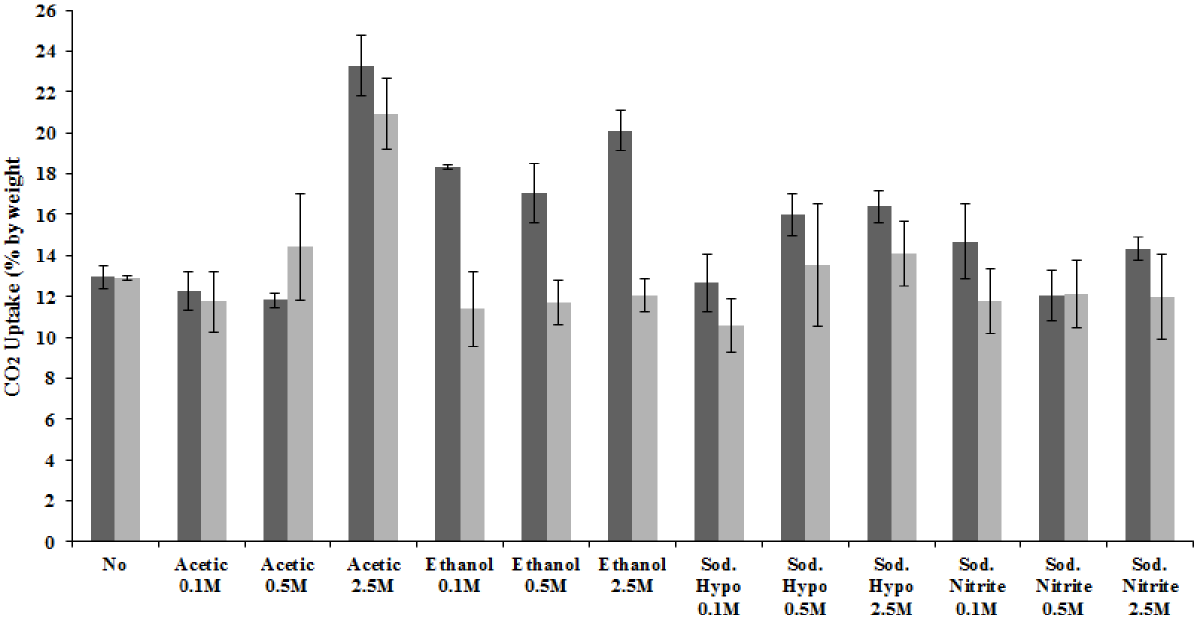


Figure 7.2: CO_2 uptake for CBD at w/s=0.6

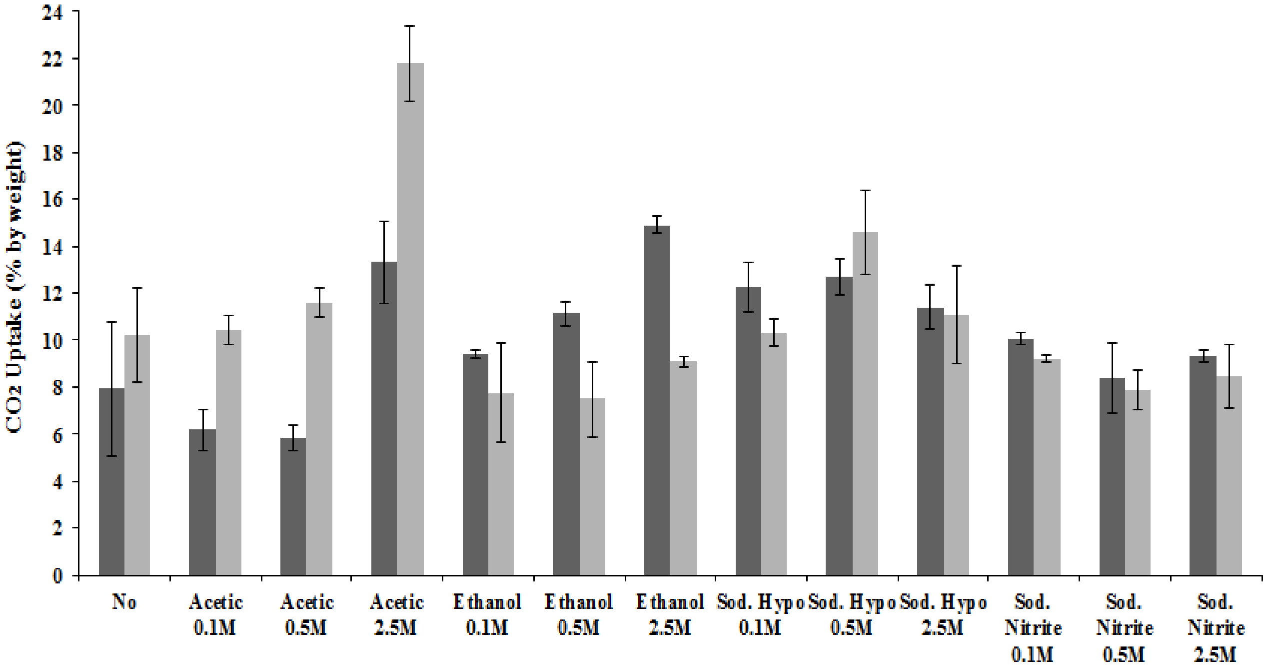


Figure 7.3: CO_2 uptake for CEM 1 at w/s=0.4

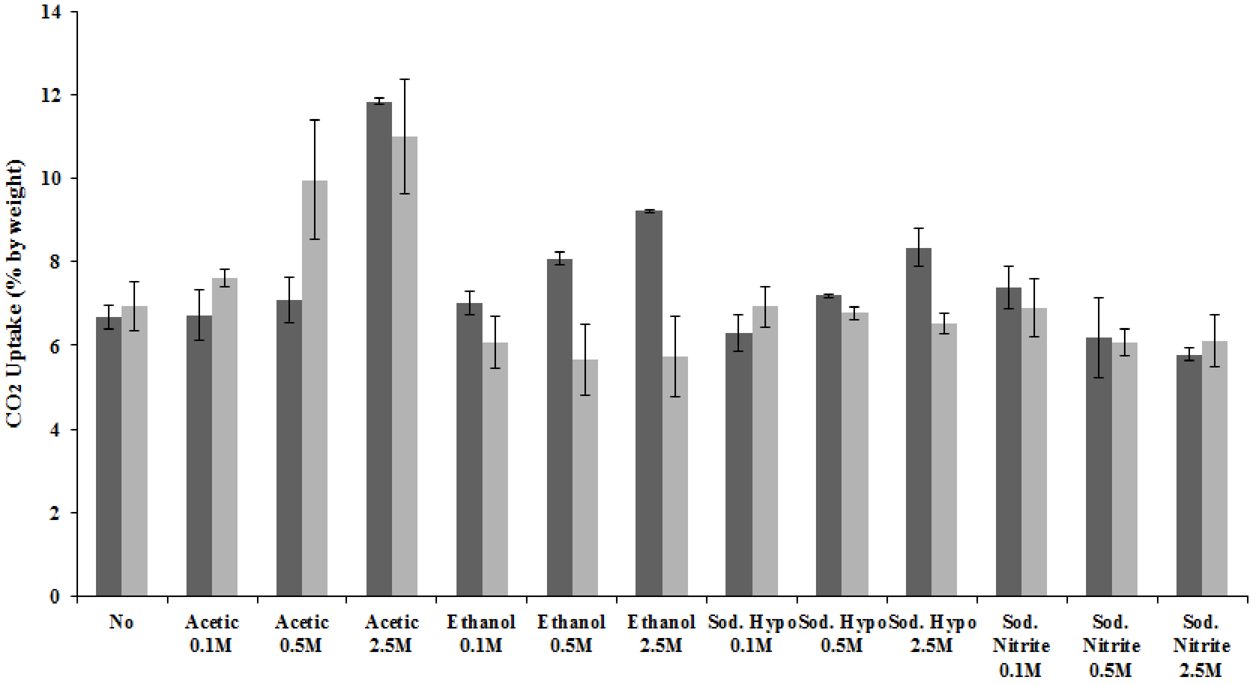


Figure 7.4: CO_2 uptake for steel-making slag at w/s=0.2

7.3.2 Phase Analysis of Dry Samples

The samples that showed the highest CO_2 uptake were analysed by XRD. The results indicated that no toxic products were identified by this method. The mineral phases of each sample after and before treatment are presented in Table 7.3.

7.3.3 Carbonation under Wet Conditions

The same waste residues were carbonated at the optimum high w/s ratios found in the previous chapter: APCr, CBD and CEM 1 at w/s=100 and steel-slag at w/s=50. The experiments were repeated under the presence of an ultrasonic field at 35 kHz to examine the combined effect of chemical acceleration and ultrasound on the CO_2 uptake of the reaction products.

The CO_2 uptakes obtained are shown in the graphs 7.5-7.8. The black columns represent the yields during chemical acceleration only, while the grey the yields during chemical acceleration with ultrasound.

The recorded yields suggested that the samples containing acetic acid gave the highest CO_2 uptake, however this was due to acid dissolution and not due to a true catalytic effect of this chemical as it is explained in the discussion section.

Table 7.3: Key mineral phases identified by XRD under dry conditions

Phases	Formula	CEM 1 ACETIC 2.5M	APCr ETHANOL 2.5M	CBD ACETIC 2.5M	S.S ACETIC 2.5M
Akermanite	$Ca_2Mg(Si_2O_7)$				●
Aluminium Phosphate	$Al(PO4)$		○		
Anhydrite	$CaSO4$		●	●	
Bassanite	$Ca(SO_4)(H_2O)0.5$		●		
Brownmillerite	$Ca_2(Al,Fe)_2O_5$	●			
Brucite	$Mg(OH)_2$				●
Calcite	$CaCO_3$	++	+++	++	+
Calcium Chloride Hydroxide	$CaClOH$				
Calcium Iron Titanium Oxide	$CaFe_3(TiO_3)_4$		○		
Chromite	$(Fe, Mg)Cr_2O_4$				●
Cristobalite	SiO_2		●		
Gehlenite	$Ca_2Al[AlSiO_7]$			●	
Gypsym	$CaSO4 \cdot 2H2O$	●			
Halite	$NaCl$		●		
Hatruite	$Ca_3(SiO_4)O$	--			
Larnite	Ca_2SiO_4	●		●	
Lime	CaO		○	-	
Magnesium Oxide Hydroxide	$Mg_5O(OH)_8$		○		
Manganolangbeinite	$K_2Mn_2+2(SO_4)_3$				●
Merwinite	$Ca_3Mg(SiO_4)_2$				●
Periclase	MgO				●
Portlandite	$Ca(OH)_2$		--	-	-
Pyrophanite	$Mn(TiO_3)$				●
Quartz	SiO_2			●	●
Rutile	TiO_2		●		
Sylvite	KCl		●	●	
Titanite	$CaTiSiO_5$				●
Vaterite	$Ca(CO_3)$		▪		

● Present in untreated/treated material
○ Absent in treated material
+ Increase after carbonation
- Decrease after carbonation
▪ New mineral phase

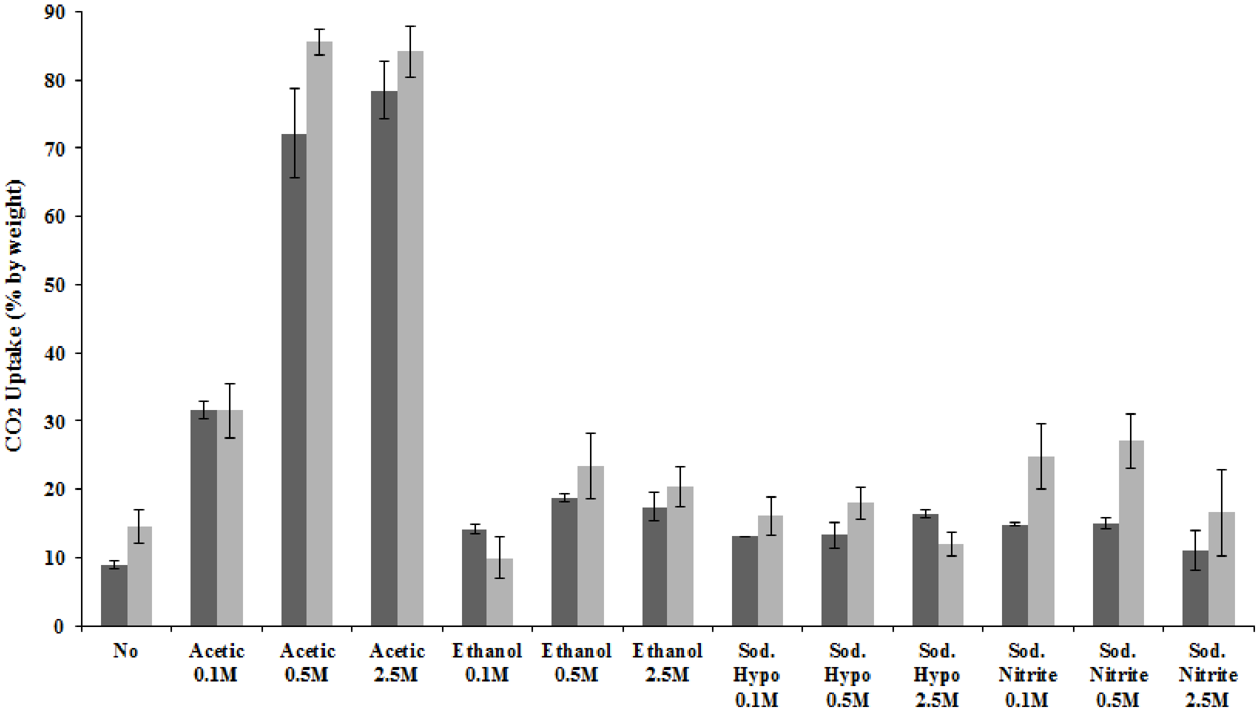


Figure 7.5: CO_2 uptake for APCr at w/s=100

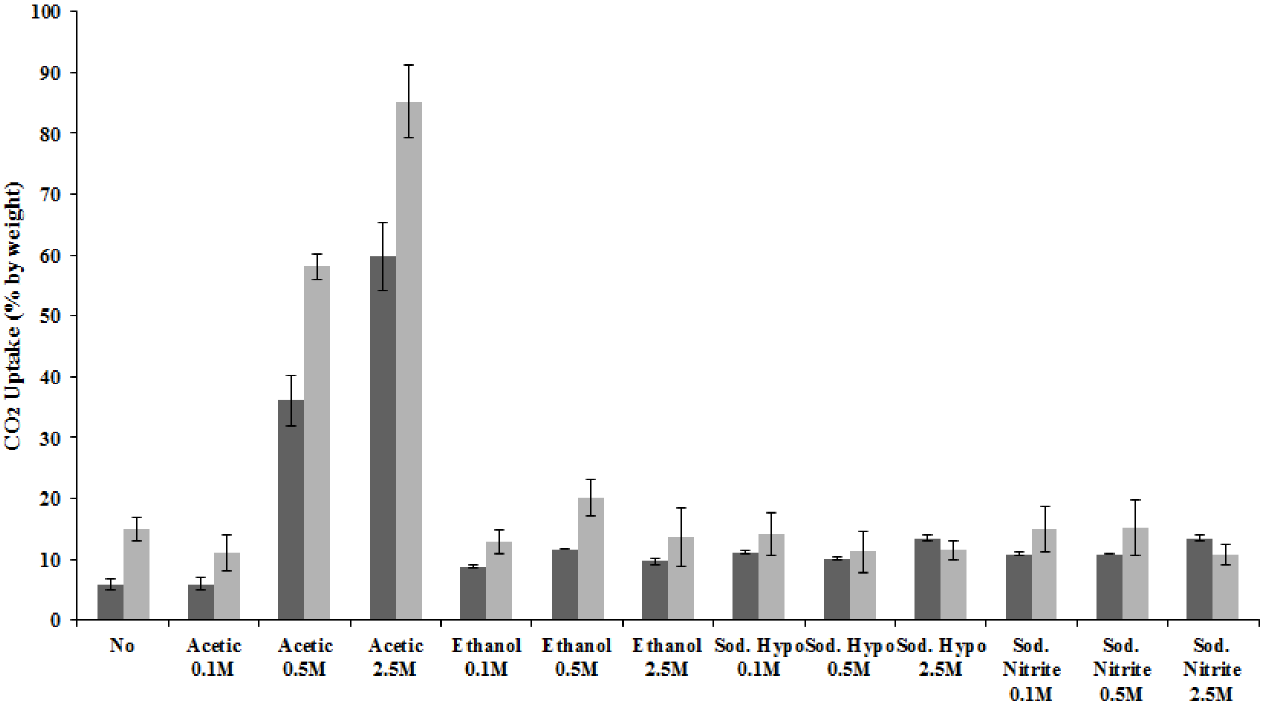


Figure 7.6: CO_2 uptake for CBD at w/s=100

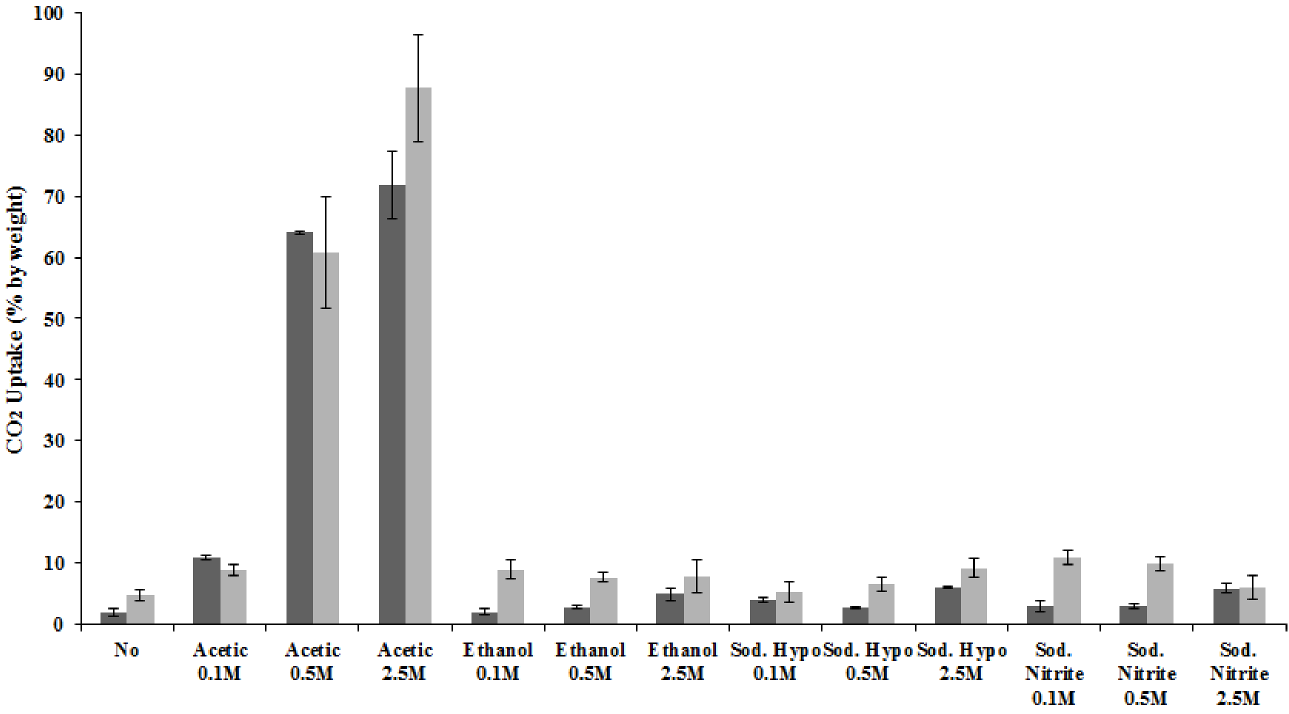


Figure 7.7: CO_2 uptake for CEM 1 at w/s=100

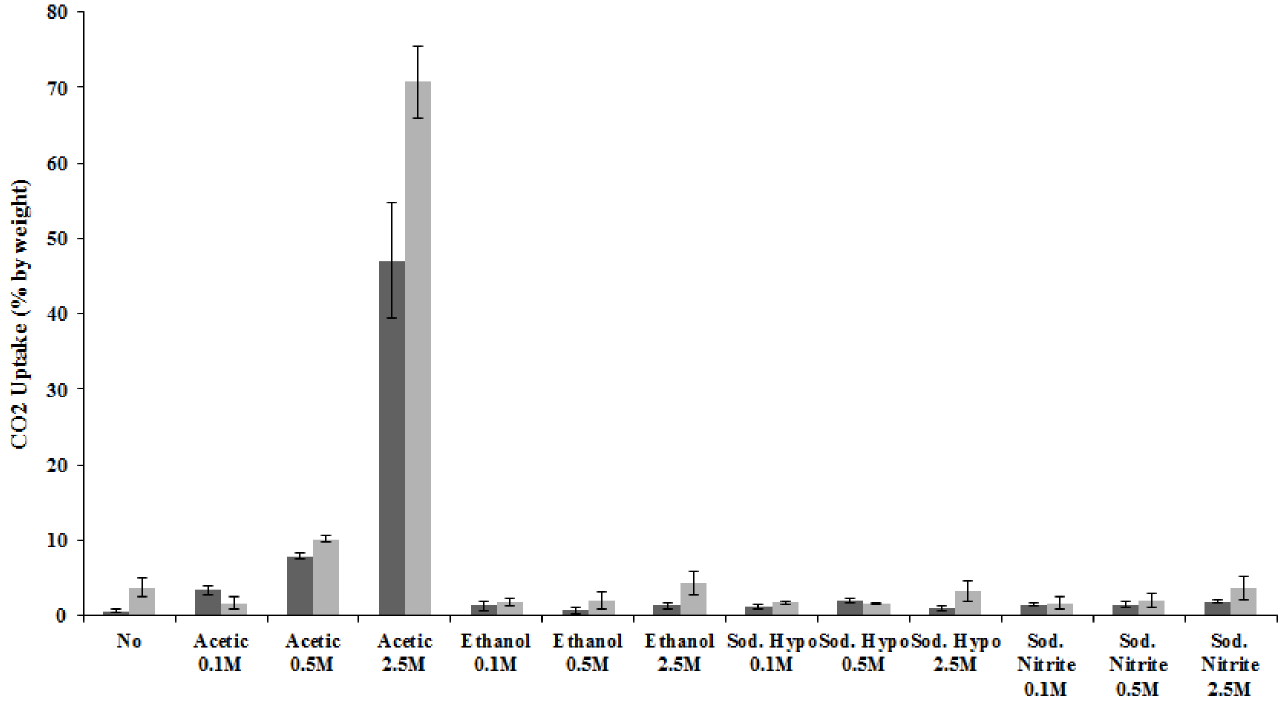


Figure 7.8: CO_2 uptake for steel-making slag at w/s=50

7.3.4 Phase Analysis of Wet Samples

The yields presented in Figures 7.5-7.8 suggest that the samples that achieved the highest CO_2 uptake were the ones containing acetic acid. Analysis by X-ray diffraction were conducted and showed that the principal mineral phase in the carbonated samples was calcium acetate hydrate.

Table 7.3: Key mineral phases identified by XRD at wet conditions

Phases	Formula	CEM 1 ACETIC 2.5M	APCr ETHANOL 2.5M	CBD ACETIC 2.5M	S.S ACETIC 2.5M
Akermanite	$Ca_2Mg(Si_2O_7)$				●
Aluminium Phosphate	Al(PO4)		○		
Anhydrite	CaSO4		●	●	
Bassanite	$Ca(SO_4)(H_2O)0.5$		●		
Brownmillerite	$Ca_2(Al,Fe)_2O_5$	---			
Brucite	$Mg(OH)_2$				○
Calcite	$CaCO_3$	--	---	---	●
Calcium acetate hydrate	$Ca(C_2H_3O_2)_2$	▪	▪	▪	▪
Calcium chloride hydroxide	CaClOH		●		
Calcium iron titanium oxide	$CaFe_3(TiO_3)_4$		○		
Chromite	$(Fe, Mg)Cr_2O_4$				●
Cristobalite	SiO_2		○		
Gehlenite	$Ca_2Al[AlSiO_7]$			○	
Gypsym	CaSO4·2H2O	○			
Halite	NaCl		---		
Hatruite	$Ca_3(SiO_4)O$	---			
Larnite	Ca_2SiO_4	○		○	
Lime	CaO		○	○	
Magnesium acetate hydrate	$Mg(CH_3COO)_2 \cdot 4H_2O$				▪
Magnesium oxide hydroxide	$Mg_5O(OH)_8$		○		
Manganolangbeinite	$K_2Mn_2+2(SO_4)_3$				--
Merwinite	$Ca_3Mg(SiO_4)_2$				--
Periclase	MgO				-
Portlandite	$Ca(OH)_2$		○	○	○
Pyrophanite	$Mn(TiO_3)$				○
Quartz	SiO_2			-	-
Rutile	TiO_2		---		
Sodium acetate	CH_3COONa		▪		
Sylvite	KCl		○	●	
Titanite	$CaTiSiO_5$				●
Vaterite	$Ca(CO_3)$		▪		

● Present in untreated/treated material
○ Absent in treated material
+ Increase after carbonation
- Decrease after carbonation
▪ New mineral phase

7.4 Discussion

7.4.1 Health, Safety and Environmental Issues

Although acetic acid, ethanol, sodium hypoclorite and sodium nitrite are characterised as non-toxic candidate catalysts of accelerated carbonation (Maries and Hills, 2013) there are some health, safety and environmental issues associated with their handling/processing.

The biggest health issue of ethanol is not related with chemical processes but with human consumption of alcoholic beverages. Ethanol is the principal ingredient of alcoholic drinks formed by fermentation of sugars and over-consumption of alcohol may lead to intoxication and other serious diseases (Rubin et al., 1970). Also, ethanol is highly flammable with flash point at 282 K and causes skin irritation, and for this reason it should be kept away from heat, sparks and flames and not mixed with strong oxidizing agents and alkali metals. Ethanol is not known to polymerise and the only decomposition products are carbon monoxide and carbon dioxide (Europe, 2001).

Acetic or ethanoic acid is widely used in various industrial activities including the production of cellulose acetate and polyvinyl acetate. This compound enters the environment from discharge and emissions from the chemical industries and is not considered toxic or harmful to the general public or the environment (Bull, 2010). However, exposure to concentrated solutions of acetic acid may cause skin burns, irritation to the eyes and nose, cough and if inhaled burning mouth or stomach and diarrhoea (CHAPD, 2010).

Nitrates and nitrites are chemicals used in fertilisers and as food preservatives. Exposure to high levels of nitrates and nitrites is harmful to humans' health as there is increased danger of cancer, brain tumours and leukaemia. Both compounds are mobile in soil and could be migrated to ground water and consumed by plants and other organisms as they do not volatilise (TEACH, 2007).

The most common use of sodium hypochlorite is as a bleaching and disinfectant agent for household purposes and the chlorination of swimming pools (Li and Blatchley, 2007). There are some health and environmental issues regarding the application of this chemical. Sodium hypochlorite is a strong oxidiser and exposure to concentrated solutions of NaClO can burn the skin and cause eye damage. The reaction of sodium hypochlorite with other compounds can form various possible toxic by-products, for example chloroform.

Chloroform is a hazardous organic substance with chemical formula $CHCl_3$, and it volatises easily form soil and water before degrading into the air to form phosgene, dichloromethane, formyl chloride, carbon monoxide, carbon dioxide and hydrogen chloride (Rossberg et al., 2000). Chloroform releases to the atmosphere after chlorination of drinking water, waste water and swimming pools, from pulp and paper mills, hazardous waste sites and sanitary landfills. Short term exposure to chloroform causes central nervous system depression, while chronic exposure may inflict more serious consequences including hepatitis and cancer (EPA, 2000).

7.4.2 Carbonation under Dry Conditions

The CO_2 uptakes depicted in Figure 7.1 suggest that ethanol was the chemical with the most beneficial effect upon the yield of APCr. The increase was proportional to the concentration of ethanol in the solutions. The 0.1M solution increased the average CO_2 uptake by 75%, the 0.5M solution by 85% and the 2.5M solution by 120%. No increase was observed for the samples combining ethanol and sonication and the same phenomenon was observed for the rest of the waste residues. It seems that the ultrasonic waves evaporated the contained ethanol and the reaction proceeded without chemical acceleration.

Ethanol is an organic compound which has been used in several chemical processes. The catalytic conversion of ethanol is widely used for the formation of value-added chemicals. For instance, ethanol is a precursor for the production of hydrogen in fuel cells at relatively low temperatures (<873 K) (Haryanto et al., 2005). Also, the dehydration of ethanol offers less expensive and more sustainable processes for producing ethylene, propylene, 1-butanol and other C3-C4 olefins without using fossil fuels (Sun and Wang, 2014, Yang and Meng, 1993).

One of the most important commercial applications of ethanol is the production of bioethanol, which could replace traditional transportation fuels and contribute to the mitigation of CO_2 emissions into the atmosphere (Hamelinck et al., 2005). Although bioethanol is considered as a sustainable energy source, the current production of this fuel relies on starch and sugars, and thus there is competence with food crops (Alvira et al., 2010).

Except for ethanol, acetic acid found to increase the average CO_2 uptake of air pollution control by 40%-80%. The results suggested that sonication with acetic acid did not enhance the reaction further. Although the addition of sodium hypochlorite and sodium nitrate increased the recorded yields by 20%-50% and 15%-40% respectively, the variability of results was high.

The yield for cement bypass dusts showed that the most effective compound was acetic acid at the 2.5M solution. The latter increased the average CO_2 uptake by 80%. The samples of CBD containing acetic acid did not achieve a higher CO_2 uptake during sonication. In addition, chemical acceleration with ethanol (without sonication) increased the recorded CO_2 uptake by up to 55%. Moreover, chemical acceleration with solutions of sodium hypochlorite (0.5M and 2.5M molarities) ameliorated the reaction and the results showed that the achieved yield increased slightly (26%). Acceleration with sodium nitrite did not show any rise of the achieved CO_2 uptake.

Acetic acid has been successfully used in the past for mineral sequestration purposes, mainly the extraction of calcium ions form calcium-based natural silicates, for example wollastonite, and the subsequent reaction of these ions with CO_2 for the formation of calcium carbonate at an estimated cost of USD200/tonne of CO_2 (Kakizawa et al., 2001). In addition to calcium ions extraction, acetic acid was also used as a solvent for the extraction of magnesium and ferric ions from serpentines, although the concentration of the extracted ions was lower compared to extraction with other acids such as sulphuric, hydrochloric and nitric acid (Teir et al., 2007b).

Moreover, there are previous findings suggesting the beneficial effects of acetic acid during catalytic chemical processes. Acetic acid found to be an effective catalyst for the production of di(indolyl)methanes (DIMs) and for enhancing the decomposition rate of sodium bicarbonate in epoxy foam (Wan Hamad et al., 2013, El-Sayed et al., 2014).

The highest increase in CO_2 uptake of CEM 1 was achieved by the samples containing acetic acid at 2.5M under the presence of ultrasound. It was the only occasion where the combined effect of ultrasound and chemical acceleration had a positive impact on the reaction efficiency at low w/s ratio. Also, ethanol found to improve the CO_2 uptake by up to 88%. The analysis of Figure 7.3 showed that the carbonated samples containing solutions of sodium hypochlorite and sodium nitrite did not show an increased yield.

Finally, the recorded yield for steel-making slags, shown in Figure 7.4, indicated that acetic acid, similarly to cement and cement bypass dusts, improved the CO_2 uptake in the solutions of 0.5M and 2.5M by 50%-77%. In addition, the samples of ethanol at 0.5M and 2.5M increased the recorded CO_2 uptake by up to 40%. Again, the effect of sodium hypochlorite and sodium nitrite upon the reaction yield was negligible.

7.4.3 Carbonation under Wet Conditions

The CO_2 uptakes that showed in Figures 7.5-7.8 suggested that the highest values obtained for the samples containing acetic acid. However, the effect of acetic acid at high w/s ratio did not seem to be catalytic for two reasons. The first reason is that a chemical compound which could be characterised as a “true” catalyst should have a similar effect over a range of water concentrations. The second reason is that according to mineral phases analysis presented in Table 7.3, several mineral phases of the un-treated materials “disappeared” after chemical acceleration with acetic acid, and hydrated salts of CH_3COOH including calcium, magnesium and sodium acetate appeared.

For the non-sonicated samples of APCr, ethanol was found to increase the average CO_2 uptake by 58% to 110%, sodium hypochlorite by 46% to 83% and sodium nitrite by 23% to 69%. For the sonicated samples of the same residues the accelerator with the biggest effect was sodium nitrite as the final carbon uptake increased by up to 200%. Despite the evaporation of ethanol observed at dry conditions, at high w/s ratio the presence of ultrasonic waves did not evaporate the chemical as the volume of ethanol in the samples was 250 to 500 times more compared to low w/s ratio samples.

Ethanol increased the average CO_2 uptake of the non-sonicated samples of cement dusts by 50% to 98%, sodium hypochlorite by 70% to 130% and sodium nitrite by 85% to 130%. For the sonicated samples of CBD the chemical with the most beneficial effect upon the CO_2 uptake of the products was ethanol as the achieved values raised by 120% to 240%, followed by sodium nitrite (82% to160%) and sodium hypochlorite (90% to 140%).

The non-sonicated samples of the reference material showed improved yield only when ethanol was present and the recorded CO_2 uptakes increased by 9% to 170%. The chemical acceleration of CEM 1 with sodium hypochlorite and sodium nitrite did not improve the reaction. On the other hand, chemical acceleration with ultrasound significantly increased the CO_2 uptakes of the products. Sodium nitrite was the most effective accelerator as it increased the yield by up to 490%, sodium hypochlorite up to 400% and ethanol by up to 380%.

Finally, the results of steel-making slag after chemical acceleration without ultrasound suggested that sodium nitrite ameliorated the reaction by increasing the CO_2 uptake between 145% and 230%. Also, sodium hypochlorite increased the CO_2 uptake between 75% and 240% and ethanol by up to 125%. During chemical acceleration with ultrasound ethanol improved the yield of steel slag by 660%, followed by sodium nitrite (530%) and sodium hypochlorite (450%).

7.4.4 Mineral Phases Analysis

The samples that showed the highest CO_2 uptake at low w/s ratio were analysed by X-ray diffraction in order to identify any toxic compounds after chemical acceleration. The mineral phases before and after treatment was presented in Table 7.3 and indicated that no toxic compounds were found after treatment for the original diffractograms).

The chemical acceleration of air pollution control with ethanol at 2.5M resulted in higher concentration of calcite since all lime and a high portion of portlandite converted into $CaCO_3$. Also, vaterite, a polymorph of calcium carbonate, was identified, in contrast to aragonite which was not found after treatment. The minerals phase analysis of APCr suggested that the minerals: aluminium phosphate, calcium iron titanium oxide and magnesium oxide hydroxide were fully carbonated.

The concentration of calcite during chemical acceleration of cement bypass dusts with acetic acid at 2.5M, similarly to APCr, increased due to the conversion of lime and portlandite into $CaCO_3$.

In the case of the reference material (acetic acid 2.5M with ultrasound), the results showed that hatruite reacted to calcite, while the concentration of the minerals brownmillerite, gypsym, and larnite remained unchanged after treatment.

Finally, the XRD analysis of steel-making slags indicated that the only change in mineralogy of this residue was the slight increase of concentration of calcite in the products due to conversion of portlandite.

The results of chemical acceleration at wet conditions suggested that the samples containing acetic acid at 2.5M achieved the highest CO_2 uptake. However, this was due to the acid dissolution rather than to an actual catalytic effect. This hypothesis was validated by the XRD analysis of the high w/s ratio samples presented in Table 7.4.

The analysis of air pollution control residues showed after treatment with acetic acid at 2.5M the majority of the mineral phases found in the un-reacted ashes was dissolved including christobalite, portlandite and sylvite, while the concentrations of calcite, rutile and halite considerably decreased. On the other hand, the predominant mineral phase after chemical acceleration was calcium acetate hydrate.

Calcium acetate is a calcium salt of acetic acid and its common form is the mono-hydrate with chemical formula $Ca(CH_3COO)_2 \cdot H_2O$. The toxicity of this compound is low and its uses include treatment of patients suffering from renal failure (Mai et al., 1989), the catalytic synthesis of oxazolones (Paul et al., 2004), while the calcination of calcium acetate was used for the removal of SO_2 from exhaust flue gases of fossil-fuel power plants (desulphurisation) (Adánez et al., 1999).

The formation of calcium acetate hydrate via the reaction of calcite or portlandite with acetic acid can be done according to equations 7.3 and 7.4.

$$CaCO_3 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + H_2O + CO_2 \quad (7.3)$$

$$Ca(OH)_2 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + 2H_2O \quad (7.4)$$

The second new mineral phase found in the carbonated APCr was sodium acetate. Sodium acetate is used in the food industry as a seasoning and for improving colour stability of fresh meat (Knock et al., 2006). This compound is also used for the utilisation of waste-streams coming from the textile industry, which could cause aesthetic problems due to the remaining colour, while the natural degradation of dyes could be proved toxic to aquatic environments (Georgiou et al., 2004).

The chemical acceleration of cement dusts with acetic acid at 2.5M resulted in the complete dissolution of gehlenite, larnite, lime and portlandite, while the concentration of calcite decreased remarkably. Again, the predominant mineral phase found in the reaction products was calcium acetate hydrate.

Calcium acetate hydrate was also the primary mineral phase after chemical acceleration of cement with acetic acid at 2.5M. The XRD analysis of the reference material suggested that lime and gypsum completely dissolved, as well as a high amount of calcite, hatruite and brownmillerite.

Finally, the mineral analysis of steel-making slags after chemical acceleration revealed the presence of magnesium acetate hydrate apart from calcium acetate.

Magnesium acetate is a magnesium salt of acetic acid, its hydrate form is the magnesium acetate tetrahydrate with chemical formula $Mg(CH_3COO)_2 \bullet 4H_2O$ and similarly to calcium acetate can be used for desulphurisation of flue gases (Adánez et al., 1999).

The formation of magnesium acetate via acetic acid and magnesium hydroxide can be done according to equation 7.5.

$$2CH_3COOH + Mg(OH)_2 \rightarrow (CH_3COO)_2Mg + 2H_2O \qquad (7.5)$$

7.5 Conclusions

In this chapter the effect of acetic acid, ethanol, sodium hypochlorite and sodium nitrite, four candidate catalysts of accelerated carbonation, on the CO_2 uptake of APCr, CBD, CEM 1 and steel-making slag was investigated. The combined effect of these chemicals and ultrasound on the carbon uptake was also explored.

At dry conditions (w/s ratio between 0.2 and 0.6) ethanol and acetic acid was the two chemicals that ameliorated the reaction efficiency. On the other hand, sodium nitrite and sodium hypochlorite did not seem to have any positive effect during chemical acceleration.

The yields recorded at low w/s ratio suggested that ethanol (without ultrasound) increased the CO_2 uptake of APCr by up to 120%. In addition, the non-sonicated solutions of acetic acid at 2.5M increased the recorded CO_2 uptakes of cement dusts and steel-making slags by 80% and 77% respectively. In the case of CEM 1 the combined effect of acetic acid and ultrasound at the 2.5M sample improved the CO_2

uptake by 88% and it was the only occasion where sonication ameliorated the chemical acceleration.

The XRD analysis of the low w/s ratio samples that achieved the highest CO_2 uptake suggested that no toxic products were formed after chemical acceleration.

The yields recorded at high w/s ratio indicated that the highest CO_2 uptake for all the input materials was given by the samples containing acetic acid at 2.5M. However, this was not due to a “true” catalytic effect but rather to acid dissolution. A real catalyst should have a similar effect over a range of water concentrations and also the XRD analysis suggested that a number of mineral phases found in the un-reacted residues dissolved after chemical acceleration with acetic acid and the principal mineral phase was calcium acetate hydrate, a calcium-based salt of acetic acid.

8 SUMMARY AND FUTURE WORK

8.1 Summary

The reduction of anthropogenic CO_2 emissions and harmful waste-streams prior to landfilling is necessary in order to mitigate environmental impacts and maintain the sustainability of the planet. In addition, carbon taxes and stricter landfill regulations are expected in the near future, forcing the industry to adopt innovative processes for carbon utilisation and waste management.

A technique which combines CO_2 utilisation and waste management is accelerated carbonation technology (ACT). Accelerated carbonation could be successfully used for the stabilisation of hazardous wastes, remediation of contaminated soils, and re-use /recycling of various waste streams. This technique, as described in Chapter 2, could also be used for the permanent storage of CO_2 into minerals via a process known as mineral carbonation technology (MCT).

Mineral carbonation is considered a promising option of mitigating the release of carbon into the atmosphere. In contrast to geological and ocean storage, mineral carbonation ensures the long-term sequestration of CO_2 in calcium and magnesium silicates, and the potential to sequester in excess of 10,000 Gtonnes of CO_2 cumulatively in stable carbonate products. However, the current associated costs are high (USD100-120/tonne CO_2), conversion rates remain low, and there are large distances between major CO_2 emitters and potential geological storage sites.

Due to the high costs of mineral sequestration another method of CCS has recently gained attention. This method is known as waste carbonation and it has particular advantages: processing is easier, handling and transport procedures are largely in place, and waste and CO_2 are often located together as a result of being produced by the same industrial process. As a result, the associated costs are lower (USD38-95/tonne of CO_2) with a potential for reduction if carbonated products with added-value could be manufactured.

The examination of 7 “common” alkaline waste residues showed that approximately 1 Gtonne of CO_2 may be sequestered each year using moderate reaction conditions. Although this figure represents only a small fraction of the World’s annual anthropogenic emissions (around 36 Gtonnes), waste carbonation is a reality, with known commercial companies, including Carbon8 and Recmix, specialising in the production of green aggregates and valorised products via this process.

The topic of mineral carbonation was examined in Chapter 4. The biggest challenge of this sequestration method is the low conversion rate of minerals into carbonates at mild reaction conditions. Samples of magnesium hydroxide were carbonated via various carbonation techniques at different w/s ratios. The achieved CO_2 uptakes suggested that the reactivity of $Mg(OH)_2$ remained low and increased only under elevated pressure (=>0.2 MPa) and long reaction time (=>24 hours). However, the processing/handling of large amounts of minerals over a prolonged reaction time or under elevated temperature and pressure results in higher overall costs.

A product development study which included the preparation of cylindrical samples of $Mg(OH)_2/Ca(OH)_2$, indicated that the newly formed products composed of pure magnesium showed improved compressive strength and bulk density. An XRD analysis of the same mixtures suggested the presence of hydromagnesite, a desirable polymorph of $MgCO_3$, and the complete absence of magnesite due to the selective precipitation of nesquehonite under ambient temperature and pressure.

The topic of waste carbonation was explored in Chapter 5. Air pollution control residues, bauxite residues, cement bypass dust, coal fly ash, MSWI bottom ash, steel-making slags and cement (as the reference material) were carbonated for 1 hour under ambient temperature and pressure and at 10 different water-to solid ratios varying from 0.2 to 100. The most reactive residues were air pollution control residues, cement bypass dusts, steel slag and cement due to their high initial concentration in calcium oxide and the presence of reactive calcium-based mineral phases.

The CO_2 uptakes for all the input residues suggested that carbonation was favoured at dry conditions (w/s=0.2-0.6). At intermediate w/s ratios (between 0.8 and 10) the yield decreased considerably due to the presence of water, inhibiting the diffusion of CO_2 by pore-blocking. However, a further rise in w/s ratio (25 to 100) resulted in higher CO_2 uptake, as the increased volume of water provided a reservoir with a larger total capacity for carbon dioxide solution and ionisation/hydration.

On every occasion, the actual CO_2 uptakes were considerably lower than the predicted ones, as the theoretical predictions are based exclusively on the initial chemical composition, mainly the concentration of CaO, of a candidate residue, whereas the actual CO_2 uptake is dependent upon several carbonation variables including mineralogy, temperature, pressure, reaction time, relative humidity as well as water content etc.

The effect of ultrasound on the CO_2 uptake of waste residues was examined in Chapter 6. The results suggested, that ultrasound did not remarkably increase the CO_2 uptake of the tested materials at low w/s ratios (0.2-0.6). In these ‘dry’ conditions the cavitation of the solid particles was unlikely to occur, as the film of water surrounding particle surfaces was generally too ‘thin’. However, it should be noted that in this study, the power of the ultrasonic device was 150W-300W and higher values of power were not considered. On the hand, at high w/s ratios (50-100) a significant increased yield was recorded (up to 400%), as the conditions were much more suited for cavitation.

The CO_2 uptakes achieved after 8 hours of sonication were compared with the theoretical (uptake) values derived from the Steinour formula. On every occasion, the actual CO_2 uptakes were considerably lower than those predicted. However, the recorded CO_2 uptakes after 1 hour of sonication indicated that a large percentage of CO_2 was bound into the products compared to 8 hours of treatment. For low w/s ratios this percentage ranged from 67%-99%, showing that carbonation occurred rapidly, while for “wet” samples (except for cement bypass dusts) the same percentage was 27%-54.8% as the high water content resulted in a slower reaction.

Analysis by X-ray diffraction showed that the amount of calcite in the sonicated samples increased and the carbonation of several mineral phases found in the un-treated samples was enhanced. Finally, SEM imaging suggested that the non-sonicated samples were characterised by a more ‘rounded’ appearance and lower relief compared to the non-sonicated ones.

In the final chapter the effect of acetic acid, ethanol, sodium hypochlorite and sodium nitrite, four candidate catalysts of accelerated carbonation, on the CO_2 uptake of APCr, CBD, CEM 1 and steel-making slag was investigated. The combined effect of these chemicals and ultrasound on the carbon uptake was also explored.

At dry conditions (w/s ratio between 0.2 and 0.6) ethanol and acetic acid was the two chemicals that ameliorated the reaction efficiency. On the other hand, sodium nitrite and sodium hypochlorite did not seem to have any positive effect during chemical acceleration. The XRD analysis of the low w/s ratio samples that achieved the highest CO_2 uptake suggested that no toxic products were formed after treatment.

The yields recorded at high w/s ratio indicated that the highest CO_2 uptake for all the input materials was given by the samples containing acetic acid at 2.5M. However, this was not due to a “true” catalytic effect but rather to acid dissolution. A real catalyst should have a similar effect over a range of water concentrations and also the XRD analysis suggested that a number of mineral phases found in the un-reacted residues dissolved after chemical acceleration and the principal mineral phase was calcium acetate hydrate, a calcium-based salt of acetic acid.

All the experiments were repeated three times and data analysis was done by applying three statistical variables: the mean, standard deviation and standard error. The latter was plotted as “error bars” in the relevant figures. Also, the impact of human error was minimised by conducting experiments, analyses and samples preparation with extreme care and any potential error could be attributed to normal deviation derived from the analytical equipment.

Finally, the following analyses could have made this thesis even stronger: a) examination of more minerals, b) examination of more wastes and c) application of ultrasonic probes. The examination of more wastes and minerals could have resulted in a “wider data-basis” covering a larger range of residues and minerals suitable for accelerated carbonation. Ultrasonic probes compared to ultrasonic baths present some advantages, especially the possibility of conducting sonication at higher power and exploring the effect of amplitude on CO_2 uptake. However, sonication with probes requires high w/s ratio samples since the probe acts as a mechanical stirrer. Thus, the sonication of dry samples is possible in ultrasonic baths only.

In conclusion, this study proved that: the carbonation of minerals is low under ambient temperature and pressure; waste carbonation involves less expensive processing as there are “common” alkaline wastes which react significantly with CO_2 under ambient conditions; ultrasound increases the CO_2 uptake of waste residues at high water content; ethanol and acetic acid could be used for catalysing the reaction of accelerated carbonation (at low w/s ratio) without forming any toxic by-products.

8.2 Future Work

Based on the main findings of this study, future work should focus on the production of magnesium-based cylinders with higher strength and density, the investigation of the impact of ultrasonic power on the CO_2 uptake and the development of a new theoretical model to replace the Steinour formula.

Although the cylinders of 100% Mg showed improved strength and bulk density, the values were inferior to the properties for normal and lightweight concrete. To increase the properties further additives/binders should be applied. Instead of using traditional binders such as ordinary Portland cement it would be reasonable to apply alkaline waste residues which are known to have a significant reaction with CO_2. Candidate residues comprising cement kiln dust, wood ash and paper ash as all of them have been successfully used for the production of sustainable lightweight aggregates (LWA) with improved properties.

In this study, the effect of ultrasonic power during sonication was not considered as the experiments were conducted in an ultrasonic bath with power at 150 W-300 W. Ultrasonic power is an important parameter regarding the strength of sound waves and it should be investigated whether the exposure of an input material to a higher power increases the CO_2 uptake.

The theoretical model that predicts the CO_2 uptake of a candidate residue is the Steinour formula. However, this model is outdated and the theoretical estimations are significantly higher than the actual recorded values. The formula is solely based on chemical composition, whereas the real CO_2 uptake depends on several reactions variables. The development of a new and more accurate theoretical model is necessary in order to evaluate the reactivity to CO_2 of an input material. This model should be purely based on experimental data. This study proved that the CO_2 uptakes of the raw materials depended highly on mineral composition. Thus, it would be reasonable to create a new formula by analysing the correlation between mineral composition and CO_2 uptake of several alkaline wastes.

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The current status of commercialisation of carbonation technology

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Abstract

Mineral carbonation technology (MCT) involves the safe long term storage of stable and carbonated products, mainly carbonates and bicarbonates. The carbonation of candidate feed-stock comprising calcium and magnesium silicates is relatively slow, is energy intensive. Processing involves the handling of significant quantities of materials Thus, the challenges to be overcome appear to be the high overall processing costs and slow reaction kinetics; both of which will hinder commercial application of MCT. The combining of CO_2 with various silicates is estimated to cost between US\$54 and US\$250 per tonne of CO_2. Further research on various carbonation routes, via organic and inorganic substances, will result in lower energy consumption and enhanced kinetics. In addition to naturally abundant silicates, an alternative approach could be the waste carbonation technology (WCT) of alkaline residues. Previous studies have shown that suitable wastes are abundant and may sequester up to 475kg of CO_2/tonne/waste at a lower cost than MCT. As the annual world production of 7 selected alkaline residues is 4.79Gt, and the availability of silicate ores is huge, the future potential of both MCT and WCT to be industrialised is promising, providing the key issues outlined by this work can be overcome.

Introduction

According to the United Nations statistics department the global CO_2 emissions in 2008 was 30.21Gt and 30.08Gt in 2009. The annual decrease of 0.41% (Table 1), although encouraging, does not comply with the obligations of the first commitment period of Kyoto Protocol, which persuades the participant members to cut their emissions by an average 5% during 2008-2012. The recent withdrawal of Japan, Canada and Russia, and the continuous reluctance of China and the US to ratify the treaty, puts the CO_2 reduction scheme at stake, and the future sustainability of Earth in great danger. During the United Nations Climate Change Conference in Doha (2012) the countries agreed to extend the commitment period of Kyoto Protocol for 8 years, until 2020, and in 2015 they pledged to sign a new treaty with more realistic targets, satisfying both rich and developing nations.

Emissions per capita index represents the individual emissions of a given population (Figure 1). The USA's emissions per capita are four times bigger than the world average (17.43 tonnes), due to high consumption of fossil fuels and public reluctance to adopt alternative energy sources. The Russian economy is heavily dependent on hydrocarbon exploitation, resulting in the second highest emissions per person (11.08 tonnes). The European population have a developed environmental awareness however, governments failed to create cleaner and more efficient energy systems and reduce carbon emissions (7.27 tonnes per capita). China's emissions, although lower compared to other countries (5.76 tonnes per capita), are increasing year after year raising additional environmental concerns.

Table 1. Total CO_2 emissions (in Gt) in 2008 and 2009

Country	Emissions in 2008 (in Gt)	Emissions in 2009 (in Gt)	% Difference
World	30.21	30.08	-0.41
China	7.03	7.68	9.22
USA	5.65	5.29	-6.31
EU 27	3.92	3.62	-7.53
India	1.80	1.97	9.83
Russia	1.71	1.57	-8.23
Rest[a]	10.07	9.91	-1.57

a: includes data from 187 countries Source: United Nations Statistics

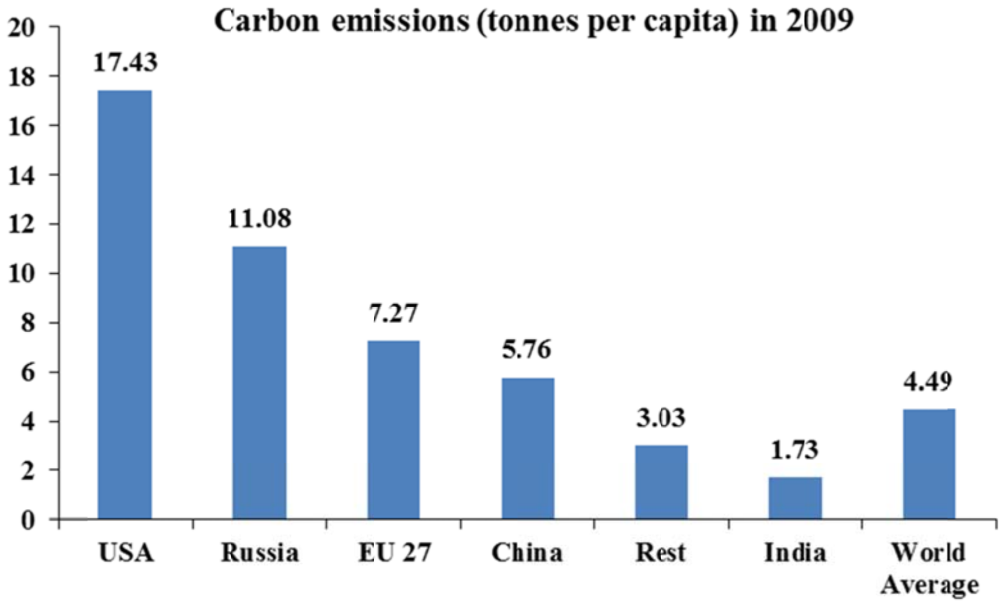

Figure 1. Global emissions per capita in 2009, based on Table 1 and the population in each region

The progress towards a less carbon-dependant society is slow, mainly due to poor improvements in energy efficiency and the low level of renewables integration into energy generation. In addition, the disaster in Fukushima in 2011 has raised significant doubts about the use of nuclear energy for electricity generation. Thus, carbon capture and storage (CCS) offers an excellent option for CO_2 reduction, providing that a high yield can be achieved at a reasonable cost. CCS includes the capture, transportation and subsequent storage of CO_2 in appropriate geological and ocean sites, or the storage as carbonates/bicarbonates via mineral carbonation[1]. Because they are similar to natural silicates, alkaline wastes can also sequester CO_2 in a process known as waste carbonation.

The main aim of this review is the progress of mineral carbonation technology (MCT) in terms of costs and processing routes, and advantages / disadvantages compared to geological and ocean storage. Furthermore, the annual production and maximum sequestration capacity of seven candidate alkaline wastes is estimated, in order to assess the potential of applying waste carbonation technology (WCT) to current and future commercial sequestration projects.

Carbon capture and storage (CCS)

Currently, there are three carbon capture technologies: post combustion, pre-combustion and oxy-combustion[2]. The average cost of these technologies is estimated at around US$55/tonne[1]. After removal from the process, CO_2 is stored at geological or aquatic locations.

In geological sequestration, carbon dioxide is injected into deep saline aquifers, depleted oil and gas fields, and un-mineable coal seams at ground depth at least 1km. The maximum storage capacity is between 1000Gt and 1800Gt, while the biggest advantage of geological method is the low environmental risk of the sequestrated products compared to ocean sequestration[3]. On the other hand, it requires continuous monitoring to spot and stop potential leakage of CO_2 coming from aquifers, and its re-emission to the atmosphere[4]. The cost of monitoring increases the overall expenses in the long term.

Countries lacking coal and/or oil and gas fields have potential to turn their attention to aquatic sequestration. The availability of oceans and deep lakes is huge, and no continuous monitoring would be required. Ocean storage involves the injection of compressed CO_2 into the seafloor at depth below 3km, where liquid CO_2 can be permanently stored as it is denser than seawater. The maximum capacity of the method is approximately 10000Gt, whereas the average cost per tonne of CO_2 is estimated at US$18 (US$5 net injected for geo-storage). The biggest potential disadvantage is the risk of ocean acidification in case of an accident; public perception is also hostile, preventing governments from supporting large scale projects of this nature[5].

Alternatively to geo and ocean sequestration, mineral carbonation ensures the environmentally benign long term storage of carbonated products. Potential feed-stocks of MCT are minerals comprising calcium and magnesium ions, for instance wollastonite, basalt, olivine and serpentine. The carbonation reaction is thermodynamically favourable and the final products are stable for a long period of time. The potential capacity exceeds 10000Gt at an average cost of US$120/tonne CO_2[6-8]. Details of feed-stocks, reaction conditions and processing routes are given in the following section. Table 2 gives an overview of carbon capture technologies, their advantages/disadvantages, their estimated capacity and the relevant costs.

Table 2. Overview of CCS technologies

Technology	Advantages	Disadvantages	Capacity[a]	Cost[b]
Geologic storage	-Established technique -Low storage cost -Positive/indifferent public perception -More eco-friendly than ocean storage	- High risk of CO_2 leakage from the aquifers -Requires continuous monitoring, increasing the overall cost -Many countries lack appropriate storage sites	1800	5
Ocean storage	-High capacity -Global availability of oceans, seas, deep lakes - No monitoring requirements	-High environmental risk - Higher cost than geo-storage -Negative/hostile public perception	10000	18
Mineral carbonation	-Environmentally benign long term storage - Exothermal reactions - Large availability of natural feed-stocks	- High sequestration and transportation costs - Pre -treatment of silicates - Unsecure future potential	>10000	120

a: maximum estimated capacity in Gt
b: average sequestration cost in US$

Mineral carbonation technology (MCT)

The overall cost of mineral carbonation includes the extraction, transportation, and processing of the reacted silicates. The formation of final products via carbonation routes can be either direct or indirect (Figure 2).

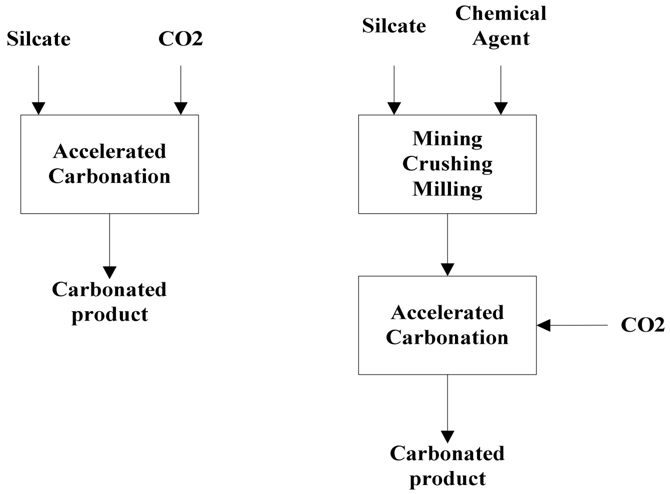

Figure 2: Schematic of direct and two-step carbonation process[10]

The direct route occurs in a single reaction, it has simple kinetics and relatively economic processing. However, the conversion rate is low due to thermodynamic constraints. Thus, large amounts of rocks need handling, in order to sequester high volumes of CO_2. On the other hand, the indirect route involves two or more steps. Initially, a chemical agent is added for the mining, crushing and milling of silicate rocks. Subsequently, CO_2 diffuses and forms carbonated products. The indirect method involves more effective reactions and high yields. However, the cost increases due to chemical additives and complex reaction mechanisms[9].

In previous studies various routes have been examined: HCl extraction, acetic acid extraction, ammonia extraction, molten salt, aqueous carbonation and bioleaching. Most of them are hampered by low conversion rates, corrosive by-products and cost. The most promising carbonation routes are acetic acid extraction and bioleaching. The former involves the addition of acetic acid as a chemical agent during silicate extraction, while the latter is based on the presence of microorganisms such as bacteria and fungi. Both are relatively cheap and environmental friendly. However, their future feasibility is un-proven and more research is urgently needed in order to achieve higher conversion rate and more favourable kinetics under moderate reaction conditions[10].

The transportation cost of silicate ore and the final carbonated products hinders the commercialisation of MCT. Picot et.al.[11] identified regions across the world that could combine emission plants with suitable ultramafic rocks, in distances less than 300km. These were found in Botswana, China, South Africa, Russia, Kazakhstan, and in some isolated places in Northern Europe, USA and Australia. Unfortunately, there is lack of suitable geological formations close to large industrial emitters (see Figure 1), and this is an impediment to investors in mineral sequestration schemes.

Appropriate feed-stocks could include basalt, olivine and serpentinite. Table 3 contains costs, energy consumption and reaction conditions for four silicates based on the works of Gerdemann et al.[12] and Ragnheidardottir et al.[13]

Table 3. Reaction conditions, costs and energy consumption for four silicates

feed-stock	T (°C)	P_{CO2} (bar)	US$/ton CO_2	US$/kWh
basalt	-	-	66[a]	0.05
olivine	185	150	54	0.06
serpentine	100	40	250	0.26
wollastonite	155	115	91	0.09

a: estimation based on full utilisation of carbon emissions from Hellisheidi plant (CarbFix project)

Waste carbonation technology (WCT)

In the EU the characterisation of wastes is dictated by the European Directive 2000/532/EC and European Waste Catalogue (EWC), which classify hazardous residues according to their origin and toxicity. Waste disposal is strictly monitored by the European Commission and local Governments, imposing expensive landfill taxes, ranging from €17 (US$21) to €130 (US$160), depending on the type of waste and domestic environmental regulations. Polluters are under high pressure to reduce or utilise their harmful disposals, and waste carbonation is an appealing option for the market[14].

The reaction mechanism of waste carbonation is similar to MCT. Instead of silicates, alkaline wastes react with CO_2 and form carbonated products. With WCT the overall costs are lower, new building materials are produced, and the leaching of various metals is reduced[15]. Suitable wastes with large availability and high storage capacity are: bauxite residues, cement kiln dust, coal fly ash, MSWI bottom/fly ashes, steelmaking slags and waste concrete.

Table 4 contains figures regarding the annual production of 7 chosen alkaline residues, and the highest sequestration capacities that have been found in previous studies. The potential amount of CO_2 that can be sequestrated is estimated globally at 875.5Mt per annum.

Table 4. Appropriate residues for waste carbonation

Waste	Annual production (Mt)	Maximum CO_2 capacity(kg/ton waste)	Potential CO_2 uptake (Mt)
Bauxite residues	120[16]	53[17]	6.3
Waste concrete[a]	2800[18]	165[19]	462
Cement kiln dust[b]	770[20]	115[21]	88.5
Coal fly ash	600[22]	264[23]	158
MSWI bottom[c, d] ashes	80[24]	475[25]	38.0
MSWI fly ashes[c]	20[24]	120[26]	2.4
Steelmaking slags	400[27]	300[28]	120
Total	**4790**	**-**	**875.7**

a: Figures refer to cement production. Every tonne of concrete contains typically 10% cement
b: For every tonne of cement, 0.25-0.30 tonnes of kiln dust are produced. Thus: 0.275×2800=770Mt
c: The annual production of municipal incineration ashes is estimated at 100Mt. If we assume that 80% comes as bottom and 20% as fly ashes then the respective figures would be 80Mt and 20Mt
d: Ambient T and P are assumed

The maximum capacities of Table 4 indicate that the selected residues may be able to sequester considerable volumes of CO_2. Unlike mineral carbonation, the absence of rock handling/processing decreases the operational and energy cost, and the waste streams of interest tend to be generated by processes emitting CO_2. Thus, the distance between the ‘plant’ and the ‘source’ is minimised, and options to directly combine captured CO_2 with the waste system are possible. Figure 3 depicts a sequestration concept of steelmaking slags proposed by Eloneva et.al.[29]

From economic point of view WCT is actually less expensive than MCT, and the final products are formed at lower temperature and pressure. Table 5 contains data for reaction conditions and cost in US$/ tonne CO_2 regarding steelmaking slag and waste cement.

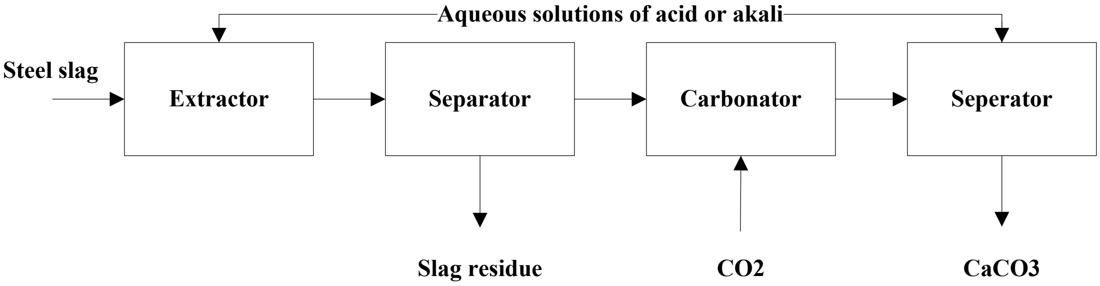

Figure 3: Carbonation concept for CO_2 sequestration using steelmaking slags[29]

Table 5: Sequestration costs and optimum conditions for steel slags and waste cement

Waste	T (°C)	P (bar)	Cost
Steelmaking Slags[30]	178	35.5	95
Waste cement[31]	80[a]	30[a]	38

a: refers to crystallisation step

The main challenges of WCT are the complexity of waste systems and the absence of adequate legislation and incentives for its wide application. Various waste residues include heavy metal traces and radioactive elements that require intensive pre-treatment before their reaction with carbon dioxide, increasing the overall cost and reaction time. Moreover, in many countries the regulation of waste disposal is weak and thus, polluters prefer to dispose their wastes instead of utilising them. Tougher regulation and governmental financial support would certainly boost development of the method.

Conclusions

Every year around 30Gt of CO_2 are emitted in the atmosphere, and unless urgent measures are taken at an international level to mitigate these, the chances of maintaining global temperature rise to lower projected limits will be lost.

In 2020 nations will agree on a new environmental treaty reviewing the targets of Kyoto protocol and propose effective means of implementation. The slow development of renewable systems and the associate risks of nuclear energy make CCS an appealing mitigating option.

Geological and ocean sequestration offer a potentially high storage capacity for CO_2 in depleted oil/gas fields and oceans/deep lakes. However, the possibility of carbon leakage in underground sites, and accidental ocean acidification fuel public and state concerns over these large-scale CCS schemes.

Recently, interest in mineral carbonation as a potential sequestration method with lower environmental risks and secured long-time storage has risen. The available carbonation routes involve the direct reaction of CO_2 with calcium/magnesium silicates or the addition of chemical agents in an indirect process. Currently the overall cost of US$120/tonne CO_2 prevents the wide application of MCT in the near future.

New carbonation pathways need to be created, ensuring the absence of corrosive by-products, moderate reaction conditions (ideally ambient) and low energy processing of the feedstock. An additional challenge to mineral carbonation is cost of transportation or rock, or CO_2 gas which is likely to be a considerable impediment to the deployment of this approach.

In order to limit the cost of moving large volumes of material by land or sea, it is necessary to identify regions combining large emitting plants with appropriate silicate rocks, thereby minimising the financial penalties associated with transportation.

At the present time, it seems that waste carbonation is more feasible than MCT, as the overall cost is lower, and suitable waste streams are widespread. As an example, 7 candidate alkaline waste streams had potential to sequestrate 875.5Mt of CO_2. This potential might be increased further, if economic incentives and appropriate legislative changes are promoted by governments, for the management of industrial emissions via their reaction with high volume waste streams.

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CARBON CAPTURE USING WASTES: A REVIEW

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Abstract

Potential key strategies for the management of anthropogenic CO_2 emissions include mineral carbonation and storage in oil wells and in the oceans. In Europe, a large-scale demonstration of carbon capture and storage (CCS) has recently been given the go-ahead, and the application of mineral carbonation technology (MCT) to serpentine and olive-type minerals. Although less controversial in its approach, MCT involves intensive pre-treatment of the mineral feedstock, and a consequent high sequestration cost USD100-120/tonne CO_2 treated.

Mineralisation by carbonation is reliant upon the long-term storage of CO_2 in thermodynamically stable and environmentally benign carbonate-based reaction products that are persistent over geological-timescales. The use of solid industrial process wastes for storing carbon (via waste carbonation technology, WCT) may provide a shorter-term gain, as the industrialisation of CO_2 mitigation technologies takes place.

With WCT, CO_2 is reacted with alkaline waste residues, to both risk-manage a high pH, and utilise waste CO_2 gas, can be used as a pre-treatment prior to landfilling, facilitate valorisation and production of new materials.

The present work examines the current status of waste carbonation and investigates the utilisation of seven ‘common’ alkaline industrial residues showing that they have potential to sequestrate 1Gtonne of CO_2 worldwide. The projected average cost of USD38-95/tonne of CO_2, is competitive with landfill and projected carbon taxes. If WCT is more widely commercially developed an option for the management of significant amounts of carbon could become more quickly established.

Keywords: CO_2 emissions; Carbon utilisation; Mineral sequestration; Waste carbonation; Accelerated carbonation

Introduction

Strategies to control anthropogenic CO_2 emissions involve meeting national-term targets, improvement in energy efficiency, alternative fuels, ‘greener’ industrial processes and the adoption of targeted tax schemes and integrated environmental policies, such as ICCP (2005, 2011, 2013b).

By way of example of tax-based initiatives, Alberta, Canada, has a carbon offset tax where large emitters are charged CD15 (€14) per tonne of CO_2 with proposals to increase this to CD40 (€37) in order to generate more revenue [4]; on the other hand in British Columbia, the carbon tax system is neutral.

The progress towards a more eco-friendly society is slow, mainly due to government inertia, industrial resistance, the investment required for energy efficiency, coupled with the slow integration of renewables into the energy supply mix.

The potential of carbon capture and storage (CCS) for managing anthropogenic CO_2 rests on the yield that can be achieved at a reasonable cost. The routes to CCS involve the capture, transportation and subsequent storage of CO_2 in appropriate geological and ocean sites, or the storage as carbonates/bicarbonates via mineral carbonation (2005).

However, it is not widely recognised that high volume alkaline waste streams can sequester CO_2. The chemical similarity of wastes to natural silicates is often overlooked and if waste carbonation can be widely achieved, then there is potential to manage significant amounts of CO_2 by this method.

The current work reviews mineral carbonation technology (MCT) and compares its potential with the other sequestration methods. In addition, the potential for waste carbonation technology (WCT) annual production and maximum sequestration capacity of seven alkaline wastes is estimated. Finally, an appraisal of companies applying mineral and waste carbonation is made via a comparison of their process routes.

Carbon Capture

Carbon capture and storage is projected to consume up to 60% of overall anthropogenic carbon emissions (Dooley et al., 2009). The process of CCS involves three steps:

1) the removal and capture of CO_2 from specific locations,
2) transportation to proper storage sites and
3) CO_2 long term storage (Praetorius and Schumacher, 2009).

Large quantities of carbon are emitted by coal and gas plants, where three capture technologies are used: Post-combustion capture, Pre-combustion capture and Oxy-combustion capture (Gibbins and Chalmers, 2008). After transportation, the captured CO_2 can be stored in appropriate geological and ocean sites (Svensson et al., 2004). In Europe, a large-scale demonstration known as the 'White Rose' CCS project centred upon the Drax coal-fired power station in the UK has been given the go-ahead. This CCS project will see CO_2 transported via a pipeline for permanent storage in the North Sea in depleted oil wells (Gunning et al., 2009).

Alternatively, mineral carbonation involves the production and disposal of environmentally benign minerals that are stable over geological timescales. Potential feedstocks for MCT comprise minerals comprising calcium and magnesium ions, including wollastonite, basalt, olivine and serpentine. The potential storage capacity exceeds 10,000Gtonnes at an average cost of USD100-120/tonne CO_2 (Goldberg et al., 2001, Lackner, 2003, Lackner, 2002).

Table 1 overviews the available carbon capture and storage technologies, their advantages/disadvantages, estimated capacity and likely costs[1].

Table 1: Overview of CCS technologies

Technology	Advantages	Disadvantages	Capacity[a] (Gt)	Cost[b] (USD)
Geological storage [11,12]	• Established technique • Low storage cost • Positive perception	• High risk of leakage • Requires continuous monitoring • Lack of appropriate sites	1800	5
Ocean storage [13]	• High capacity • Global availability • No monitoring requirements	• High environmental risk • Higher cost than geo-storage • Negative/hostile perception	10000	18
Mineral carbonation [8-10]	• Environmentally benign • Exothermal reactions • Wide availability of feedstocks	• High costs • Pre-treatment • Unsecure future potential	>10000	120

a: maximum estimated capacity, b: average sequestration cost

Mineral Carbonation Technology (MCT)

In countries with large reserves of suitable rock resources i.e. Finland, Australia, USA and Canada, the potential for future carbon mitigation depends upon future research advancement.

Mineral carbonation mechanisms

Mineral carbonation involves the formation of stable carbonates and bicarbonates which are chemically equivalent to calcite, magnesite and dolomite [9]. Silicates naturally abundant in rocks and mining ores can be used as feed stocks e.g. peridotite, serpentine, olivine, wollastonite, gabbro and basalt. After appropriate treatment, carbonated products may be used as paper fillers and coating materials (Teir et al., 2010, Sanna et al., 2012b). The

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[1] Costs expressed in US Dollars. At current exchanges rates x0.77 for Euros, x0.61 for British Pounds Sterling

following equations show the principal reactions occurring for calcium and magnesium silicates; wollastonite (1), olivine (2) and serpentine (3) (Huijgen and Comans, 2003).

$$CaSiO_4 + CO_2 \rightarrow CaCO_3 + SiO_2 \qquad \Delta H = -90 kJ/mol \qquad (1)$$

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 \qquad \Delta H = -89 kJ/mol \qquad (2)$$

$$Mg_3SiO_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \qquad \Delta H = -64 kJ/mol \qquad (3)$$

All the reactions are exothermic and no energy is added to the system. However, slow kinetics, low yield under mild conditions, heat pre-treatment of silicates adversely impact on the cost of the processing (Maroto-Valer et al., 2005). The cost of transportation accounts for 77-94% of the total costs involved in MCT (Renforth, 2012).

During the mining of silicate ores, the cost of grinding, crushing and milling must also be considered. It is estimated that, in order to be applied at industrial scale, the maximum cost of mineral carbonation should range between USD20 and USD30 per tonne of CO_2 (Lackner, 2002). Indicative costs of wollastonite and serpentine were estimated at USD200 and USD126-185 respectively (Lackner, 2002, Kakizawa et al., 2001).

Carbonation of mineral residues

Mineral sequestration can be achieved close to emitting plants by transporting the raw materials to site (ex-situ MCT), or via direct diffusion of CO_2 into rocks containing calcium and magnesium minerals (in-situ MCT).

The ex-situ carbonation of feed-stock occurs in three stages (Prigiobbe and Mazzotti, 2011):

1. Thermal and mechanical pre-treatment of the mineral
2. Reaction of CO_2 with ions of Ca^{2+} and Mg^{2+} accompanied by energy release
3. Disposal/reuse of the final carbonated products

One of the biggest challenges of ex-situ processing is the distance that often exists between CO_2 emitters and the location of mineral sources, as invariably they do not coincide. The need for handling large quantities of CO_2 and mineral silicates impacts negatively on the costs of material transportation.

Therefore, the location of bespoke carbonation plants should be as close to the natural mineral resources as possible. Picot *et al.* (Picot et al., 2011) investigated candidate locations around the world, which combine coal-fired plants emitting more than 1Mtonne of CO_2, with available minerals within a distance of 300km. The identified regions are located at Botswana, China, South Africa, Russia, Kazakhstan, and in some isolated places in Northern Europe, USA and Australia. Unfortunately, there is lack of mineral availability in industrial regions with vast carbon emissions.

Although ex-situ processing is a preferred option, the slow kinetics (unless finely ground feedstock is used), the pre-treatment of feedstock, and the elevated temperature and pressures required, have focussed attention towards in-situ treatments (Kelemen et al., 2008).

CarbFix is an ex-situ MCT research project, using CO_2 emitted from a geothermal plant in Iceland. The mineral 'host' is basalt, a silicate rich in calcium, magnesium and ferrite ions (Matter et al., 2009). The installation consists of a CO_2 separation plant and injection facility, with a 3km pipeline for the carbon transportation and monitoring systems. The current overall capacity of CO_2 injection is estimated at 2.2ktonnes CO_2/per year (Matter et al., 2011) and it can reach 60ktonnes at overall cost of USD66/tonne of CO_2 sequestrated (Ragnheidardottir et al., 2011).

The Samail ophiolite in Oman is composed of peridotite, which naturally reacts with an estimated 0.1Mtonnes of CO_2 per year. The potential for reaction with carbon dioxide may reach 1Gtonne, if accelerated carbonation were to be applied at elevated temperature and pressure (Kelemen and Matter, 2008). Other relevant research has been made at Mount

Keith Nickel Mine in Canada, Linnajavri in Norway and various locations in Italy (Dipple et al., 2008, Boschi et al., 2010, Beinlich et al., 2012).

Routes for mineral carbonation

Carbonation routes (for mineral carbonation) are classified into two main categories: direct and indirect. During the direct route, silicates react with gaseous or aqueous CO_2 in a single step, without the extraction of calcium or magnesium ions (Priggiobbe et al., 2008). Via the indirect route involves more than one step, including ion extraction. Table 2 summarises the available carbonation routes (Zevenhoven et al., 2008a).

Table 2: Routes for direct and indirect carbonation

Route	**Description**	**Advantages**	**Disadvantages**	**Cost US$/t**
Gas-solid (Sipilä et al., 2008, Lackner et al., 1997, Baciocchi et al., 2009b).	Particulate metal oxides react directly with CO_2,	• Simplicity • Production of steam and electricity • Mining integration potential	• Slow reaction • Thermodynamic constraints • Industrially unfeasible	
Aqueous (Huijgen and Comans, 2003, Sipilä et al., 2008, O'Connor et al., 2000, Chen et al., 2006, Ghoorah et al., 2010, Bonfils et al., 2010, Krevor and Lackner, 2008,	Mixing (minerals) with a liquid medium such as bicarbonate/salt before the reaction with CO_2.	• Conversion rate	• High energy requirements • Requires extra chemicals • No recycling • High costs	50-100

Gerdemann et al., 2003, Krevor and Lackner, 2009, Bobicki et al., 2012).				
HCl extraction (Lackner, 2003, Huijgen and Comans, 2003, Huijgen and Comans, 2005a).	Hydrochloric acid used to extract ions of Ca+ and Mg+ from a silicate matrix	• Recoverable reactants	• High energy requirements • Expensive	>188
Acetic acid extraction (Kakizawa et al., 2001, Huijgen and Comans, 2005a, Teir et al., 2007b, Teir et al., 2007a).	Similarly to HCl extraction, the use of acetic acid is used	• Less energy intensive • Economical	• Higher recoverability needs to be achieved	78
Molten Salt (Bobicki et al., 2012).	Molten salt as a less energy intensive sorbent than HCl.	• Less energy intensive than HCl	• Extremely corrosive • Undesirable by-products	
Ammonia extraction (Kodama et al., 2008,	Ammonium salts used to promote the CO_2-silicate reaction	• High purity carbonates • Good kinetics • Recoverable reactants	• High current costs • More research needs to be done	

Wang and Maroto-Valer, 2010)				

Waste Carbonation Technology (WCT)

As an alternative to natural minerals, solid wastes can be reacted with carbon dioxide (Araizi et al., 2013). This process is known as waste carbonation technology (WCT) and the most significant advantage, compared to MCT, is that pre-treatment is rarely necessary and the general proximity of these residues to point sources of anthropogenic CO_2 (Huijgen and Comans, 2003).

Wastes such as those from bauxite processing, cement manufacture, coal combustion, iron and steel manufacture and the incineration of municipal waste, are composed of a significant proportion of calcium and magnesium. These wastes are widespread around the world. A number of the high volume waste streams with potential for WCT are identified in Table 3:

Table 3: Characterisation of alkaline wastes according to European Directive 2000/532/EC (Gerdemann et al., 2004)

Code	Main Category	Code	Sub-category	Waste
01	Wastes resulting from exploration, mining, dressing and further treatment of minerals and quarry	01 03	Wastes from further physical and chemical processing of metalliferous minerals	Bauxite residues
10	Inorganic wastes from thermal processes	10 01	Wastes from power stations and other combustion plants	Coal fly ash
		10 02	Wastes from the iron and steel industry	Steel slags
		10 13	Wastes from manufacture of cement, lime and plaster and articles and products made from them	Cement kiln dust
19	Wastes from waste treatment facilities, off-site waste water treatment plants and the water industry	19 01	Wastes from incineration or pyrolysis of waste	MSWI bottom ash
				MSWI fly ash

Bauxite residue (Red Mud)

'Red mud' is the solid waste produced by the Bayer process when alumina is extracted from bauxite ores. The transport, re use and disposal of red mud is extremely difficult due to its high alkalinity (pH>13) and elevated sodium concentration (Johnston et al., 2010).

The carbonation of bauxite residues can be achieved by neutralisation involving the reaction of aqueous solutions of red mud with carbon dioxide (Sahu et al., 2010, Renforth et al., 2012). The carbonation capacity of the process is estimated at 53kg of CO_2/tonne of red mud (Yadav et al., 2010).

Cement kiln dusts

Cement kiln dust (CKD) is formed during the manufacture of cement clinker at high temperature (around 1400°C) and it is a mixture of fine particles, unburned and part-burned raw materials and contaminants. Many cement manufacturing processes involve CKD recycling. However, the degree of recycling depends on various parameters including dust composition, particularly alkali content, and the standards that need to be met (Huntzinger and Eatmon, 2009, Huntzinger et al., 2009, Gunning et al., 2010b).

Historically, large amounts of CKD have been landfilled and could be a potential resource for CO_2 sequestration. Depending on the type of cement kiln, 250-300kg of cement kiln dust is formed per tonne of cement.

Pulverised fuel ash

Pulverised fuel ash (PFA) is produced from the burning of coal. PFA is classified as either Class C or Class F, differentiating between those with high and low calcium contents, respectively (Blissett and Rowson, 2012, Muriithi et al., 2013). Where high CaO containing PFA is available, there is great potential to capture CO_2 with minimal handling and transport costs (Sun et al., 2012).

MSWI bottom ash and APCr

The incineration of municipal solid wastes produces bottom (grate) ash and fly ash. Depending upon the composition, the two residues may or may not be combined. Air pollution control residues (APCr) are also produced as a result of flue gas treatment. APCr is sometimes combined with the fly ash.

Bottom ash former comprises 80% of the total incineration residue and is composed of ash powder along with glass and metal fragments. Bottom ashes are invariably used in road pavement construction, glass and ceramics, and in agriculture and waste water treatment (Lam et al., 2010, Li et al., 2006). The presence of heavy metals is a concern, and an accelerated carbonation treatment-step has been shown to be a promising management option (Sakita et al., 2006, Shimaoka et al., 2006, Cornelis et al., 2006, Santos et al., 2013a).

Fly ash is a fine grained airborne material which is removed via electrostatic precipitators. Typically, the heavy metal loading is higher than bottom ashes, which is often the determining factor whether it can be combined with the bottom ash.

APCr is typically a mixture of lime and activated carbon, that is injected into the flue gas to remove volatile heavy metals and neutralise acidic gasses (Fernandez Bertos et al., 2004).

Steelmaking slags

Steel manufacture generates slag, comprised of calcium, iron, silicon, aluminium, magnesium and manganese oxides. These residues are highly alkaline (pH 12) and when they react with carbon dioxide, stable products comprising carbonates are produced (Kodama et al., 2008, Bonenfant et al., 2008). Moreover, slag production is around 400Mtonnes worldwide (2010), with 45Mtonnes in the EU (Euroslag, 2012) and 5.2Mtonnes in the UK (Böhmer et al., 2008). Their carbon-uptake potential is promising whilst transportation costs are negligible, assuming the CO_2 can be captured.

Carbon Sequestration Potential

Based upon available data (between 2007 and 2011), it is possible to sequester up to 1Gtonne of CO_2 by carbonating 6 alkaline residues found widespread around the world (Table 4).

WCT ensures the utilisation of both CO_2 and solid waste residues (arising from the same plant) without additional transportation and monitoring costs. The average cost of WCT is estimated at USD67/tonne of CO_2, which is considerably lower than MCT. Furthermore, process operating conditions including temperature and pressure are generally lower. However, the complexity of waste systems and the frequent presence of heavy metals and/or radioactive elements in some residues necessitate pre-treatment, which may increase the cost of handling and processing these wastes. Finally, in many countries the regulation of waste does not lend itself to treatment and valorisation at this time, and this is an impediment to utilising waste for the sequestration of CO_2 gas.

Table 4: Alkaline residues suitable for waste carbonation

Waste	**Annual world production in million tonnes**	**Sequestration capacity in kg CO_2/tonne of waste**	**Max potential CO_2 utilised[c] (MTonnes)**	**Min potential CO_2 utilised (MTonnes)**
Bauxite (Johnston et al., 2010, Gunning, 2010, Power et al., 2011, Poulin et al., 2008, Association, 2010, Sahu et al., 2010, Renforth et al., 2012, Yadav et al., 2010)	120	53	6.36	6.36
CKD[a] [50, 70-73]	990	15-115	113.85	14.85
PFA [51-53, 74-75]	600	8-264	158.4	4.8
MSWI bottom ash[b,c] [54-60, 76-80]	80	247-475	38	19.76
MSWI fly ash[b] [57-59, 76-78, 80-81]	20	30-120	2.4	0.6
Steel slags [61-64, 81-84, 85-88]	400	227-300	120	90.8

a: estimated based upon 0.25-0.30 tonnes of kiln dust per tonne of cement. b: annual production is estimated at 100Mt. Assumed 80% as bottom ash and 20% as fly ash. c: estimated using the highest and lowest sequestration capacities identified

Commercial Applications

Several companies are already using mineral and waste carbonation to produce valuable products, including aggregates and secondary building materials. Table 5 presents data on these commercial/near commercial companies and their processes, using data/ metrics (CO_2 utilised, products value, energy penalty) taken from two reports from Carbon Sequestration Leadership Forum (2012, 2013a), companies web-sites and other information sources.

Summary

There is great potential to manage carbon emissions to protect the environment. Technologies capable of doing this are in development, but cost reduction remains a priority.

The application of Carbon Capture and Storage (CCS) and Mineral Carbonation Technology (MCT) have the greatest potential to manage large volumes of CO_2, but in the shorter-term the use of waste may provide significant gains as the often waste and CO_2 are emitted by the same process and are generated near to industrial centres, where the carbonated products might be used, or disposed of with reduced impact on the environment.

Many industrial residues exist which have the potential to act as capture mediums, including wastes from bauxite extraction, cement manufacture, coal combustion, municipal waste incineration, and steelmaking. Applying Waste Carbon Technology (WCT) to these six residues alone has the potential to sequester up to 1Gtonne of CO_2.

Several companies have been established to develop WCT processes. Currently, there are two, Carbon8 and Recmix, who are operating commercially to produce construction materials from wastes treated using WCT. Several others are in the process of bringing new technologies to the market.

Table 5: Summary of ventures applying mineral and waste carbonation

Name	Activities and Technology	Raw Materials	Key Process Steps	Output materials
Commercially Active				
Carbon8	Carbon8 produces carbon negative construction aggregates from hazardous wastes including MSWI ashes, CKD, and steel slags. (Gunning et al., 2013)	1. Alkaline wastes 2. CO_2 3. Reagents	1. Pre-treatment of waste 2. Blending reagents 3. Pelletising 4. Aggregate production	1. Aggregates
Recmix	Stainless steel-slag is carbonated to produce aggregates, fillers for concrete and asphalt and blocks. [93]	1. Stainless steel slag 2. CO_2	1. Granulation 2. Mixing 3. Carbonation 4. Shaping and curing	1. Aggregates 2. Concrete/asphalt fillers 3. Artificial aggregates
Commercialising				
Solidia	Production of low-energy cement from blended calcium silicates, and hardening using CO_2. (Picot et al., 2011)	1. Solidia cement 2. CO_2	1. Kiln treatment 2. Mixing with water 3. Curing with CO_2	1. Solidia concrete
Pilot Scale				
Calix	Enhanced calcination technology offering the potential for efficient mineral sequestration of carbon. Sorbent is regenerated and recycled (Prigiobbe and Mazzotti, 2011)	1. Limestone/Dolomite/ Magnesite/Kaolin/Gypsym/ Diatomite/Bauxite	1. Minerals Grinding 2. Minerals pre-treatment 3. Calcination 4. Separation of products	1. Steam 2. Magnesium Oxide 3. Semidolime 4. Metakaolin 5. Organic Phosphate
Carbon Engineering	Direct air capture (DEC) and production of high quality carbon dioxide for enhanced oil recovery, algae growth in industrial-scale ponds, and synthesis of liquid hydrocarbons. [98-99]	1. Atmospheric air 2. Energy 3. Chemicals	1. Air capture 2. Separation of CO_2 3. Regeneration cycle	1. Pure CO_2
CO_2 Solutions	Utilises the enzyme catalyst carbonic anhydrase for removing carbon from flue gases at emitting plants. (Penders-van Elk et al., 2012, Penders-van Elk et al., 2013, Huijgen and Comans, 2005a)	1. Flue gas 2. Low energy solvents	1. CO_2 Absorption 2. Enzyme catalysis 3. Thermal heating	1. Pure CO_2
ICS	The novelty of ICS approach is that integrates the flue gasses capture step with the carbonation of silicate minerals. (Hunwick, 2009, Hunwick, 2010)	1. Flue gas 2. Mineral silicates	1. Capture of flue gas 2. Mineral preparation 3. Carbonation 4. Storage	1. Mineral Carbonates
Laboratory Scale				
CCC	Mineralisation of magnesium and calcium silicates to carbonated products, along with generation of zero carbon electricity (Streit et al., 2012, Wilson et al., 2014)	1. Silicate minerals/wastes 2. Flue gas	1a. Digestion of the process fluids 1b. Carbon capture & power generation 2. Carbonation 3. Fluid regeneration	1. Silica by-products 2. Carbon free electricity 3. Carbonate materials

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