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Master Thesis

Assessing the Mineral Carbonation Science and Technology

MSc program in Chemical and Bioengineering

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ABSTRACT

The principal focus of this report will be to review and assess the currently available literature about the developments on the carbonation routes mention in previous literature reviews (4-5) and new routes that have been proposed in the meanwhile. A complete update of the literature from January 2008 until March 2010 was done, to compile, discuss, and compare the current stage of the mineral carbonation science and technology. Key elements that were compiled and compared include pre-treatment and activation processes of feedstock, raw material used (mineral or residue), route used (gas-solid or aqueous), source of CO₂ (pure CO₂ or flue gas), kinetic information, recovery of media (additives, solution, raw material), product handling, and gaps in the processes.

This report reviews the mentioned period of time with a summarization of the present work around mineral carbonation for the purpose of CO₂ mitigation published in peer reviewed journals, grey literature if publicly available (such as reports), patents, proceedings from the second International conference on Accelerated Carbonation for Environmental and Materials Engineering (ACEME) held in 2008 in Rome, Italy, since it is the only conference focusing on mineral carbonation within the period under review, and the proceedings of the ninth International Conference on Greenhouse Gas Control Technologies (GHGT) held in 2008 in Washington, DC, USA, since these are publicly available through Elsevier (Energy Procedia).

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1. INTRODUCTION

Since the industrial revolution, increase in the anthropogenic CO₂ emissions, hence in the concentration of atmospheric CO₂ can be observed. Global warming has been recognize very likely to be a result of this ongoing increase in the concentration of greenhouse gases such as CO₂. Carbon dioxide capture and storage (CCS) is a process that uses technology to capture the CO₂ from large point sources such as fossil fuel combustion power plants, its transport to a suitable storage location and its storage away from the atmosphere (1). This could reduce anthropogenic emissions of CO₂ into the atmosphere, coming from the fossil fuel combustion for energy generation, avoiding the consequences of climate change and global warming, serving as a bridge on the way to the use of sustainable energy systems. The storage methods include the injection of the CO₂ in underground geological formations, injection into the deep ocean (not really an option today), or industrial fixation in inorganic carbonates (1).

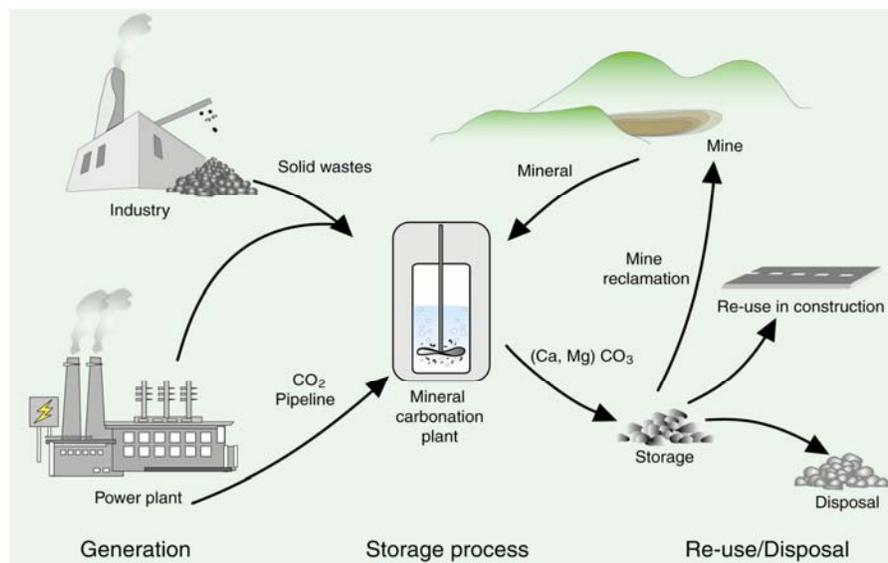


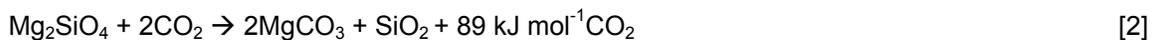
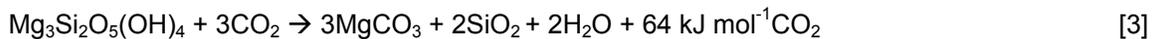
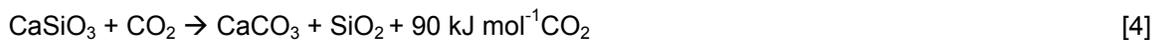
Figure 1 Basic scheme of ex-situ mineral carbonation of silicate rocks or industrial residues (1).

The mineral carbonation option (also known as mineral sequestration) tries to imitate natural rock weathering and it is described as the exothermic reaction between a metal oxide bearing material and CO₂, to form the corresponding thermodynamically stable and environmentally benign carbonate minerals (2), as shown in the following general reaction scheme:



Where M is a metallic element, preferably an alkaline earth metal, such as calcium and magnesium and the amount of heat released depends on the mineral used. Reaction 1 has been

exploited to improve the environmental quality of materials and as waste stream remediation. Alkaline residues from industrial processes such as steelmaking slags, fly- and bottom ashes, or waste cement have been used as feedstock. They contain high amounts of these metal alkaline oxides, making them suitable to fix CO₂, hence the increasing interest of using these materials for CO₂ sequestration. However, due to their lack of abundance, they are not considered in the perspective of climate change mitigation. Therefore, the most suitable sources of these metal oxides are natural magnesium or calcium silicate minerals, such as olivine, wollastonite, and serpentine; this last one has a large availability worldwide (see fig. 1). The reactions and heat release for these minerals are given in the following equations:

Olivine:**Serpentine:****Wollastonite:**

The reactions [2, 3, and 4] are thermodynamically favorable, but the reaction rates are slow (geologic time scales). Therefore, extensive studies have focused on accelerating the rates and exploiting the heat of reaction. Some limitations include the energy penalty and costs that comes from the big amount of rock that needs to be mined and transported (not the case for alkaline residues), the need of high temperatures and pressure, pre-treatment of the material and the use of additives, such as acids or bases, that are not recovered or recycle (3). These drawbacks result in a high price per ton of CO₂ sequestered and make mineral carbonation less attractive as compared to other CCS options. However a major benefit of this option is its virtually inert, leakage-free, and permanent trapping, without the necessity of a post-storage monitoring program.

Mineral carbonation is not a mature technology since most of the studies are still in the laboratory experimental phase and only few pilot plants projects have been mention. This immaturity could be seen in the fact that there has been in average 31 publications on mineral carbonation per year, the main drawbacks of the process have not been resolved yet, and there is still a lot of room for improvements.

2. MINERAL CARBONATION

2.1. Overview of carbonation processes

Mineral carbonation has been divided in several process routes for its better understanding and study. A main classification that has been given is to separate the process in direct or indirect carbonation. Another one is the use of gaseous or aqueous phase. Based on previous literature reviews (2, 4-5), figure 2 shows an updated version of the carbonation process routes that have been investigated in the period of time for this report.

No route reported by (5) has completely been abandoned, just modified as originally proposed. An example is the direct gas-solid carbonation that now is only used with industrial residues and not with minerals anymore. The routes in the diagram are basically the same ones mentioned before, but they have some modifications and/or have been grouped together. To the right of the figure it is written the chapter number where the information about the specific route is given.

In the figure we can see a clear separation for most of the routes into the use of pure CO₂ or the use of flue gas instead; this is an important point in order to lump the capture and storage processes in a single step avoiding the CO₂ capture and transportation costs. The indirect aqueous carbonation is now divided in double-(all two step processes) and multi-step (more than two steps) processes. In these double and multi-step routes are also included all the routes that use additives for the extraction or precipitation steps (e.g. acetic acid, HCl, NaOH, etc.). Other CO₂ routes will discuss briefly the processes that are not considered as ex-situ mineral carbonation, but that are strongly linked to a carbonation process, which include in-situ carbonation, coastal spreading, ultramafic mine tailings with biomineralization, accelerated weathering of limestone (AWL), and the use of brines.

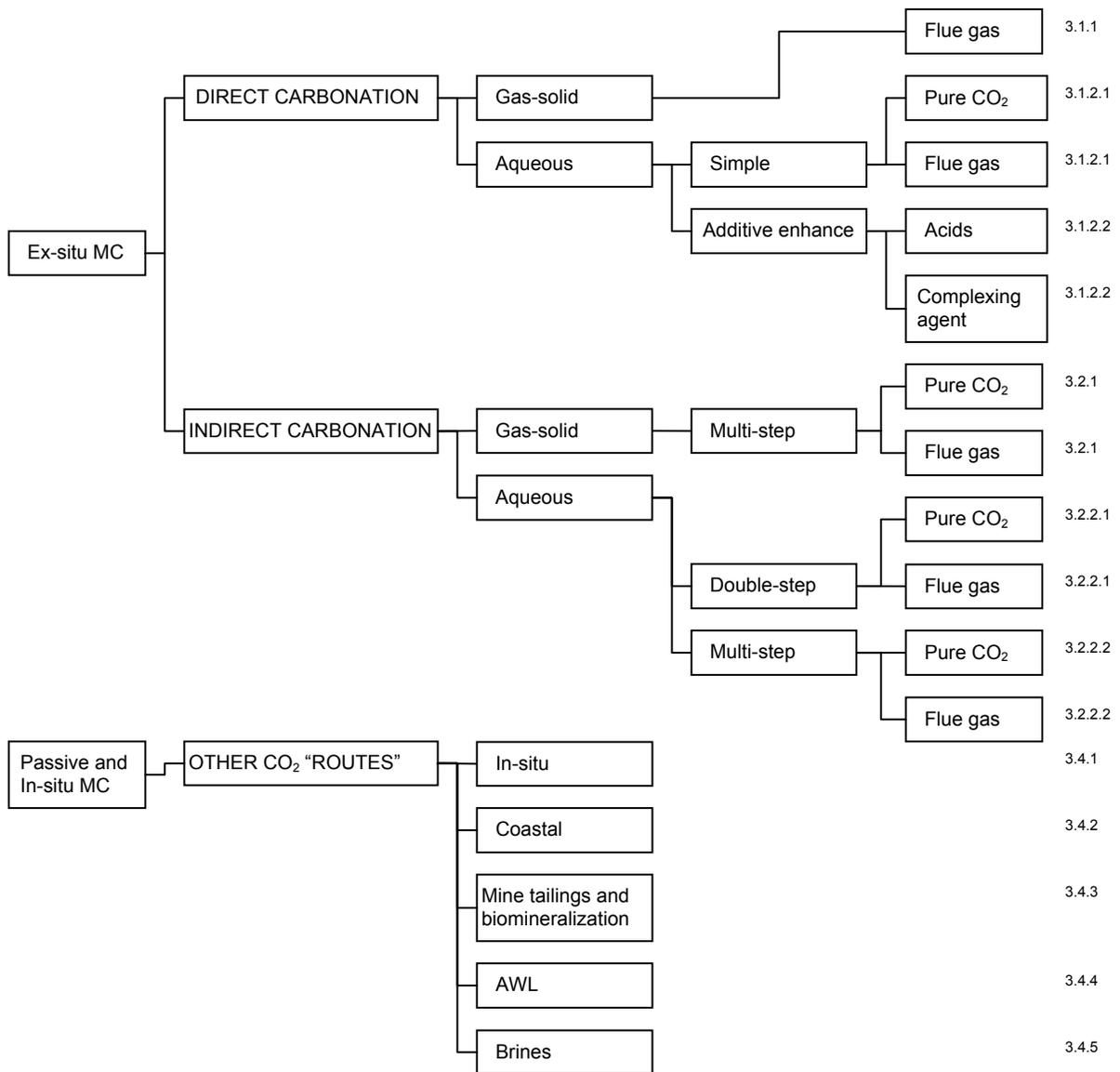


Figure 2 Mineral carbonation route tree (2008-2010).

2.2. Statistical review: trends on mineral carbonation

Oxides and hydroxides of calcium and magnesium would be the ideal source material, but as such they are rare in nature. Therefore, mafic and ultramafic silicate rocks, or alkaline industrial residues containing these metal oxides, are the most suitable for the carbonation process. The latter are limited in quantity but readily available having higher reactivity than the former that are abundant but not readily available.

The importance and need of a detailed evaluation of suitable minerals deposits worldwide was indicated by (2, 4-5). Prior to 2007 we found this kind of evaluation only for the United States (6) and Finland (7). From 2008 only in the US is found an assessment covering the entire country that was carried out to gain the understanding of the potential CO₂ storage capacity from the deposits within the US (8). A digital geologic database was developed of magnesium-silicate ultramafic rocks in the entire country that are suitable and could be exploited for mineral carbonation, which consisted primarily of olivine and serpentine minerals. In another study, the viability of Central Atlantic magmatic province (CAMP) basalts from the eastern seaboard of the United States, such as the Georgia, the New York, and the Sandy Hook basins, was studied as potential target for geological CO₂ sequestration (9). There is still a gap in assessing the silicate ores that can be exploited for CO₂ mineral sequestration worldwide.

The most important natural, synthetic and residue materials investigated in the articles reviewed are listed in tables 1, 2, and 3. From these tables it can be concluded that the Magnesium bearing silicates, such as olivine and serpentine, are the ones that are being investigated the most, although the interest in basalts for in situ mineral carbonation is increasing and to be noted. From the alkaline solid residues, steelmaking slag is still the one receiving the most attention. The different types of fly ash are also sources of material having a lot of research.

There is a long list of additives that have been used or mention in the literature lately. This can be explained with the idea that research is focusing on the acceleration of the dissolution and precipitation steps, in order to enhance the carbonation process, trying to do this with the help of additives. A list of all the additives used or mention in the research papers reviewed is also given (see table 4). The acid that is has been used the most is HCl, and the base is NaOH, in a lot of the cases these two are used in the same process for different steps.

Table 1 Mineral types investigated for carbonation in literature under review (2008-2010).

Mineral	Formula	Reference
Basaltic glass	Depends on basaltic formation	(9-15)
Brucite	Mg(OH) ₂	(16)
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	(17-18)
Dunite	90 % olivine	(19-20)
Forsterite	Mg ₂ SiO ₄	(21)
Harzburgite	CaMgSi ₂ O ₆ + (Mg, Fe) ₂ SiO ₄	(20)
Olivine	(Mg, Fe) ₂ SiO ₄	(17, 22-31)
Orthopyroxene	CaMgSi ₂ O ₆ + (Fe,Al)	(17)
Peridotite	Depends on rock formation	(14, 32-33)
Pyroxenite	Mixture of pyroxene rocks	(20)
Sandstones	Depends on rock formation	(34-35)
Serpentine	Mg ₃ Si ₂ O ₅ (OH) ₄	(36-40)
Serpentinite	Depends on rock formation	(41-44)
Wollastonite	CaSiO ₃	(45-48)

Table 2 Solid alkaline industrial residue investigated for carbonation with CO₂ mitigation purposes in literature under review (2008-2010).

Residue	Reference
Air pollution control fly ash	(49-51)
Biomass ash	(52-53)
Blast furnace slag	(54)
Bottom ash	(52-53, 55)
Cement wastes	(48, 52-53, 56)
Chrysotile milling and mining tailings	(57-59)
Coal combustion fly-ash	(60-61)
Lignite combustion fly ash	(62-63)
MSWI ash	(52-53)
Nirex reference vault backfill	(64)
Oil shale ashes	(65-67)
Paper mill waste	(68)
Paper wastewater incineration ash	(52-53)
Pressed lime-waste composites	(69)
Steelmaking slag	(70-77)

Table 3 Synthetic materials investigated in literature under review (2008-2010).

Synthetic Material	Formula	Reference
Calcium acetate	Ca(COO) ₂	(78)
Cement curing		(79)
Larnite	Ca ₂ SiO ₄	(80)
Lime	Ca(OH) ₂	(81-82)

Table 4 Additives used or mentioned in literature under review (2008-2010).

Additive	Formula	Publication
Acetic acid	CH ₃ COOH	(43, 45, 54, 71, 73)
Acidithiobacillus sp.	(Microbial catalyst, to produce acid)	(58)
Aluminum nitrate	Al(NO ₃) ₃	(73)
Aluminum sulfate	Al ₂ (SO ₄) ₃	(73)
Ammonium acetate	CH ₃ COONH ₄	(73)
Ammonium chloride	NH ₄ Cl	(36, 73-74)
Ammonium di-hydrogen phosphate	NH ₄ H ₂ PO ₄	(73)
Ammonium hydroxide	NH ₄ OH	(43)
Ammonium nitrate	NH ₄ NO ₃	(73)
Ammonium sulfate	(NH ₄) ₂ SO ₄	(43, 58, 73)
Carbonic anhydrase	(enzyme)	
Calcium chloride	CaCl ₂ *2H ₂ O	(58)
Citric acid	C ₆ H ₈ O ₇	(29-30)
Diammonium hydrogen phosphate	(NH ₄) ₂ HPO ₄	(73)
Dipotassium phosphate	K ₂ HPO ₄	(58)
EDTA	C ₁₀ H ₁₆ N ₂ O ₈	(36)
Formic acid	HCOOH	(43)
Hydrochloric acid	HCl	(16, 29-30, 37-38, 43-44, 75-76)
Lithium hydroxide	LiOH	(28-30)
Nitric acid	HNO ₃	(43-44, 72-73)
Potassium bicarbonate	KHCO ₃	(25)
Propionic acid	CH ₃ CH ₂ COOH	(73)
Rubidium bicarbonate	RbHCO ₃	(25)
Sodium acetate	CH ₃ COONa	(36)
Sodium bicarbonate	NaHCO ₃	(19-20, 25)
Sodium citrate	C ₃ H ₄ OH(COOH) ₂ COONa	(36)
Sodium chloride	NaCl	(17, 19-20, 28-30, 36-37)
Sodium hydroxide	NaOH	(37-38, 43-44, 46-47, 54, 72-73)
Sodium nitrate	NaNO ₃	(28-30)
Sodium oxalate	Na ₂ (COO) ₂	(36)
Succinic acid	C ₄ H ₆ O ₄	(45)
Sulfuric acid	H ₂ SO ₄	(43, 72-73)
Tributyl phosphate (TBP)	C ₁₂ H ₂₇ O ₄ P	(71, 73)
Urea	(NH ₂) ₂ CO	(73)

In table 5, it is given a list of other type of publications that could not be listed in tables 1, 2, and 3, and also the ones that are in the tables above but have specific work focusing on one step of the mineral carbonation process or other topics that are related to it.

Table 5 Other type of publications included in the review (2008-2010).

Step on mineral carbonation:	Reference
Mineral resource study	(10, 36)
Mechanical activation	(22-24, 31)
Heat activation	(37, 40, 83)
Feedstock dissolution	(28-30, 67, 71, 75-76)
Carbonate precipitation	(30, 84-85)
Passive carbonation	(32, 41-42, 57, 59, 86-87)
In-situ	(3, 9, 11-14, 32-33, 35, 42)
Other	(88-90)

Since the use of flue gas is gaining interest in the field (like said before to avoid the costs of capturing CO₂), a list with the publications that mention the use of pure CO₂ or flue gas with minerals or residues is shown in table 6. From this table it can be concluded that even though flue gas is increasing its use as a source of CO₂, the use of pure CO₂ is still by far the most studied.

Table 6 Use of pure CO₂ or flue gas with minerals or residues investigated in literature under review (2008-2010).

	PureCO₂		Flue gas	
	Mineral	Residue	Mineral	Residue
Reference	(15-21, 25-27, 36, 39-40, 43-47)	(49, 52-55, 60, 62-63, 68-70, 73, 91)	(37-38, 83)	(49-51, 61, 65-66, 74, 77)

2.3. Chronological review: milestones

This report will be centered principally on the open literature found for the years 2008 until March 2010; however a brief chronological review is given in this section in order to list the milestones of mineral carbonation that have been mentioned and considered as important findings or reports throughout the past 20 years.

- **1990:** Mineral carbonation with calcium silicates as a way of binding and storing CO₂ was first mentioned by Seifritz (92).
- **1993:** The first patent on “treatment of calcium silicates” which included its carbonation was introduced in Japan by “Asahi Chemical Ind.” (93).
- **1995:** The process was first investigated with more detail by Lackner et al. (94) at Los Alamos National Laboratory (LANL) who considered two approaches: the direct gas-solid carbonation and aqueous carbonation with hydrochloric acid (HCl).
- **1999:** The single step aqueous carbonation was investigated at the Albany Research Center (ARC), using a solution of 0.64 M NaHCO₃ and 1M NaCl to enhance the carbonation rates.
- **2000:** The International Energy Agency (IEA) Greenhouse Gas R&D Programme published a report on mineral carbonation. They assessed the feasibility of the technology for CO₂ sequestration routes, concluding that there was no competitive process as compared with other CCS options, such as geological storage and use of aquifers (95). The use of alkaline industrial residues as an alternative feedstock for mineral carbonation was first considered in by Devoldere et al. (96). They proposed the carbonation of municipal solid waste incinerator (MSWI) bottom ash with liquid and supercritical CO₂.
- **2001:** Kakizawa et al. (97) suggested a double step carbonation process which involves the extraction of calcium ions by acetic acid and the crystallization of calcium carbonate by injecting CO₂ and recovering the acetic acid, but it was never proven how to actually recover the acid.
- **2002:** The Separation Processes Laboratory (SPL) of the Swiss Federal Institute of Technology Zurich (ETH) started its mineral carbonation research. The first patent on mineral carbonation with CO₂ was introduced by Shell internationale research maatschappij B.V (98).
- **2003:** Huijgen and Comans (2) from the Energy research Centre of the Netherlands (ECN) presented the first literature review discussing the publications on mineral carbonation prior to January 2003.
- **2004:** In Finland, Zevenhoven et al. (99), suggested the multi-step gas-solid carbonation, which involved three steps: MgO production, MgO hydration, and Mg(OH)₂ carbonation.
- **2005:** The ARC now called the National Energy Technology Laboratory (NETL) presented its final report on aqueous mineral carbonation where they presented the optimal conditions they found using the solution mentioned before for olivine and serpentine, and pure water for

wollastonite (100). In the same year, Huijgen and Comans rendered a literature review update for the years 2003-2004 (4). Also the Intergovernmental Panel on Climate Change (IPCC) published a special report on CCS in which chapter 7 was particularly focus on the mineral carbonation option (1).

- **2006:** The first International conference on Accelerated Carbonation for Environmental and Materials Engineering was held in London, England.
- **2008:** The latest literature review update for the years 2005-2007 was presented by Sipilä et al. (5). The second International conference on Accelerated Carbonation for Environmental and Materials Engineering was held in Rome, Italy.
- **2010:** The third International conference on Accelerated Carbonation for Environmental and Materials Engineering will be held in Turku, Finland in November 2010.

The interest in studying mineral carbonation can be based on the number of publications that were published per year. A chronological review of the number of publications on mineral carbonation can be seen in figure 3. From this figure we can observe an increasing trend on the number of publication from the years 1990 to 2002, after that period, a trend it is not really appreciable anymore, but it can be calculated an average of 31 publications per year in the last ten years. In the past 3 years (2007-2009) it looks like the increasing trend is coming back, but still no more than 50 publications per year are found.

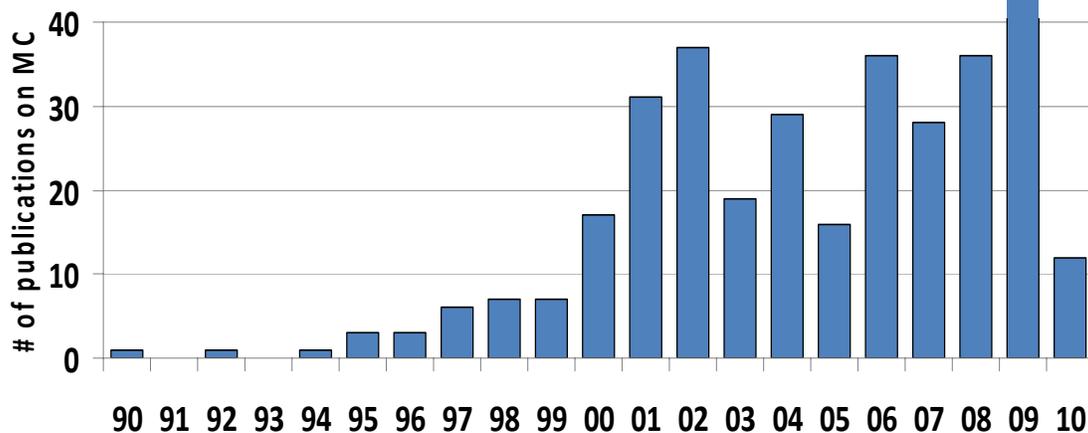


Figure 3 Chronological review of publication throughout the years. Publications prior to 2007 were based on the bibliography on the previous literature reviews.

Patents are a measure for industry's interest in a topic, also the interest of academia on protecting the rights of their inventions. In figure 4 we can observe the number of projects that were patented through the years. There are seven patents on mineral carbonation found after 2008 from a total of 26 since 1993. A chronological trend on patents cannot be seen in the figure, and it can be calculated that an average of three patents were granted per year since 2001. For a complete chronological list of all the patents see the **appendix 7.1**.

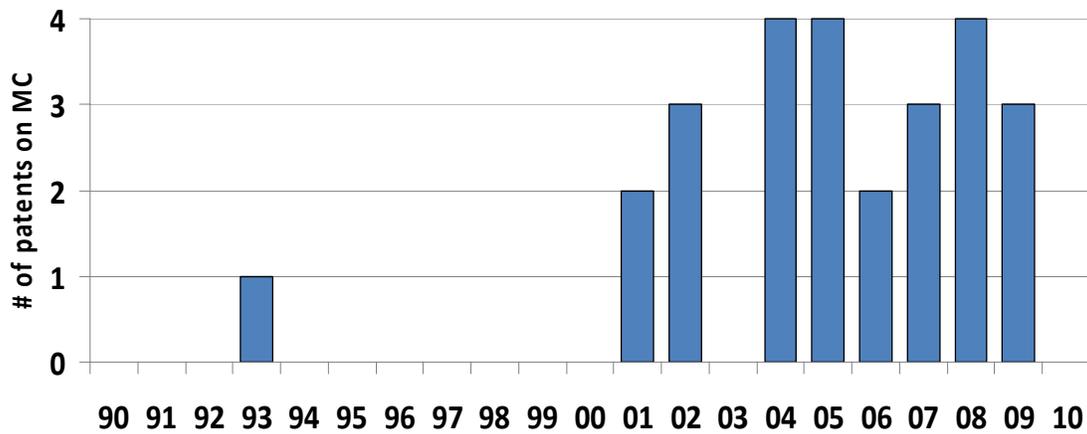


Figure 4 Chronological review of patents throughout the years.

3. PROCESS ROUTES

As reported in section 2.1, sequestering CO₂ to form carbonates can be accomplished in many ways, from the simplest direct gas-solid route all the way to complex multi-step aqueous routes. In this chapter all routes are described regarding the developments and results obtained in the research papers and reports on mineral carbonation found for the years 2008-2010.

This chapter follows the tree scheme showed in figure 2; a sub chapter is dedicated to each category presented in the tree and whether it was used with naturally occurring minerals or industrial residues, with pure CO₂ or flue gas as a source of CO₂.

3.1. Direct carbonation (single-step)

3.1.1. Gas-solid carbonation

Direct gas-solid carbonation is the simplest approach of contacting the metal oxide bearing material in its solid state with the CO₂ in its gaseous form. It was described as the most straightforward approach for mineral carbonation (4). However, the reaction rates achieved were too slow as compared to other routes such as multi-step or aqueous processes.

Investigation on this route has almost been abandoned, especially when using minerals no literature was found for the years 2008-2010. But, research on the dry process with solid residues is still carried out at University of Rome (49-50) and the university of Wyoming (61) (see below). These studies continue mainly because the dry process has a simple design (no issues dealing with high amounts of solution) and the heat generated by the reaction could possibly be exploitable to reduce energy penalties in the whole process. Other research institutes are focused or have switched to other more promising routes (39, 43).

Direct gas-solid carbonation of industrial residues with flue gas

The use of waste streams as feedstock instead of minerals has some benefits. First, these wastes are highly reactive and are readily available at the CO₂ source. Second, the produced carbonate minerals are known to immobilize contaminants through surface adsorption and co-precipitation processes (61). Therefore the solubility of pollutants from the waste streams could be lowered. However, the total amounts of industrial wastes are too small to reduce CO₂ emissions substantially (1).

The kinetics of direct gas-solid carbonation of Air Pollution Control (APC) residues has been studied by Baciocchi et al. (49-50) in a thermogravimetric system (TGA). They observed that the kinetics were characterized by a rapid chemically-controlled reaction, followed by a slower product layer diffusion-controlled process. Conversions between 60 and 80 % were obtained, depending on the conditions. The temperature had no influence on the maximum conversion at temperatures equal or above 400 °C, whereas the CO₂ concentration had only a small influence. The maximum conversion was achieved in 1 minute at 400°C and 50 vol% of CO₂ concentration. However, they suggested the use of 10 vol%, which had also fast reaction rates and high conversion in 3 minutes. With this the costs of capturing the CO₂ could be avoided. When we compare figure 5a with 5c, we can see that there is not a big difference in the final conversion.

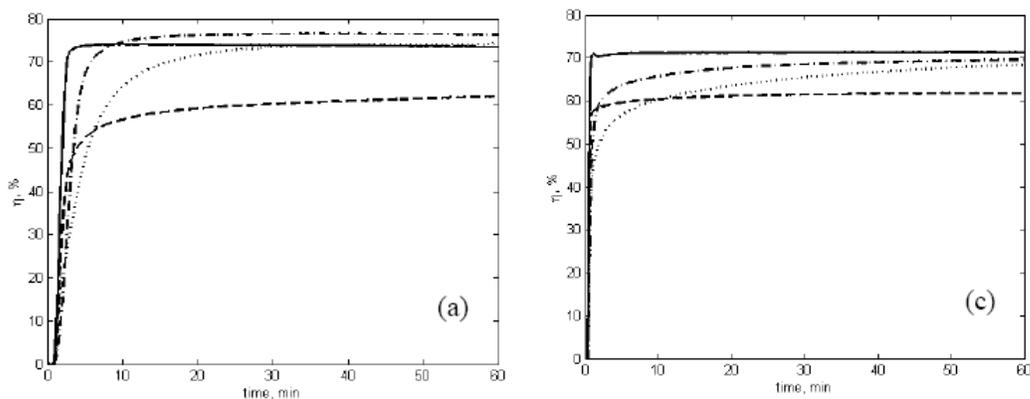


Figure 5 Gas-solid carbonation kinetics measured at different operating temperatures: dashed line at 350 °C; continuous line at 400°C; dotted line at 450°C; dashed-dotted line at 500 °C. (a) 10% vol., (c) 50% vol. CO₂ concentration (50).

The use of a self-design and fabricated fluidized bed gas-solid reactor with another industrial solid residue (fly ash) was conducted by Reddy et al. (61). Who subjected the fly ash to fluxes of flue gas with a CO₂ concentration of 12-17 % at temperatures between 43 and 54 °C and total pressure between 0.88 and 1.14 bar. Based on the typical composition of fly ash it was calculated that the capacity of CO₂ sequestration by fly ash could be of 20 kg of CO₂ per 100 kg of ash. The production of calcium carbonate was observed for reaction times of 8 minutes. The yield obtained was small but it was concluded that this could be improved by optimizing the operating conditions. An important point to be highlighted was that the reaction products need to be continuously separated to avoid their dissolution by acid gases in the flue gas (e.g. SO_x).

3.1.2. Aqueous carbonation

Water is a key element in the natural weathering processes, and it has been proven that it enhances the reaction rates of mineral carbonation processes. Because of that, the major part of the current research has focused in aqueous carbonation. In this report direct aqueous

carbonation is divided in two categories depending in the type of aqueous solution used: simple, which involves only the use of water, and additive enhanced, which involves the use of acids or complexing agents to enhance the reaction rates.

Direct aqueous carbonation has been described as the most promising CO₂ mineralization option (5), in which three mechanisms (CO₂ dissolution, silicate dissolution, and precipitation of carbonates) takes place in the same reactor. It has been proven that the silicate dissolution is the rate-limiting reaction step. Therefore, there is a big interest on enhancing this step with additives, which will be discussed later in this paper (see ***Dissolution, extraction, or leaching of the reactive components*** below). Not only the use of these additives, but also, in order to maximize the reaction rates, operating conditions such as temperature, CO₂ concentration and pressure, water-to-solid ratio, and particle size need to be optimized.

A major disadvantage and criticality of the aqueous approaches that has not been completely addressed is the great amounts of water that need to be manage and treated in an industrial scale. This means, the recycle of the aqueous media needs to be considered in order to make the process more cost-effective.

In situ carbonation could be considered as a direct aqueous carbonation of minerals, because aqueous CO₂ is injected directly into porous ultramafic formations with the aim of reacting the CO₂ with the host rocks. However, in this chapter only ex-situ processes are considered and in situ carbonation will be addressed later as a separate topic (see section 3.4.1).

3.1.2.1. Simple

Direct simple aqueous carbonation of minerals

In order to understand better the processes of aqueous ex-situ mineral CO₂ sequestration, Lopez-Periago et al. (81) investigated the effect of ultrasonic agitation on the carbonation of Ca(OH)₂ by using scCO₂. Experiments were performed with ultrasonic agitation in the batch mode at 313 K and 13 MPa. An overall degree of conversion of 85-90 % was obtained with typical rhombohedral morphology of CaCO₃ and small particle size. Regnault et al. (82) studied the impact of water content on the kinetic rate of portlandite carbonation with CO₂-rich fluids. The experiments were conducted in the presence of liquid water and CO₂/H₂O vapor, with dry scCO₂ that either stayed in the one-phase gas region, or change to the two-phase liquid-gas region. In the presence of liquid water complete carbonation was observed and no calcite coating was found. On the other hand, in the absence of liquid water, calcite formed a passivating layer on the portlandite surface

leading to incomplete carbonation. This proved that the water content influences the overall final amount of carbonation.

Also using a synthetic material Santos et al. (80) synthesized larnite powders to be dispersed in distilled water in a glass reactor with pure CO₂ bubbling for 15 min at room temperature and atmospheric pressure. The silicate to carbonate transformation rate was 100% in 15 min, and according to the stoichiometry of the reaction, it was calculated that 550 kg of CO₂ could be eliminated with 1 t of larnite.

It was recently studied by Kwak et al. (21) who used magic angle spinning (MAS) NMR, combined with XRD, TEM, SAED, and EDX to study the reaction extent of forsterite with water at 80 °C and 96 atm. They obtained only 8, 47, and 67 % conversion in 20h, 4, and 7 days, respectively. This study was mostly to use the technology to characterize the reaction pathways of metal carbonation in the presence of supercritical CO₂ (scCO₂) and water, concluding that (MAS) NMR could be used to study fundamental mineral carbonation.

In another study by Zhao et al. (16) experiments were performed dissolving natural brucite with distilled deionized water (DDW) at ambient temperature and 15 atm for 2.5 h, observing that nesquehonite was the most abundant species of the mineral products and fitting the results to a pseudo-first order rate law. The carbonation extent based on the total carbon content achieved divided by the maximal carbon content was 94.3 %.

In Brazil studies were performed with sandstones from the Rio Bonito formation to understand geochemical interactions of water-rock-CO₂ that could be useful for the geological storage of CO₂ by mineral trapping. When reacting the sandstones with CO₂ and deionized water at 200 °C and initial pressure of 10 MPa for 100 h they observed initial dissolution of k-feldspars and carbonates with further precipitation of calcium and iron carbonates, silica, kaolinite, and calcium sulfate (34-35).

Direct simple aqueous carbonation of residues

The differences in the composition of the industrial residues make them difficult to generalize the process conditions for all wastes. For example the influence of operating parameters, such as temperature, pressure, and liquid to solid ratio (L/S), on the wet process of APC, stainless steel slag (SSS) and bottom ash (BA) was studied by Baciocchi et al. (49, 55, 70). The Maximum CO₂ uptakes found were 130, 140, and 250 g of CO₂ per kg of residue for SSS, BA, and APC, respectively. And it could be achieved at 50 °C, 3 bar, 0.4 L/S, and grain size <0.105 μm in 2 h for

SSS. For BA was done at 30 °C, 10 bar, 0.3 L/S, and grain size <0.150 µm in 8 h. Finally for APC at 30 °C, 3 bar, and 0.2 L/S in 8 h. it was suggested that this route could also be used for other residues with high content of calcium oxides and hydroxides, in order to increase the impact of this process on the CO₂ sequestration. This demonstrates that different conditions for different kinds of residues need to be applied to optimize the CO₂ uptake due to a difference in the composition of the residue and in the reaction kinetics.

In France, Perez-Lopez et al.(68) and Montes-Hernandez et al. (60, 91) used the same methodology and operating conditions, for alkaline paper mill waste (55 wt% Ca(OH)₂) and coal combustion fly ash (4.1 wt% CaO). It was calculated that approximately 26.19 and 218.37 g of CO₂ per kg of residue could be sequestered into stable calcite, with coal combustion fly ash and paper mills waste, respectively. They also proved the big differences on CO₂ uptake depending on the type of waste used.

Sequestration of CO₂ in waste cement kiln dust (CKD) under ambient temperature and pressure was also investigated (56). Carbonation extents greater than 70 % of its theoretical capacity without any prior modification in the waste material could be achieved. The overall extent of carbonation appeared to be inversely related to the water content of the columns, probably due to a greater gas pore volume and lower diffusion limitations when the water content is low. More detailed material characterization was needed to determine if heterogeneity in the columns influenced their ability to sequester CO₂.

In another study carried out with lignite fly ash, Back et al. (62), achieved a maximum CO₂ uptake of 230 g of CO₂ sequestered per kg of fly ash at 75 °C, 50 g/L, 0.01 MPa of CO₂ partial pressure, and stirring rate of 600 rpm for 270 min. They separated the reaction in three consecutive phases, the dissolution of CO₂, the calcium carbonation reaction, and the dissolution of MgO reacting with CO₂ to magnesium bicarbonate. The CO₂ uptake could be increased with longer phases I and II. Using lignite fly ash also, Uliasz-Bochenczyk et al. (63), concluded that CO₂ absorption by ash-aqueous suspension depended mainly on the ash type.

In a general study made by Gunning et al. (53), several industrial wastes from the cement, metallurgical, paper, waste disposal and energy industries were treated with pure CO₂ to improve their environmental properties, while sequestering CO₂. The experiments were performed with water at 2 bar and 75 % of relative humidity for 72 h. The wastes had wide ranging in CO₂ uptake, related to the total calcium content and the mineralogy of the residue. Cement dust and paper incinerator ashes were the most reactive waste streams. On the other hand, clinical waste incineration ash, steel wastewater sludge and pulverized fuel ash showed little or no reaction.

Another way of reducing CO₂ emissions, by a factor of 2 or 3, from the conventional process of producing some ceramic components (hot-curing) is to change it with a carbonation process using a combination of lime and waste (SS, PFA) as binders (69). These were treated with scCO₂ at 60 °C and 200 bar for 24 hr obtaining a complete conversion of lime to calcite.

Direct aqueous carbonation of industrial residues with flue gas

An aqueous process similar of that used by Baciocchi (49) was presented by Sun et al. (51) to obtain the kinetic data of the carbonation process for APC fly ash. They calculated that 8-12 % of CO₂ could be trapped in APC residues at 20-30 °C, 3 bar, 0.3 L/S, and 20 % of CO₂ concentration for 2.5 h. The reaction rate was found to be fast in the first 5 to 10 minutes with an activation energy (E_a) of 14.84 kJ/mol, the phase boundary was the controlling step, were CO₂ had a positive effect. As the reaction proceeded, the diffusion through product-layer was the new rate-controlling step and the new E_a was 30.17 kJ/mol. They in another study (64), also investigated the capacity of the Nirex Reference Vault Backfill (NRVB) to absorb CO₂ from radioactive wastes at conditions similar of those underground. It was found that the degree of water saturation of the NRVB pores influenced more the rate of carbonation as compared to the effects of CO₂ pressure and temperature.

In another study using large grains of two kinds of SS, the presence of elementary carbon in the carbonation products was found and the amount of carbon that comes from CO₂ was estimated that could be comparable to the amount of CO₂ capture as carbonate (77). The CO₂ uptake due to carbonation at 90 °C with water saturated synthetic combustion gas (20 % CO₂, 80 % Ar) was found to be 15 and 6 g of CO₂ per kg of SS for the two different slags used.

Experiments using alkaline ash-transportation water from oil shale transportation system were carried out in a dispergator-type device or a barboter-type column at ambient temperature and atmospheric pressure. A decrease of the water pH from 13 to <9 was observed. The dispergator-type had 50 times higher specific intensity than the barboter-type column. The size and structure of the final CaCO₃ were different depending on the end-point pH value, the flue gas composition and the reactor type. This could be use for the production of PCC but further optimization is needed to have a fine and homogeneous particle size (65-66).

3.1.2.2. Additive enhanced

Direct additive enhanced aqueous carbonation of minerals

Silicate dissolution has been proven to be the rate limiting step on the carbonation processes, and to be dependent on pH. Therefore many studies have focused on enhancing this step by using additives, for example the use of dilute HCl for the carbonation of brucite showed that at the beginning of the reaction the fraction of reacted brucite increased rapidly, but then stabilized (16). It was found that the extent of carbonation was lower in HCl than in DDW. suggesting that the process started with the dissolution of brucite and CO₂, enhanced by the HCl, leading to nesquehonite crystallization hindered by the acidic pH.

The carrier solution that has been used the most in aqueous carbonation is the one proposed by the ARC (100), which consist of an aqueous solution of 1M NaCl +0.64 M NaHCO₃. Recent studies using this solution were made by Koukouzas et al. (20), who investigated the carbonation of pyroxenite, dunite and harzburgite from Greece, obtaining low levels of carbonation (5 to 10 % of the stoichiometric value) at 155°C and 158.6 bars for 2 h. They suggested changing the set of reaction conditions but no further studies were shown. Andreani et al. (19), also used the carrier solution for a flow-through dunite percolation experiment at conditions analogue to those of an in situ CO₂ sequestration. It was concluded that with low flow rates the permeability of the rock could be reduce irreversibly close to the injection point, whereas with high flow rates the surface passivation would increase and reduce the carbonation potential of the rock. Moderate flows would lead to partial carbonation of the rock without altering the permeability, being optimal for the process.

Experiments were performed by Jarvis et al. (25), who adjusted the carrier solution composition and increased the reaction rates. They concluded that by increasing the bicarbonate activity, the hydrogen ion activity was increased which yielded in faster olivine dissolution and increased the rate passivating-reaction layer exfoliation. Maximum conversion of 63% with a solution of 5.5M KHCO₃ at 185 °C and 13.5MPa for 1 hour was obtained which is greater than the one obtained with the standard solution (49.5 %).

The reactivity of olivine, orthopyroxene, and chrysotile carbonation using oxalic acid as CO₂ source was studied by Dufaud et al. (17), who used a NaCl-rich water, at 400 °C and 1 kbar for 4 h. The carbonation levels achieved, increased from orthopyroxene, to chrysotile and then to olivine with the largest CO₂ mineral sequestration levels (57 mol%). They suggested the formation of a poorly crystalline graphite phase that could be up to 22 mol % of the total sequestered

carbon. Although a more precise quantification of this phase was needed and the use of CO₂ instead of oxalic acid is an important point to study the actual potential to sequester CO₂.

At specific conditions, the carbonation process gets limited by other factors others than the dissolution step. The impact of a passivating silica layer on the mineral particles has been studied. In a study made by Daval et al. (46-47), who showed that wollastonite carbonation in water was not dramatically slowed by the formation of a thick silica layer and the calcite crystal had large size, however, when using 0.44 M NaOH or scCO₂, smaller crystal sizes were favored filling in the silica pores. They proposed that the transport of species was not hindered by the silica layer but for the formation of nano particles in the pores and cracks within it, or because the layer becomes overlain by dense homogenous packing of small crystals.

3.2. Indirect carbonation (multi-step)

Indirect carbonation is when the mineral carbonation process is divided in two or more steps, this means that the extraction of the metal oxide or hydroxide (Mg or Ca usually) from the alkaline feedstock, the precipitation of the carbonates with CO₂, and/or the dissolution of the CO₂ (in the case of aqueous carbonation) are performed in separated steps or vessels.

3.2.1. Gas-solid carbonation

Indirect gas-solid carbonation of minerals

Since the reaction kinetics of a single step gas-solid carbonation were found to be too slow, an indirect staged gas-solid dissolution/carbonation reaction was proposed to overcome some of the issues of the direct route. In Finland the gas-solid carbonation has been studied since the year 2000, trying to take advantage of the heat produced by the exothermic reaction, avoiding the energy requirement that involves an aqueous process (43).

With an exergy analysis zevenhoven et al. (39), tried to find an optimal energy efficiency were the excess heat exergy ($\Delta Ex(Q)$) had a negative value. Two carbonation schemes were compare: A two-step serpentine carbonation with MgO extraction followed by MgO carbonation, and a three-step serpentine carbonation with MgO extraction followed by MgO hydration and Mg(OH)₂ carbonation. From all the tests performed, it was found that Mg(OH)₂ could be carbonated faster than MgO, and that carbonation via Mg(OH)₂ is preferable from an energy efficiency point of view. They tried to extract magnesium from Mg-silicate minerals without the consumption of chemical or the need of significant energy input for the carbonation process via Mg(OH)₂ (43) proposing a three-step process: 1) The thermal activation of serpentine was done by heating-up

to 630 °C in air, 2) The hydroxylation of MgO to Mg(OH)₂ with steam at 35 bar, and 380 °C, and 3) The carbonation of Mg(OH)₂ to MgCO₃ at 35 bar and 495 or 525 °C. However the conversions obtained were still lower than the results obtained with aqueous processes. Work on the carbonation of Mg(OH)₂ in a fluidized bed to enhance particle-particle collision and a uniform temperature in the reactor are future studies proposed by the authors, as well as the use of scCO₂ (see fig. 6).

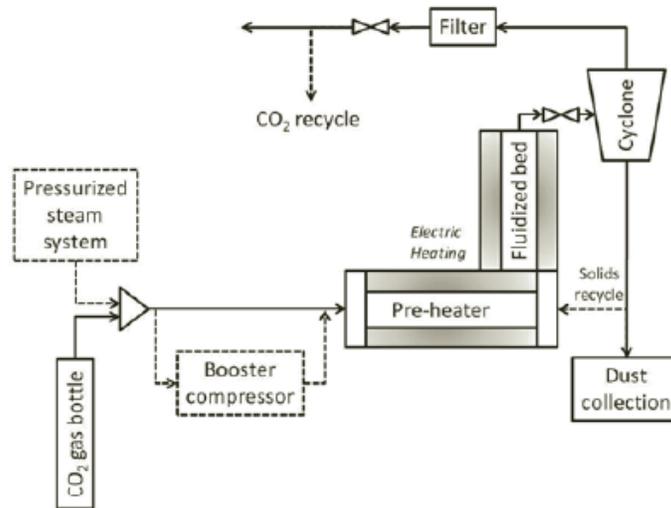


Figure 6 Schematic diagram of a fluidized bed proposed by (43).

Indirect gas-solid carbonation of minerals with flue gas

A three step route for extracting Mg(OH)₂ from serpentine in an aqueous solution followed by a gas-solid carbonation was proposed by Lin et al. (38). 1) The extraction step was carried out in an autoclave, with serpentine powder and a 1N HCl solution at 150 °C for 24 h, followed by a change in the pH to 8 with a 0.1N NaOH solution to precipitate and remove silica. Finally, more NaOH was added until a pH of 11. 2) The Mg(OH)₂ powder was dried at 100 °C for 3 h. 3) The carbonation experiments were conducted in a fixed bed reactor under atmospheric pressure with a gas mixture of 10 vol% CO₂ and 90 %N₂ with a flow rate of 200 cm³/min at 325 °C for 2 h. They suggested that the crystal domain size of the Mg(OH)₂ was the principal factor governing inversely proportional the CO₂ fixation. Carbonation reached 26 % of the stoichiometric limit, concluding that the gas-solid carbonation of Mg(OH)₂ was restricted under atmospheric pressure. Nothing was addressed on the recovery of the HCl or NaOH used for the extraction and precipitation steps.

3.2.2. Aqueous carbonation

The Aqueous carbonation process can be divided in two principal steps: the dissolution of the metal oxide bearing mineral, and the precipitation of the carbonate. Normally enhancing one step means limiting the other one. Research has moved to an indirect process where these two steps take place in separate vessels at different optimized operating conditions. This can be done in two (double-step) or more stages (multi-step). In these processes the use of additives to accelerate each of the stages or steps is common. In this section it is also included the investigations carried out for one of the steps only (mostly dissolution), but that was done aiming on an indirect carbonation process.

3.2.2.1. Double-step

Indirect double-step aqueous carbonation of minerals

Teir et al. (43-44), studied the feasibility of a process producing magnesium carbonate from serpentinite using either HCl or HNO₃ to extract magnesium and iron from the mineral at 70 °C, and using NaOH to precipitate iron oxide, adjust the pH, and precipitate hydromagnesite with CO₂ at 30°C. With a mass balance they found that 3.1 t of serpentinite, 2.3 t of NaOH and 3.6 or 2.1 t of HNO₃ or HCl, respectively, are required to store 1 ton of CO₂. This process demanded large amounts of acid and base, in order to reduce the cost associated with these chemicals, they have to be recycled. This recovery, could be done via electrolysis of NaCl, however, it would release bigger amounts of CO₂ than the ones bound. Also a lot of heat was needed in order to evaporate the solvent before precipitating the magnesium salts and iron oxides. It was then concluded that the process could be feasible for production of valuable minerals and metal products, but probably not for capturing and storing CO₂.

Following the approach by Kakizawa et al. (97), who used acetic acid as extraction medium of calcium, Baldyga et al. (45), proposed a process consisting of two stages using succinic acid instead of acetic acid. First, the extraction of calcium (Ca²⁺) from wollastonite by the carboxylic acid in a glass reactor at 80 °C, ratio 1:1 acid to calcium. Second, the crystallization of calcium carbonate (CaCO₃) with CO₂ in a high-pressure titanium reactor at 80 °C, and pressure ≥ 30 bar. They concluded that succinic acid yielded better results than acetic acid, leading to a 90% of calcium conversion. However the problem of recycling the acid was not mentioned.

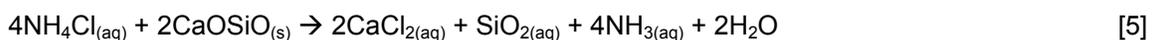
Indirect double-step aqueous carbonation of residues

Another expansion of the acetic acid process was proposed by Eloneva et al. (54), who studied the suitability of precipitating calcium carbonate from solutions of calcium acetate derived from blast furnace slag. The extraction step was carried out dissolving the slag in an aqueous solution of acetic acid at 70 °C and 1 bar for 2h, and the precipitation was performed by adding NaOH and pure CO₂ at 30 °C and 1 bar. Process calculations showed that 4.4 kg of blast furnace slag, 3.6 l of acetic acid, and 3.5 kg of NaOH, would be required to bind 1 kg of CO₂, resulting in 2.5 kg of 90% calcium carbonate which was not suitable to use as precipitated calcium carbonate (PCC). They concluded that the energy input requirements for the recovery of the acetic acid and the NaOH would generate from 6 to 13 times more the amount of CO₂ stored by the carbonation, making this process unsuitable for CO₂ sequestration.

Indirect double-step aqueous carbonation of residues with flue gas

Another double-step carbonation is the pH swing process (101), where the dissolution of the metal ions from the mineral is performed at low pH (acidic conditions), and the precipitation of the carbonates is carried out at elevated pH (basic conditions).

Kodama et al. (74), in their study proposed a pH-swing process under mild conditions, with recycling of the reaction solution utilizing steelmaking slag as the calcium source and NH₄Cl as the extraction medium. The regeneration of NH₄Cl was done when precipitating CaCO₃ with CO₂ as shown in the following reactions:



The extraction experiments were performed with the slag with a NH₄Cl solution (pH = 4.63) at 80 °C, 1 atm, and particle size < 64 μm having 99.6 selectivity of the calcium ion. The precipitation was carried out with the extracted solution (pH = 9.41) and a mixture of CO₂ (13 %) and N₂ (87 %) introduced at 17 sccm, at 80 °C and 1 atm for 2 h with a yield of 59.5 %. The total energy consumption of the whole process was estimated to be 300 kWh/t-CO₂. They concluded this process could be feasible if problems related to the high cost of crushing the slag and the recovery (downstream of the CO₂ absorption tower) and supply of the lost NH₃ could be overcome, but no process was proposed or showed to do so.

3.2.2.2. Multi-step

Indirect Multi-step aqueous carbonation of minerals

A cost model of a continuous industrial process was developed by Machenbach et al. (26), for the aqueous carbonation of olivine in a three-step process. The first step was the dissolution of olivine at 130 °C and 100 bar. The second step was the precipitation of magnesite at 250 °C and 100 bar. The final step was the precipitation of silica at ambient pressure. The cost estimation was developed base on mass balances for 50,000 t of CO₂ treated. The biggest investment cost was associated to the first reactor due to high mass flows and retention times. However, a positive NPV was predicted, assuming the sales of magnesite and silica. The recycling of water and heat were not considered, the conversion in the first reactor was assumed at 50 %, and the net CO₂ storage efficiency taken was 69%. Other issues like kinetics and product qualities need to be verified, since this was just a rough estimate.

Another process alternative was proposed later by Munz et al. (27) who proposed that the CO₂ was dissolved and mixed in the first reactor at 130 °C. The solution was then fed into the second reactor which contained the olivine for the dissolution process. Finally it was fed to the third reactor for precipitation at 250 °C. This change in temperatures led to an increase in the saturation index of magnesite from 0 to 2 which enabled its precipitation. The pressure was kept constant at 150 bar for the whole process. In order to also precipitate silica the outlet solution needed evaporation. However no kinetic information or final conversions were given.

Indirect Multi-step aqueous carbonation of minerals with flue gas

Li et al. (37), proposed a method to form HCl (for the extraction of Magnesium ions) and NaOH (for the dissolution of CO₂) solutions by the electrolysis of a NaCl solution, this was carried out in a self made electrolysis apparatus with a current of 0.5 A for 2 h. The carbonation process consisted of 3 steps: First, the heat pre-treated serpentine was placed in a reactor, for its dissolution, with the HCl solution at 90 °C for 2 h. Second, the simulated flue gas (CO₂ 11.3%, N₂ 88.7 %) was introduced to the NaOH solution for CO₂ dissolution. Finally, same volumes of both solutions were mixed at 85 °C for 15 min. A carbonation efficiency of 97.1 % could be achieved. However the feasibility of this process should be investigated, since no energy or cost considerations for the electrolysis step were addressed.

Hunwick in his patent (102) described a process using a slurry of serpentine (-40µm) with 30 wt% of water that is mixed with chilled ammonia to produce an ammonia/water/metal silicate slurry. This is after used to absorb CO₂ from a flue gas stream to form ammonium carbonates and later it

passes to a reactor at 280 °C and 120 bar to produce the metal carbonates. The ammonia could be recover and recycle in this last step up to 99.23 %. Only 0.67 % for make-up ammonia is needed at the beginning of the process. 90 % capture of the CO₂ was assumed and a long chain of heat exchangers to recover all the possible heat from the process (see fig. 7).

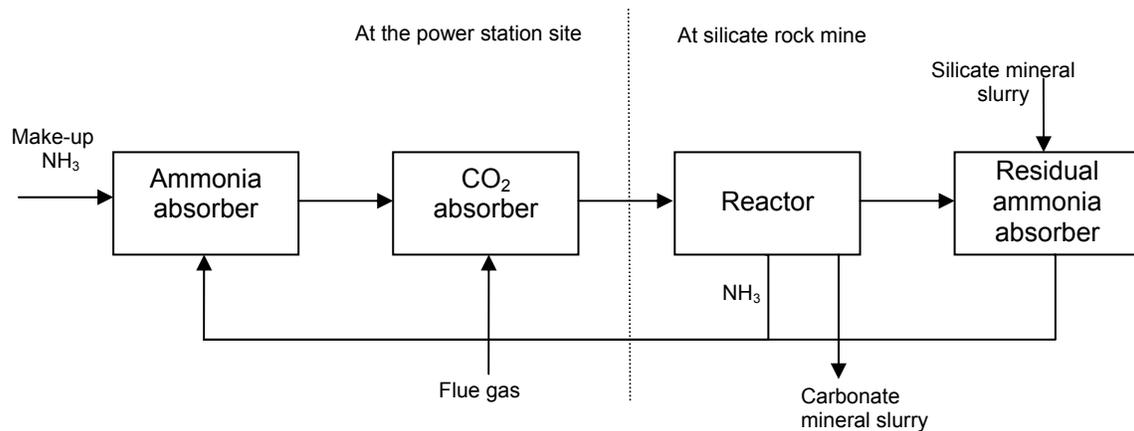


Figure 7 Schematic illustration of CO₂ sequestration via ammonia. (102)

Indirect Multi-step aqueous carbonation of residues with flue gas

In Estonia a process of direct carbonation of oil shale ash suspension in a series (multi) of reactors was proposed by Uibu et al. (65-66), based on their results from batch experiments (67). The experiments with the ash suspension of two different ashes (pulverized firing (PF) or circulating fluidized bed combustion (CFBC)) were conducted in a cascade of reactor columns with pH alkaline (reactors I and II) and almost neutral (reactor III), which was adjusted with the incoming CO₂ flow rate (see fig.8). The binding degree of CO₂ (BD_{CO2}) was calculated comparing the final content of CO₂ with the theoretical maximum with respect to CaO content. It was found that 65-70 % and 55-65 % of the initial CaO was utilized in the first reactor by the CFBC and PF ashes, respectively. Values over 100 % of BD_{CO2} were observed concluding that other components such as MgO or Ca-silicates could also bound CO₂. The used of circulating process water instead of tap water had a negative influence on the results for PF but not for CFBC. They proposed a flowsheet of a pilot-scale ash carbonation plant in the SC Narva Power plants that could capture 1-1.2 million tons of CO₂ from flue gases with this technology.

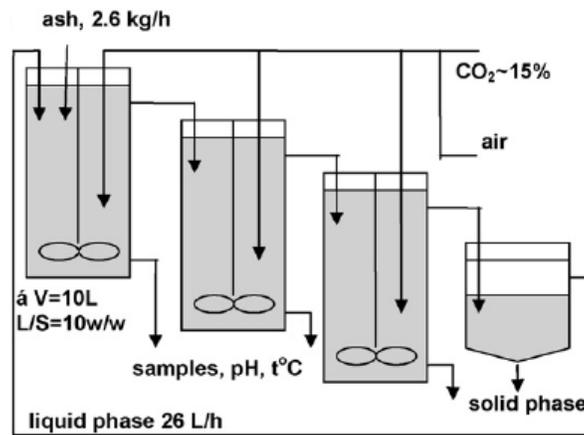


Figure 8 Schematic diagram of a flow reactor system for treating oil shale ash (65-66).

Dissolution, extraction or leaching of the reactive components of minerals

Aiming at the design and optimization of an effective mineral carbonation process, where the dissolution of the silicate mineral is considered to be the rate limiting step, experiments trying to enhance the dissolution of minerals, such as olivine and serpentine, have been studied for a long time. The dissolution of serpentine in weakly acidic solutions was studied by Krevor et al. (36), who used solutions of 1M NaCl, 1m NH₄Cl, 0.5M sodium acetate, 0.1M sodium citrate, 0.1M sodium oxalate, or 0.1M sodium EDTA, under 20 bars of pressure at 120°C in a batch autoclave. In the experiments with citrate, EDTA, or oxalate the dissolution achieved was more than 60% within 2 hours, more than 80 % in 7 hours, and 100% between 10 and 20 hours with no discernible difference in the rate of dissolution between them. The enhancement was most pronounced at neutral to weakly basic conditions, which could be also optimal for the precipitation of carbonate and they could be done together.

Studying the effects of CO₂, temperature, pH, and salinity on the dissolution kinetics of olivine, Prigiobbe et al. (28-30) using a population balance equation model (mention before by Hänchen et al.(103)) coupled with a mass balance equation estimated the dissolution rate from experimental data. The logarithm of the specific dissolution rate values, r , were regressed over pH (see fig. 9). The rate law applied was of the form:

$$r = a_{H^+}^n A e^{\left(\frac{-E_a}{RT}\right)}$$

Where $a_{H^+}^n$ is the activity of protons (mol l⁻¹) A the pre-exponential factor, E_a is the activation energy estimated for the olivine dissolution reaction equal to 52.9 ± 6.9 kJ mol⁻¹, R is the gas constant (kJ mol⁻¹ K⁻¹), and T is the temperature (K). The dissolution rate of olivine, at a given temperature, depended on pH only. CO₂, NaCl and NaNO₃ did not have a significant effect on the

dissolution kinetics. Further dissolution experiments using weak organic acids aiming at a neutral pH to have dissolution and precipitation in the same batch is ongoing at the SPL from ETH.

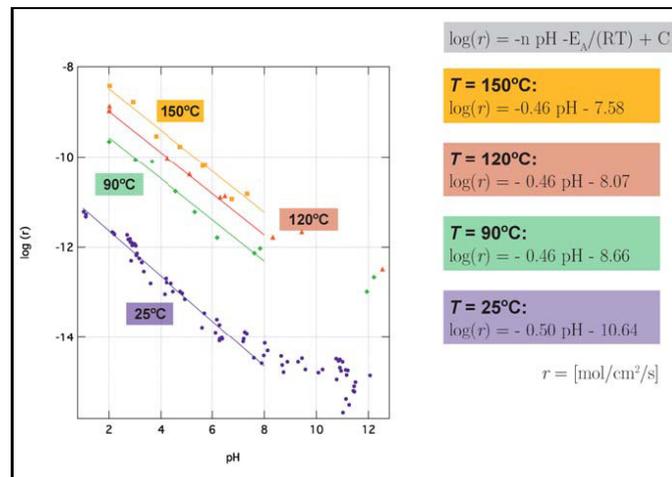


Figure 9 Logarithm of the specific dissolution rate r as a function of pH and at different temperatures (29). In violet literature data by Pokrovsky and Schott (104)

Dissolution, extraction or leaching of the reactive components of residues

Doucet (72) investigated the dissolution behavior of calcium and magnesium phases from four different steel slags generated in South Africa. The experiments were carried out with the slag samples (<150 μm) in aqueous solution of either pure H_2O , 0.5M NaOH, 0.5 M H_2SO_4 or 0.5M HNO_3 with liquid-to-solid ratio of 10 kg/kg at 22 °C for 60 min. The slags were non reactive in NaOH and leached rapidly in HNO_3 . The hydrolysis/dissolution properties, the heat production, the rate and extent of Ca and Mg extraction, the buffering capacity, and the mineralogical composition of the non-dissolved residues were different for each slag. Also working with steel slag Nienczewski et al. (75-76) proposed the extraction of calcium and magnesium with HCl. They found optimal conditions using an acid concentration of 0.8 mol/L, a liquid-to-solid ratio of 10:1 and temperatures lower than 40°C for 15 min. The extraction of magnesium was highly dependent on temperatures, while for calcium was not the case. The particle size was not the main factor determining the yield of extraction of calcium, but it was important for magnesium extraction.

The use of a leaching medium consisting of acetic acid, TBP, and water was introduced by Bao et al. (71). They studied the selective leaching of calcium and magnesium from SS, and proposed how to recover the organic solvent. It was observed that the leaching of calcium, magnesium, iron, aluminum, and silicon was affected by the acid to slag ratio, temperature, and time. High reaction temperatures, long reaction times, and acid to solid ratio below 1 g/g were preferred to

selectively leach calcium and magnesium from steelmaking slag. Research is needed to prove that the recovery of the solvent it is actually possible.

To simplify the first step in modeling a PCC process using oil shale ash Velts et al. (67), developed models to describe Ca^{2+} equilibrium distribution between phases and to determine an effective diffusion coefficient which characterizes the resistance of mass transfer in Ca leaching. It was observed that leachability increased with increasing temperature, but the Ca equilibrium concentration in the solution decreased. The effective diffusion coefficient for pulverized firing ashes was 1×10^{-12} - 1.46×10^{-12} and for fluidized bed combustion ash was 0.73×10^{-14} - 1.25×10^{-14} m^2/s , determined using a single sphere diffusion model.

Precipitation of magnesium carbonates

The precipitation of different forms of magnesium carbonates was studied by Hänchen et al. (84) and Prigiobbe et al. (30). Particularly they studied the effects of temperature and partial pressure of CO_2 . Precipitation was possible for all the temperatures and pressures used by creating supersaturation when mixing a solution of Na_2CO_3 , in equilibrium with CO_2 , with a solution of MgCl_2 . At low temperature and pressure, supersaturation with respect to nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) governed the precipitation kinetics, therefore only nesquehonite precipitated. At high temperature and low pressure, the formation of hydromagnesite ($(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) was observed, but it transformed into magnesite (MgCO_3) within 5 to 15h. At high temperature and high pressure, the direct precipitation of magnesite occurred at low levels of supersaturation, however, at high levels the co-precipitation of magnesite and hydromagnesite was observed, followed by the transformation of the latter into the former after 2 h. According to the results from dissolution and precipitation (30), It was suggested that both processes, could be feasibly carried out in one step at 120 °C, 100 bar, supersaturation of 20, and pH of 5.7

3.4. Pre-treatment and activation options

With the aim of enhancing the carbonation reaction kinetics, which has proven to be slow, a lot of emphasis has been given to accelerate it by changing the process conditions (see chapters above). But sometimes, the process could not be enhance enough only by this option, therefore, research on how to activate the mineral source has received a lot of interest and attention for a long time. These treatments included chemical, mechanical, and heat pre-treatment, generally with the aim of increasing the specific surface area and reducing the crystalline phase of the minerals. The options found in the literature from 2008-2010 are discussed in this chapter.

The use of chemical activation with or without a mechanical treatment since the last review has not been addressed in publications. Probably due to the loss of chemicals, and the high costs that could not be compensated with the faster carbonation reaction (4-5).

In general, mechanical activation is used for olivine, while heat activation is used for serpentine. The mechanical activation of olivine in an attritor mill was studied to determinate the adsorption properties of the mineral (22-23, 31). The particles were rounded, fractured and diminished in size. They could increase the specific surface area from 0.25 to 35 m²/g after 120 minutes of milling, and decrease the crystalline phase from 100 to 12 % with an energy consumption of 2.31 kWh/kg. The capacity of CO₂ adsorption was increased from 0.61 to 79.9 μmol/g of sample for CO₂. The application of this attrition milling for further studies on CO₂ sequestration from an industrial point of view was suggested to be promising because attritors are scalable. In another study, Haug et al. (24) studied the effects of mechanical activation in a planetary mono mill on olivine dissolution rates. The milling was performed either dry or wet for different times. The dissolution of activated olivine was carried out with a solution of 0.01 M HCl at room temperature and 1 atm. It was again observed that the crystallinity decreased and the specific surface area increased with milling time, thus increasing the reaction rates. Wet milled olivine was the least reactive material, whereas dry milling was the most efficient with respect to the dissolution rates giving 3.8 x 10⁻⁶ mol/m²s for dry olivine milled for 30 minute. However from the energy consumption point of view nothing was discussed.

The heat activation process to enhance the carbon sequestration capacity of serpentine was studied in the ARC for a long time. Li et al. (37) also studied by heating the serpentine at 10 °C/min from ambient temperature to different temperatures up to 950 °C for 30 min and after cooled rapidly. They observed that below 600 °C, hydroxyl groups were still present in the heat-activated material, which became less with heating until completely disappeared at 950 °C. The magnesium solubility was found to increase first and then decrease with increasing the heat-treatment temperature, with a maximum solubility at 650 °C, which is in agreement with previous studies (105). But as concluded by (4-5) this treatment has been found to be too energy intensive.

In patents by shell, Boerrigter (40) and Geerlings and Wesker (106) proposed a heat activation method by in-situ combustion of fuels which are typically available where CO₂ is produced. This is done by combusting the fuel inside of a fluidized bed of silicate mineral (150-200 μm), producing the necessary heat (temperature between 620-650 °C) to activate the mineral for 55 to 65 min. This serpentine is later carbonated with a CO₂ containing flue gas at temperatures between 100 to 200 °C and total pressure of 1 to 75 bar. In another patent, Brent (83) also proposed serpentine's thermal activation, by contacting a pre-heated serpentine slurry (either with water,

acids, or salts) with combustion gases from coal, oil or natural gas, and may be heated via radiation, conduction or convection from the fuel combustion chamber. The pre-heating of serpentine is done with the heat liberated by the later carbonation process. These processes would avoid the use of external hot gases and reduce the cost related to the heat pre-treatment of serpentine.

3.4. Other routes for CO₂ carbonation

This chapter will discuss other applications or process that were found in the papers reviewed that are also being considered as CO₂ mineral sequestration, but that are better introduced in a separate section, since they do not really fit in the categories mention above.

3.4.1. In-situ mineral carbonation

In-situ carbonation can be performed with silicate minerals; these are primarily found in basalts and peridotites which together have the potential for CO₂ mineralization storage of billions of tons of CO₂. The dissolution and reaction rates were found to be, for peridotite in a bicarbonate-rich solution greater than those for the basalt glass and these last ones greater than the ones for crystalline basalt (14).

In-situ mineral carbonation could overcome some of the limitations of an ex-situ process, such as mining, transporting, and pre-treatment of the minerals as well as the use and recovery of additives (3), it may be one of the best options for sequestering CO₂. However, this approach has also some challenges that need to be overcome. These include:

- 1) The availability of water, since the CO₂ needs to be dissolved in water and the injection costs would depend on the energy required to pump the CO₂-rich water. To overcome this Oelkers et al. (3) suggested the injection of CO₂ into oceanic basalts.
- 2) The need for impermeable cap rocks, which is needed to keep the CO₂ in contact with the host rock, but these are not common over basalt or ultramafic formations and when they exist, they might be fracture or altered.
- 3) The possible release of trace and toxic metals into solution, which would need to be immobilized with further reactions

3.4.1.1. Basaltic rocks

Basalt forms the top igneous layer in oceanic crust, an occurs in large continental provinces, such as the Siberian Traps and the Columbia River Basalt Group (14). CO₂-fluid-rock reactions during

an aqueous CO₂ injection field test were studied in the Palisades sill. The dominate process was suggested to be the carbonate dissolution, with some cation exchange reaction and/or Ca-Mg silicate mineral dissolution, and even less mixing of the injected solution with formation water. The relative contributions of CO₂-fluid-rock reactions were difficult to determine and more studies are needed (11)

Basalt-CO₂-H₂O interactions for five basalt samples during long term, static, high pressure supercritical CO₂ experiments were studied by Schaef et al. (15). Differences in the carbonation rates of each sample were found and also chemical differences in the precipitates. They concluded this was due to the unique dissolution behavior of each sample, which changed the fluid chemistry. But, all samples had the ability to convert CO₂ into a carbonate mineral.

The CarbFix project is a multinational research field-scale project to assess the feasibility of in-situ mineralization by injecting CO₂ into subsurface basalts close to the Hellisheidi geothermal power plant in SW Iceland, it includes also laboratory based experiments on dissolution and precipitation kinetics, reactive transport modeling studies, and study of natural CO₂-rich waters as a natural analogue (13). A study on the underground stratigraphy of the injection site for the Carbfix project was done in order to select the most suitable horizons to inject CO₂ (10).

Previous to the CO₂ injection, soil CO₂ flux measurements, systematic monitoring of groundwater chemistry, borehole geophysical measurements, and tracer tests were conducted. The waters in the aquifer above 400 m depth were found to be at 8-12 °C, pH of 7.7-8.4, atmospheric CO₂ pressure, and undersaturated with respect to calcite. Deeper waters were at 19-33 °C, pH of 8.4-9.4, below atmospheric CO₂ pressure and saturated with calcite. From the tracer test it was concluded that most of the basaltic bedrock consists of relatively homogeneous porous media, providing high tortuosity and large reactive surface area (12, 89).

The injection experiments should be performed with the CO₂ from the geothermal gas that would be separated (CO₂ 98% and H₂S 2%) and then injected at a depth of 400-800 m, temperature of 30 to 50 °C, CO₂ rate of 0.5 to 0.7 kg/s, partial pressure around 25 bars, and groundwater rate of 20 to 28 l/s. A setup of several observation wells would allow monitoring the injection reservoir and the shallow aquifer along the hydraulic gradient (13). Results have not been given yet on the injection tests.

3.4.1.2. Peridotite

Ultramafic rocks such as peridotite are less abundant than basalt, but occur on almost every continent, with the largest volumes in the Sultanate of Oman, and small ones along the east and west coast of North America (14).

Kelemen et al. (32) proposed a method to enhance the natural CO₂ uptake of the peridotite in the Sultanate of Oman, by heating and raising the partial pressure of CO₂. First, drilling and hydrofracture of peridotite at depth, followed by a pre-heating of the peridotite to 185 °C with a hot fluid, and finally, the injection of pure CO₂ at 300 bars and 25 °C with a flow rate of 0.04 m/s. A constant volume fraction of 0.01% was assumed. They calculated that at these conditions the temperature could be kept constant by the exothermic carbonation reactions. The estimated carbonation rate could be 4 x 10⁹ tons of CO₂/year. The major energy investment would be for drilling, hydraulic fracturing, pumping fluid, preheating fluid and purification of CO₂. This is just a first step on understanding in-situ mineral carbonation; more elaborated models combined with field test are needed to optimize the process.

In another study, a model was applied to understand some of the controls on the rate of serpentinization and carbonation of peridotite during weathering. This model was developed for the physical processes involved in the weathering reactions that cause volume changes which can increase stress in the rock leading to fractures of the rock, which in turn enhance the transport of the mobile phase through the rock and thus accelerates weathering. The main aim of this analysis was to determine the propagating weathering front velocity v and the typical crack length L as a function of the given parameters, and also to find a relationship between them. The model suggested that with heating to 185°C, increasing partial pressure of CO₂ to 300 bar, hydrofracturing the rock at depth, and force flow by a pressure gradient could increase the front velocity going from the natural weathering rate of tenths of mm/year to an industrial rate of hundreds of m/year (33). This model was meant to be a first step towards better understanding of the system and more sophisticated models.

3.4.2. Coastal spreading

The concept of “beach weathering” was introduced before by Schuiling and Krijgsman (107), based on spreading crushed olivine rock along large parts of the Earth’s coastlines above the wave base. Hangx and Spiers (88) analyzed this concept to qualitatively demonstrate whether or not it could contribute to reduce atmospheric CO₂ concentrations. The reaction times they obtained assuming that olivine dissolution follows a shrinking core model with a rate of (1.58 ±

$1.4) \times 10^{-10} \text{ mol/m}^2 \text{ s}$ were long. The results showed it would take 700 and 2130 years to reach a steady state CO_2 uptake with grain size of $300 \mu\text{m}$ at $25 \text{ }^\circ\text{C}$ and $15 \text{ }^\circ\text{C}$, respectively. For a grain size of $10 \mu\text{m}$ would take only 23 years, but a public health risk could be a problem when using such a small grain size. When the cost for mining, crushing and grinding the olivine to $10 \mu\text{m}$ is taking into account, they calculated that the process efficiency would be reduce by 5-11 % for pure olivine, plus additional 0.1-1 % per 100 km reduction for transportation.

It was concluded that an impractical amount of 5 Gt of $6 \mu\text{m}$ grain size olivine coastal spreading per year are needed to achieve the Netherland's global target of a 30 % emissions reduction. Instead it was suggested spreading of 100 to $300 \mu\text{m}$ crushed olivine to reduce 1-3 % the emissions. This method could not replace other CCS technologies, but could contribute with perhaps a 1% reduction of CO_2 , especially in tropical regions where the beach temperature is higher and therefore the reaction rates are faster.

3.4.3. Mine tailings and biomineralization

The weathering of mine tailings occurs relatively rapidly as a result of their high surface area and the release of cations, such as magnesium and calcium. The application of a biogeochemical model, this means biological processes in conjunction with physical and chemical ones, were suggested to sequester CO_2 artificially by creating similar conditions of those of natural environments, with potential application at mine facilities (87).

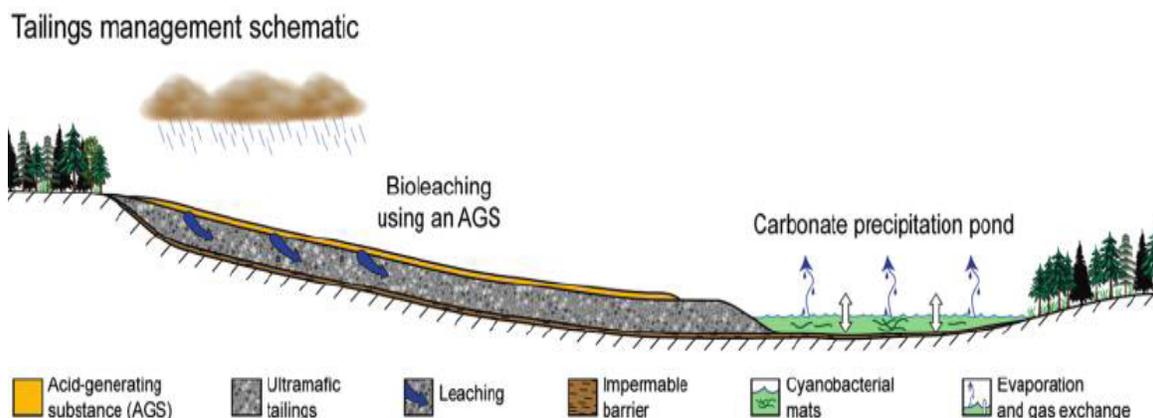


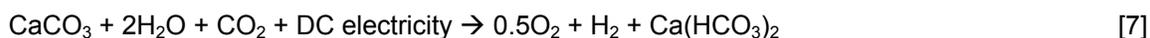
Figure 10 A schematic representation for a geoengineered tailings management for CO_2 sequestration.

It was suggested, from the mineralogy, isotope values, and spatial distribution of the samples, that cyanobacteria and sulphate reducing bacteria promoted the precipitation of dypingite and aragonite from wetland and groundwater of the site, which would later form hydromagnesite via

dehydration (87). The use of *Acidithiobacillus spp.* to accelerate the oxidation of acid-generating substances (AGS) in order to enhance chrysotile tailing's dissolution (by decreasing the pH) for further carbonation was proposed by Power et al. (58). The authors suggested a scheme of a geoengineered tailings facility where these leachate waters could be directed into a closed basin where carbonate precipitation can be promoted to sequester CO₂ either by evaporation or by cyanobacteria (see fig. 10). Cyanobacteria, such as *Synechococcus sp.* can induce the precipitation of carbonate minerals by making their microenvironment more alkaline and it may be able to mediate carbonate precipitation in waters produced from leaching mine tailings like mention before.

3.4.4. Accelerated weathering of limestone

Rau continued his studies on accelerated weathering of limestone described in (5). Now proposing the electrolysis of CaCO₃ to produce Ca(OH)₂ for its further carbonation to form calcium bicarbonate (Ca(HCO₃)₂) (108). This option could capture one mol of CO₂ per mol of CaCO₃ as shown in reaction 7:



The H₂ produced could be capture and used as an energy source or chemical feedstock and the bicarbonate could be store in the ocean or saline reservoirs either on land or underground. The amounts of CO₂ avoided with this H₂ production could be increased when using electricity from low or non-CO₂ producing energy, such as wind, wave, solar, geothermal or nuclear, or by oxidizing the H₂ on site.

This process could be seen as a source of renewable electrolytic H₂ with a CO₂ mitigation option. An environmental benefit would be the neutralization of ocean acidity and to maintain marine calcification via the bicarbonate. The net cost was estimated to be \$ 74/ton of CO₂ mitigated, but due to some uncertainties on the process a precise assessment could not be done.

3.4.5. Carbonation using brines

Significant quantities of brine are brought to the surface as a byproduct of oil and natural gas production. These brines could be used to sequester CO₂ by carbonating the ions within the brine. Previous studies have focused on finding favorable conditions, such as raising the pH, to carry out the carbonation.

Dilmore et al. (109) proposed the addition of caustic byproducts, such as bauxite residue slurry, flue gas desulfurization (FGD) spray drier ash, and class C fly ash, to an oil and gas well produced brine to enlarge its carbonation capacity. Neutralizing the caustic byproduct and the acid brine to a nonhazardous range would be also a benefit from the process. The experiments were performed in a flow-through reactor at room temperature and atmospheric pressure with a gas mixture of CO₂ (29.46 vol %) and N₂ (70.54 vol %). It was found that with increasing concentration of caustic byproduct the CO₂ capture capacity was increased with a small impact of brine addition as compared to deionized water addition. They suggested that calcium and magnesium from the brine helped little to increase the mineralization capacity in the short term. The most effective CO₂ sequestration reagent (the one with the greatest capacity) was found to be FGD spray drier ash, follow by bauxite residue and after class C fly ash.

4. OTHER ASPECTS OF MINERAL CARBONATION

4.1. Passive mineral carbonation

Passive carbonation is a very common process in nature, which is the interaction of CO₂-rich fluids and ultramafic rocks. Many ultramafic-hosted magnesite deposits, in different places around the world have been studied and characterized as natural analogues of in-situ CO₂ mineral carbonation. This is done to evaluate the rate of natural carbonation and the amount of CO₂ fixation from this passive carbonation. The steps of this natural carbonation could be reproduced to propose a process of in-situ mineral carbonation with less amounts of energy necessary to maintain optimal temperature and pressure than for an ex-situ process.

In a recent study by Gislason et al. (86), who showed that chemical and mechanical weathering fluxes depend on climate via changing the temperature, demonstrated a feedback between climate and earth's surface weathering and that these weathering rates have increased with time over the past 40 years due to global warming.

The rate of natural carbonation of mantle peridotite in the Samail ophiolite, Sultanate of Oman was evaluated by Kelemen and Matter (32). They calculated an average ¹⁴C age of 26,000 years for the carbonated veins of the peridotite in Oman and estimated that the carbonation rate was around 4 x 10⁴ tons of atmospheric CO₂ per year that is consumed via mineral carbonation in the ophiolite. In another ophiolite at Malenrata, Tuscany, Italy it was concluded, based on field observations, petrography, and mineral chemistry, that several processes took place in the formation of the major veins. Boschi et al. (41-42) proposed the following sequence:

- 1) The dissolution of the serpentinites by acidic CO₂ fluids at low temperature.
- 2) Silica precipitation.
- 3) Hydraulic fracturing, loss of CO₂, and local magnesite precipitation.
- 4) Migration of fluids into the fractures.
- 5) Boiling of the fluids and massive precipitation of magnesite and dolomite.

Finally they conclude that high fracture permeability was maintained by cyclic hydraulic fracturing during carbonation.

The production of secondary magnesium carbonate minerals from mine tailings rich in magnesium silicates were documented for four mines from Canada and Australia (57). The amount of CO₂ fixation from this passive carbonation was studied using X-ray powder diffraction data and the Rietveld method. It was concluded that the Mg-carbonate minerals that predominated in the tailings were nequehonite, dypingite, and hydromagnesite. They suggested

with the preliminary data that CO₂ uptake rate was about 50,000 t CO₂/year for the Mount Keith tailings and around 500 t CO₂/year for the Diavik ones. With the data from carbon and oxygen isotope composition, it was concluded that bedrock waste carbonate was the predominant source of carbon being fixed. With a simple mixing calculation the authors derived that 10,000 t of CO₂/year was fixed from the atmosphere for all the for mine places.

Another study on milling and mining waste from southern Quebec, Canada, was done by Beaudoin et al.(59), who calculated that there are approximately 796 Mt of milling residues and 125.1 Mt of mining waste with a total of 2.047 Gt of waste that have a potential CO₂ storage of 0.76 Gt of CO₂. They suggested that the exposed surface of the wastes starts to cement within a week of exposure to weather, where the chrysotile fibers surface is cover by hydromagnesite crystals and the replacement of chrysotile an lizardite aggregates occurs by dissolution-precipitation processes. It was calculated that since the beginning of mining more than 125 years ago 3.4 Mt of CO₂ have been sequestered in this wastes in Canada.

Later a multistep carbonation mechanism was elaborated to explain the role of water, temperature and CO₂ partial pressure during chrysotile carbonation (18). First chrysotile undergoes monodehydroxylation, a proton is transfer by the exiting water, MgO is freed, and finally the hydromagnsite is formed in the surface of the chrysotile. The highest CO₂ uptake occurred at 375 °C in moist atmosphere, but a passivation layer of hydromagnesite atop the materials made the process slow with low reaction extent.

4.2. Handling of products and environmental assessment

Environmental issues have not been addressed in the latest literature. As noted by previous literature review (4) this is due to a lack of real cost-effective processes for natural minerals. However, for the mineralization of alkaline solid residues, these processes are used as mention above also as a remediation tool, that could improve their environmental and heavy metal leaching properties in order to be able to dispose of safely as a non hazardous material (49, 52, 55-56, 60, 68, 70, 77).

The handling or fate of the products is another issue that has also not been pointed out. How are the products being transported? Are they solid or a slurry? How and where are they going to be disposed of? Can they be re-utilized? This is some questions that still have no answer and they need to be taken into account when thinking of a cost-effective process.

Some re-use possibilities have been mentioned, but in some cases the product needs to meet certain properties that not only with the carbonation process can be achieved. An example is the production of PCC (54, 65-67, 73, 81) that needs to have a 99 % purity in order to be used. In other cases it was considered that the product (silica and magnesite) could be sold, since they have a price in the market (26-27). Also it was proposed that carbonation can enable the recycling of waste materials in, for example, construction products (52). The use of the carbonated products is an important issue, because it could increase the public acceptance and lower the sequestration costs (4). The use of monodispersed aragonite microspheres, made via mineral carbonation, as a value-added product in ceramics, catalysis, pigments, recording materials, medical diagnostics, and other areas was mentioned by Bao et al. (78).

Niven (79) proposed a process for accelerated concrete curing using CO₂, where not only reduces the CO₂ emissions but also the water consumption, cement requirements, air particulate matter, and NO_x and SO_x emissions. This could be done by replacing the conventional steam or heat accelerated curing methods with the use of flue gases (12-15 CO₂ %) for the carbonation at 25 °C, 1 atm for less than 1 hour.

5. DISCUSSION AND CONCLUSIONS

Some trends that could be observed in ex-situ research for the years 2008 to 2010 are:

The lost of interest in single-step gas processes, the gain of interest in multi step processes and the use of flue gas. The single step aqueous carbonation with minerals is still the predominant route under investigation. We also see the increased interest in in-situ carbonation. Considering only the last three years, we could speak of a trend on increasing the number of publication per year in the field.

The direct gas-solid carbonation route has been abandoned for minerals, and research has focus mainly in other more promising routes. However, the research from industrial residues has shown potential as a CO₂ sequestration option. More studies are still needed with waste streams other than the mentioned above to determine whether this could be true.

During the years 2008-2010, the direct aqueous route was the most studied process, some of them making improvements in the carrier solution, or by increasing temperature and pressure, but no major breakthroughs have been reported. New ways to study fundamental mineral carbonation processes were proposed and there is still room for improvements, such as the recovery of the additives that has not been completely addressed yet.

Several studies have been performed with industrial solid residues in order to understand the influence of different factors (mention above) on CO₂ sequestration. Many different residues can be used for mineral carbonation but the final conversion is affected by their mineral composition. Using residues could be the first step on applying mineral carbonation in the industry, to understand the technology for further development in the use of natural minerals on already running plants.

One difficulty of a direct mineral carbonation process is the trade-off that exists on the optimal process conditions for each step, for example, the CO₂ dissolution is enhanced at low temperatures, whereas the silicate dissolution is better at high ones. Another example is the dissolution of the silicate needs low pH, while the carbonation step is better at high pH. Due to these trade-offs research has focus on indirect processes, where the different steps are carried out at the optimum conditions of the specific step. But, even though it has been pointed as an important critical point to the process, the recycle of water and additive solutions has only been mention by a few authors and even lees have actually tried to solve this problem.

Some heat activation could be done by in-situ combustion of fuels, as proposed in some patents, taking advantage of the already high temperatures that the combustion creates. This would reduce the high cost of the pre-treatment and would make serpentine ready for carbonation without this extra energy penalty to the process.

In-situ mineral carbonation has started to increase the attention during the years 2008-2010, two major geological formation have been investigated, basalts and peridotites, the latter being more reactive but less abundant than the former. Also some studies on natural analogous for in-situ carbonation have helped to understand and accelerate the rates of CO₂ sequestration. Still clear results and better analysis of the projects are needed to evaluate if this carbonation route is actually feasible.

There is no state of the art process route yet. In order to find one promising route, it is needed to start looking on up- and downstream processing as well. For example the use of flue gas instead of pure CO₂, avoiding capture costs, but costs for transporting the material to the CO₂ source has to be considered then. Another example is the transportation or utilization of the final products. No company will make a very big investment in something that does not bring an immediate return. Therefore, studies on energy and water consumption are needed if these aqueous or gas-solid processes want to be applied in a large-scale.

All this, makes an assessment and comparative work of the technology a difficult task. Work is ongoing on building a systematic approach to gain the overview over the mineral carbonation options. This could be done by ranking the different mineralization routes based on some system boundaries for different aggregation levels and a tabular aggregation of quantitative and qualitative characteristics, summable for their ranking. And maybe then we will be able to reasonably make a comparison of mineral carbonation with other CCS option. It is possible that mineral carbonation would be never a cheaper option than geological storage, but there is a key benefit coming from mineral carbonation; the solid storage compare to the gaseous storage.

6. BIBLIOGRAPHY

1. IPCC. (2005) Special report on carbon dioxide capture and storage, Cambridge University Press., Cambridge, UK., and New York, NY, USA.
2. Huijgen, W. J. J., and Comans, R. N. J. (2003) Carbon dioxide sequestration by mineral carbonation: Literature review, Energy Research Centre of the Netherlands, Petten, The Netherlands.
3. Oelkers, E. H., Gislason, S. R., and Matter, J. (2008) Mineral Carbonation of CO₂, *Elements* 4, 333-337.
4. Huijgen, W. J. J., and Comans, R. N. J. (2005) Carbon dioxide sequestration by mineral carbonation: Literature review update 2003-2004, Energy Research Centre of the Netherlands, Petten, The Netherlands
5. Sipilä, J., Teir, S., and Zevenhoven, R. (2008) Carbon dioxide sequestration by mineral carbonation: Literature review update 2005-2007, Abo Akademi University, Turku, Finland.
6. Goff, F., Guthrie, G., Lipin, B., Fite, M., Chipera, S., Counce, D., Kluk, E., and Ziock, H. (2000) Evaluation of ultramafic deposits in the Eastern United States and Puerto Rico as sources of magnesium for carbon dioxide sequestration, In *Other Information: PBD: 1 Apr 2000*, p Medium: P; Size: 46 pages.
7. Kohlman, J. (2001) The Removal of CO₂ from Flue Gases Using Magnesium Silicates in Finland, Helsinki University of Technology Espoo, Finland.
8. Krevor, S. C., Graves, C. R., Van Gosen, B. S., and McCafferty, A. E. (2009) Delineation of Magnesium-rich Ultramafic Rocks Available for Mineral Carbon Sequestration in the United States, *Energy Procedia* 1, 4915-4920.
9. Goldberg, D. S., Kent, D. V., and Olsen, P. E. (2010) Potential on-shore and off-shore reservoirs for CO₂ sequestration in Central Atlantic magmatic province basalts, *Proceedings of the National Academy of Sciences* 107, 1327-1332.
10. Alfredsson, H. A., Hardarson, B. S., Franzson, H., and Gislason, S. R. (2008) CO₂ sequestration in basaltic rock at the Hellisheidi site in SW Iceland: stratigraphy and chemical composition of the rocks at the injection site, *Mineral Mag* 72, 1-5.
11. Assayag, N., Matter, J., Ader, M., Goldberg, D., and Agrinier, P. (2009) Water-rock interactions during a CO₂ injection field-test: Implications on host rock dissolution and alteration effects, *Chemical Geology* 265, 227-235.
12. Gislason, S. R., Wolff-Boenisch, D., Stefansson, A., Oelkers, E. H., Gunnlaugsson, E., Sigurdardottir, H., Sigfusson, B., Broecker, W. S., Matter, J. M., Stute, M., Axelsson, G., and Fridriksson, T. (2010) Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project, *International Journal of Greenhouse Gas Control In Press, Corrected Proof*.
13. Matter, J. M., Broecker, W. S., Stute, M., Gislason, S. R., Oelkers, E. H., Stefansson, A., Wolff-Boenisch, D., Gunnlaugsson, E., Axelsson, G., and Björnsson, G. (2009) Permanent Carbon Dioxide Storage into Basalt: The CarbFix Pilot Project, Iceland, *Energy Procedia* 1, 3641-3646.

14. Matter, J. M., and Kelemen, P. B. (2009) Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation, *Nature Geosci* 2, 837-841.
15. Schaefer, H. T., McGrail, B. P., and Owen, A. T. (2009) Basalt- CO₂-H₂O interactions and variability in carbonate mineralization rates, *Energy Procedia* 1, 4899-4906.
16. Zhao, L., Sang, L., Chen, J., Ji, J., and Teng, H. H. (2010) Aqueous Carbonation of Natural Brucite: Relevance to CO₂ Sequestration, *Environmental Science & Technology* 44, 406-411.
17. Dufaud, F., Martinez, I., and Shilobreeva, S. (2009) Experimental study of Mg-rich silicates carbonation at 400 and 500 °C and 1 kbar, *Chemical Geology* 265, 79-87.
18. Larachi, F., Daldoul, I., and Beaudoin, G. (2010) Fixation of CO₂ by chrysotile in low-pressure dry and moist carbonation: Ex-situ and in-situ characterizations, *Geochimica et Cosmochimica Acta In Press, Corrected Proof*.
19. Andreani, M., Luquot, L., Gouze, P., Godard, M., Hoisé, E., and Gibert, B. (2009) Experimental Study of Carbon Sequestration Reactions Controlled by the Percolation of CO₂-Rich Brine through Peridotites, *Environmental Science & Technology* 43, 1226–1231.
20. Koukouzas, N., Gemeni, V., and Ziocok, H. J. (2009) Sequestration of CO₂ in magnesium silicates, in Western Macedonia, Greece, *International Journal of Mineral Processing* 93, 179-186.
21. Kwak, J. H., Hu, J. Z., Hoyt, D. W., Sears, J. A., Wang, C., Rosso, K. M., and Felmy, A. R. (2010) Metal Carbonation of Forsterite in Supercritical CO₂ and H₂O Using Solid State ²⁹Si, ¹³C NMR Spectroscopy, *The Journal of Physical Chemistry C* 114, 4126-4134.
22. Baláz, P., Turianicová, E., Fabián, M., Kleiv, R. A., Briancin, J., and Obut, A. (2008) Structural changes in olivine (Mg, Fe)₂SiO₄ mechanically activated in high-energy mills, *International Journal of Mineral Processing* 88, 1-6.
23. Fabian, M., Shopska, M., Paneva, D., Kadinov, G., Kostova, N., Turianicová, E., Briancin, J., Mitov, I., Kleiv, R. A., and Baláz, P. (2010) The influence of attrition milling on carbon dioxide sequestration on magnesium-iron silicate, *Minerals Engineering In Press, Corrected Proof*.
24. Haug, T. A., Kleiv, R. A., and Munz, I. A. (2008) Importance of particle size, specific surface area and crystallinity of mechanically activated olivine for HCl dissolution., In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 83-92, Rome, Italy.
25. Jarvis, K., Carpenter, R. W., Windman, T., Youngchul, K., Nunez, R., and Alawneh, F. (2009) Reaction mechanisms for enhancing mineral sequestration of CO₂, *Journal Name: Environmental Science and Technology; Journal Volume: 43; Journal Issue: 16, Medium: X; Size: page(s) 6314-6319*.
26. Machenbach, I., Brandvoll, Ø., Kihle, J., Munz, I. A., and Johansen, H. (2008) Development of an industrial process concept for CO₂ sequestration by mineral carbonation., In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 459-461, Rome, Italy.

27. Munz, I. A., Kihle, J., Brandvoll, Ø., Machenbach, I., Carey, J. W., Haug, T. A., Johansen, H., and Eldrup, N. (2009) A continuous process for manufacture of magnesite and silica from olivine, CO₂ and H₂O, *Energy Procedia* 1, 4891-4898.
28. Prigiobbe, V., Costa, G., Baciocchi, R., Hänchen, M., and Mazzotti, M. (2009) The effect of CO₂ and salinity on olivine dissolution kinetics at 120°C, *Chemical Engineering Science* 64, 3510-3515.
29. Prigiobbe, V., Hänchen, M., Costa, G., Baciocchi, R., and Mazzotti, M. (2009) Analysis of the effect of temperature, pH, CO₂ pressure and salinity on the olivine dissolution kinetics, *Energy Procedia* 1, 4881-4884.
30. Prigiobbe, V., Hänchen, M., Werner, M., Baciocchi, R., and Mazzotti, M. (2009) Mineral carbonation process for CO₂ sequestration, *Energy Procedia* 1, 4885-4890.
31. Turianicová, E., Baláz, P., Fabián, M., Shopska, M., Kostova, N. G., and Kadinov, G. (2008) CO₂ sequestration on olivine activated in an industrially-scalable mill., In *2nd international Conference on Accelerated Carbonation for Environmental and Materials Engineering*, pp 439-442, Rome, Italy.
32. Kelemen, P. B., and Matter, J. r. (2008) In situ carbonation of peridotite for CO₂ storage, *Proceedings of the National Academy of Sciences* 105, 17295-17300.
33. Rudge, J. F., Kelemen, P. B., and Spiegelman, M. (2010) A simple model of reaction-induced cracking applied to serpentinization and carbonation of peridotite, *Earth and Planetary Science Letters* 291, 215-227.
34. Iglesias, R. S., Lima, V., Dullius, J., Ligabue, R., Einloft, S., and Ketzer, J. M. (2008) Experimental and modeling studies on mineral carbonation in the rio bonito aquifer, Parana basin, Brazil., In *2nd international Conference on Accelerated Carbonation for Environmental and Materials Engineering*, pp 433-438, Rome, Italy.
35. Ketzer, J. M., Iglesias, R., Einloft, S., Dullius, J., Ligabue, R., and de Lima, V. (2009) Water-rock-CO₂ interactions in saline aquifers aimed for carbon dioxide storage: Experimental and numerical modeling studies of the Rio Bonito Formation (Permian), southern Brazil, *Applied Geochemistry* 24, 760-767.
36. Krevor, S. C., and Lackner, K. S. (2009) Enhancing process kinetics for mineral carbon sequestration, *Energy Procedia* 1, 4867-4871.
37. Li, W., Li, W., Li, B., and Bai, Z. (2009) Electrolysis and heat pretreatment methods to promote CO₂ sequestration by mineral carbonation, *Chemical Engineering Research and Design* 87, 210-215.
38. Lin, P.-C., Huang, C.-W., Hsiao, C.-T., and Teng, H. (2008) Magnesium Hydroxide Extracted from a Magnesium-Rich Mineral for CO₂ Sequestration in a Gas-Solid System, *Environmental Science & Technology* 42, 2748-2752.
39. Zevenhoven, R., Teir, S., and Eloneva, S. (2008) Heat optimisation of a staged gas-solid mineral carbonation process for long-term CO₂ storage, *Energy* 33, 362-370.
40. Boerrigter, H. (2009) A process for preparing an activated mineral, Shell Internationale Research Maatschappij B.V.

41. Boschi, C., Dini, A., Dallai, L., Gianelli, G., and Ruggieri, G. (2008) Mineralogical sequestration of carbon dioxide: new insights from the malentrata magnesite deposit (Tuscany, Italy). In *2nd international Conference on Accelerated Carbonation for Environmental and Materials Engineering*, pp 55-62, Rome, Italy.
42. Boschi, C., Dini, A., Dallai, L., Ruggieri, G., and Gianelli, G. (2009) Enhanced CO₂-mineral sequestration by cyclic hydraulic fracturing and Si-rich fluid infiltration into serpentinites at Malentrata (Tuscany, Italy), *Chemical Geology* 265, 209-226.
43. Fagerlund, J., Teir, S., Nduagu, E., and Zevenhoven, R. (2009) Carbonation of magnesium silicate mineral using a pressurised gas/solid process, *Energy Procedia* 1, 4907-4914.
44. Teir, S., Eloneva, S., Fogelholm, C.-J., and Zevenhoven, R. (2009) Fixation of carbon dioxide by producing hydromagnesite from serpentinite, *Applied Energy* 86, 214-218.
45. Baldyga, J., Henczka, M., and Sokolnicka, K. (2010) Utilization of carbon dioxide by chemically accelerated mineral carbonation, *Materials Letters* 64, 702-704.
46. Daval, D., Martinez, I., Corvisier, J., Findling, N., Goffé, B., and Guyot, F. (2009) Carbonation of Ca-bearing silicates, the case of wollastonite: Experimental investigations and kinetic modeling, *Chemical Geology* 265, 63-78.
47. Daval, D., Martinez, I., Guigner, J.-M., Hellmann, R., Corvisier, J., Findling, N., Dominici, C., Goffe, B., and Guyot, F. (2009) Mechanism of wollastonite carbonation deduced from micro- to nanometer length scale observations, *American Mineralogist* 94, 1707-1726.
48. Kawatra, S. K., Eisele, T. C., and Simmons, J. J. (2009) Capture and sequestration of carbon dioxide in flue gases, Michigan technological university.
49. Baciocchi, R., Costa, G., Polettini, A., Pomi, R., and Prigiobbe, V. (2009) Comparison of different reaction routes for carbonation of APC residues, *Energy Procedia* 1, 4851-4858.
50. Prigiobbe, V., Polettini, A., and Baciocchi, R. (2009) Gas-solid carbonation kinetics of Air Pollution Control residues for CO₂ storage, *Chemical Engineering Journal* 148, 270-278.
51. Sun, J., Fernandez-Bertos, M., and Simons, S. J. R. (2008) Kinetic study of accelerated carbonation of municipal solid waste incinerator air pollution control residues for sequestration of flue gas CO₂, *Energy & Environmental Science* 1, 370-377.
52. Gunning, P. J., Hills, C. D., and Carey, P. J. (2008) Production of lightweight aggregate from industrial waste and carbon dioxide., In *2nd international Conference on Accelerated Carbonation for Environmental and Materials Engineering*, pp 291-298, Rome, Italy.
53. Gunning, P. J., Hills, C. D., and Carey, P. J. (2010) Accelerated carbonation treatment of industrial wastes, *Waste Management* 30, 1081-1090.
54. Eloneva, S., Teir, S., Salminen, J., Fogelholm, C.-J., and Zevenhoven, R. (2008) Fixation of CO₂ by carbonating calcium derived from blast furnace slag, *Energy* 33, 1461-1467.
55. Baciocchi, R., Costa, G., Marini, C., Polettini, A., Pomi, R., Postorino, P., and Rocca, S. (2008) Accelerated carbonation of RDF incineration bottom ash: CO₂ storage potential and environmental behavior., In *2nd international Conference on Accelerated Carbonation for Environmental and Materials Engineering*, pp 201-210, Rome, Italy.

56. Huntzinger, D. N., Gierke, J. S., Sutter, L. L., Kawatra, S. K., and Eisele, T. C. (2009) Mineral carbonation for carbon sequestration in cement kiln dust from waste piles, *Journal of Hazardous Materials* 168, 31-37.
57. Dipple, G. M., Wilson, S. A., Power, I. M., Thom, J. M., Raudsepp, M., and Southam, G. (2008) Passive mineral carbonation in mine tailings., In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 119-122, Rome, Italy.
58. Power, I. M., Dipple, G. M., and Southam, G. (2010) Bioleaching of Ultramafic Tailings by Acidithiobacillus spp. for CO₂ Sequestration, *Environmental Science & Technology* 44, 456-462.
59. Beaudoin, G., Hebert, R., Constantin, M., Duchesne, J., Cecchi, E., Huot, F., Vigneau, S., and R., F. (2008) Spontaneous carbonation of serpentine in milling and mining waste, southern Quebec and Italy., In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 73-82, Rome, Italy.
60. Montes-Hernandez, G., Pérez-López, R., Renard, F., Nieto, J. M., and Charlet, L. (2009) Mineral sequestration of CO₂ by aqueous carbonation of coal combustion fly-ash, *Journal of Hazardous Materials* 161, 1347-1354.
61. Reddy, K. J., Argyle, M. D., and Viswatej, A. (2008) Capture and mineralization of flue gas carbon dioxide (CO₂). In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 221-228, Rome, Italy.
62. Back, M., Kuehn, M., Stanjek, H., and Peiffer, S. (2008) Reactivity of Alkaline Lignite Fly Ashes Towards CO₂ in Water, *Environmental Science & Technology* 42, 4520-4526.
63. Uliasz-Bochenczyk, A., Mokrzycki, E., Piotrowski, Z., and Pomykala, R. (2009) Estimation of CO₂ sequestration potential via mineral carbonation in fly ash from lignite combustion in Poland, *Energy Procedia* 1, 4873-4879.
64. Sun, J., and Simons, S. J. R. (2008) Accelerated carbonation of the nirex reference vault backfill., In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 305-312, Rome, Italy.
65. Uibu, M., Velts, O., and Kuusik, R. (2010) Developments in CO₂ mineral carbonation of oil shale ash, *Journal of Hazardous Materials* 174, 209-214.
66. Uibu, M., Velts, O., Trikkel, A., Kallas, J., and Kuusik, R. (2008) Developments in CO₂ mineral carbonation by oil shale ash., In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 421-430, Rome, Italy.
67. Velts, O., Uibu, M., Rudjak, I., Kallas, J., and Kuusik, R. (2009) Utilization of oil shale ash to prepare PCC: Leachability dynamics and equilibrium in the ash-water system, *Energy Procedia* 1, 4843-4850.
68. Pérez-López, R., Montes-Hernandez, G., Nieto, J. M., Renard, F., and Charlet, L. (2008) Carbonation of alkaline paper mill waste to reduce CO₂ greenhouse gas emissions into the atmosphere, *Applied Geochemistry* 23, 2292-2300.
69. Purnell, P., Farahi, E., and Short, N. R. (2008) Super-critical carbonation of pressed lime-waste composites., In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 299-304, Rome, Italy.

70. Baciocchi, R., Costa, G., Poletini, A., and Pomi, R. (2009) Influence of particle size on the carbonation of stainless steel slag for CO₂ storage, *Energy Procedia* 1, 4859-4866.
71. Bao, W., Li, H., and Zhang, Y. (2010) Selective Leaching of Steelmaking Slag for Indirect CO₂ Mineral Sequestration, *Industrial & Engineering Chemistry Research* 49, 2055-2063.
72. Doucet, F. J. (2009) Effective CO₂-specific sequestration capacity of steel slags and variability in their leaching behaviour in view of industrial mineral carbonation, *Minerals Engineering* 23, 262-269.
73. Eloneva, S., Teir, S., Salminen, J., Revitzer, H., Kontu, K., Forsman, A. M., Zevenhoven, R., and Fogelhom, C.-J. (2008) Pure calcium carbonate product from the carbonation of a steel making slag., In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 239-248, Rome, Italy.
74. Kodama, S., Nishimoto, T., Yamamoto, N., Yogo, K., and Yamada, K. (2008) Development of a new pH-swing CO₂ mineralization process with a recyclable reaction solution, *Energy* 33, 776-784.
75. Nienczewski, J. R., Alves, S. M. S., Costa, G. S., Amaral, L. C., Dullius, J. E. L., Ligabue, R. A., Ketzer, J. M., and Einloft, S. (2008) Improving the extraction of calcium and magnesium oxides of the steel slag aiming carbonates for mitigation of climate changes., In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 249-256, Rome, Italy.
76. Nienczewski, J. R., Alves, S. M. S., Costa, G. S., Amaral, L. C., Dullius, J. E. L., Ligabue, R. A., Ketzer, J. M., and Einloft, S. (2008) Analysis of the influence of the size of carbon steel slag particle on the carbonation reaction., In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 447-450, Rome, Italy.
77. van der Laan, S. R., van Hoek, C. J. G., van Zomeren, A., Comans, R. N. J., Kobesen, J. B. A., and Broersen, P. G. J. (2008) Chemical reduction of CO₂ to carbon at ambient conditions during artificial weathering of converter steel slag while improving environmental properties., In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 229-238, Rome, Italy.
78. Bao, W., Li, H., and Zhang, Y. (2009) Preparation of monodispersed aragonite microspheres via a carbonation crystallization pathway, *Cryst. Res. Technol.* 44, 395-401.
79. Niven, R. (2008) Industrial pilot study examining the application of precast concrete carbonation curing., In *2nd international Conference on Accelerated Carbonation for Environmental an Materials Engineering*, pp 411-420, Rome, Italy.
80. Santos, A., Ajbary, M., Morales-Flórez, V., Kherbeche, A., Piñero, M., and Esquivias, L. (2009) Larnite powders and larnite/silica aerogel composites as effective agents for CO₂ sequestration by carbonation, *Journal of Hazardous Materials* 168, 1397-1403.
81. López-Periago, A. M., Pacciani, R., García-González, C., Vega, L. F., and Domingo, C. (2009) A breakthrough technique for the preparation of high-yield precipitated calcium carbonate, *The Journal of Supercritical Fluids In Press, Corrected Proof*.
82. Regnault, O., Lagneau, V., and Schneider, H. (2009) Experimental measurement of portlandite carbonation kinetics with supercritical CO₂, *Chemical Geology* 265, 113-121.

83. Brent, G. F. (2008) Integrated chemical process, Orica Explosives Technology Pty Ltd.
84. Hänchen, M., Prigiobbe, V., Baciocchi, R., and Mazzotti, M. (2008) Precipitation in the Mg-carbonate system--effects of temperature and CO₂ pressure, *Chemical Engineering Science* 63, 1012-1028.
85. Saldi, G. D., Jordan, G., Schott, J., and Oelkers, E. H. (2009) Magnesite growth rates as a function of temperature and saturation state, *Geochimica et Cosmochimica Acta* 73, 5646-5657.
86. Gislason, S. R., Oelkers, E. H., Eiriksdottir, E. S., Kardjilov, M. I., Gisladottir, G., Sigfusson, B., Snorrason, A., Elefsen, S., Hardardottir, J., Torssander, P., and Oskarsson, N. (2009) Direct evidence of the feedback between climate and weathering, *Earth and Planetary Science Letters* 277, 213-222.
87. Power, I. M., Wilson, S. A., Thom, J. M., Dipple, G. M., Gabites, J. E., and Southam, G. (2009) The hydromagnesite playas of Atlin, British Columbia, Canada: A biogeochemical model for CO₂ sequestration, *Chemical Geology* 260, 286-300.
88. Hangx, S. J. T., and Spiers, C. J. (2009) Coastal spreading of olivine to control atmospheric CO₂ concentrations: A critical analysis of viability, *International Journal of Greenhouse Gas Control* 3, 757-767.
89. Flaathen, T. K., Gislason, S. R., Oelkers, E. H., and Sveinbjörnsdóttir, Á. E. (2009) Chemical evolution of the Mt. Hekla, Iceland, groundwaters: A natural analogue for CO₂ sequestration in basaltic rocks, *Applied Geochemistry* 24, 463-474.
90. Hufton, J. R., Quinn, R., White, V., and Allam, R. J. (2009) Carbon dioxide separation via partial pressure swing cyclic chemical reaction, Air Products and Chemicals, Inc.
91. Montes Hernandez, G., Perez Lopez, R., Renard, F., Charlet, L., and Nieto, J. M. (2009) Process for the sequestration of CO₂ by reaction with alkaline solid wastes, Universite J. Fourier; Centre National de la Recherche Scientifique; Universidad de Huelva.
92. Seifritz, W. (1990) CO₂ disposal by means of silicates, *Nature* 345, 486.
93. Akiyama, T., and Nomura, M. (1993) Treatment of hydrated calcium silicate and treating apparatus, (ind, A. C., Ed.), Japan.
94. Lackner, K. S., Wendt, C. H., Butt, D. P., Joyce, E. L., and Sharp, D. H. (1995) Carbon dioxide disposal in carbonate minerals, *Energy* 20, 1153-1170.
95. IEA GHG. (2000) CO₂ storage as carbonate minerals, prepared by CSMA consultants Ltd, PH3/17, Cheltenham, United Kingdom.
96. Devoldere, K., Weyten, H., Vrancken, K., and Ginneken van, L. (2000) Accelerated weathering of MSWI bottom ash by means of liquid and supercritical CO₂, In *Proceedings of the 7th meeting on supercritical fluids*.
97. Kakizawa, M., Yamasaki, A., and Yanagisawa, Y. (2001) A new CO₂ disposal process via artificial weathering of calcium silicate accelerated by acetic acid, *Energy* 26, 341-354.
98. Geerlings, J. J. C., Mesters, C. M. A., and Oosterbeek, H. (2002) Process for mineral carbonation with carbon dioxide Shell Internationale Research Maatschappij B.V.

99. Zevenhoven, R., and Teir, S. (2004) Long term storage of CO₂ as magnesium carbonate in Finland,, In *Proceedings of the Third Annual conference on Carbon Capture and Sequestration*, Alexandria (VA), USA.
100. O'Connor, W. K., Dahlin, D. C., Rush, G. E., Gerdemann, S. J., Penner, L. R., and Nilsen, D. N. (2005) Final Report: Aqueous Mineral Carbonation, National Energy Technology Laboratory (formerly Albany Research Center).
101. Park, A.-H. A., and Fan, L.-S. CO₂ mineral sequestration: physically activated dissolution of serpentine and pH swing process, *Chemical Engineering Science* 59, 5241-5247.
102. Hunwick, R. J. (2008) System, apparatus and method for carbon dioxide sequestration, Hunwick, R.J.
103. Hänchen, M., Krevor, S., Mazzotti, M., and Lackner, K. S. (2007) Validation of a population balance model for olivine dissolution, *Chemical Engineering Science* 62, 6412-6422.
104. Pokrovsky, O. S., and Schott, J. (2000) Kinetics and mechanism of forsterite dissolution at 25°C and pH from 1 to 12, *Geochimica et Cosmochimica Acta* 64, 3313-3325.
105. O'Connor, W. K., Dahlin, D. C., Rush, G. E., Gerdemann, S. J., Penner, L. R., and Nilsen, D. N. (2004) Aqueous mineral carbonation: mineral availability, pretreatment, reaction parametrics and process studies, Albany Research Centre, Albany, OR, USA.
106. Geerlings, J. J. C., and Wesker, E. (2008) A process for sequestration of carbon dioxide by mineral carbonation, Shell Internationale Research Maatschappij B.V.
107. Schuiling, R. D., and Krijgsman, P. (2006) Enhanced Weathering: An Effective and Cheap Tool to Sequester Co₂, *Climatic Change* 74, 349-354.
108. Rau, G. H. (2009) Electrochemical CO₂ capture and storage with hydrogen generation, *Energy Procedia* 1, 823-828.
109. Dillmore, R. M., Howard, B. H., Soong, Y., Griffith, C., Hedges, S. W., DeGalbo, A. D., Morreale, B., Baltrus, J. P., Allen, D. E., and Fu, J. K. (2009) Sequestration of CO₂ in Mixtures of Caustic Byproduct and Saline Waste Water, *Journal Name: Environmental Engineering Science; Journal Volume: 26; Journal Issue: 8, Medium: X; Size: page(s) 1325-1333.*

7. APENDIX

7.1. List of patents on mineral carbonation

Here it is presented a complete list of all the patents found on mineral carbonation. The patents are listed chronologically from 2009 to 1993.

1) CAPTURE AND SEQUESTRATION OF CARBON DIOXIDE IN FLUE GASES

Publication number(s): WO2009139813 (A3); US2009202410 (A1).

Inventor(s): KAWATRA SURENDRA KOMAR; EISELE TIMOTHY C.; SIMMONS JOHN J.

Assignee(s): MICHIGAN TECHNOLOGICAL UNIVERSITY [US/US].

2) A PROCESS FOR PREPARING AN ACTIVATED MINERAL

Publication number(s): WO2009092718 (A1); WO2008142025 (A2) (A3); EP2158159 (A2); CA2687620 (A1); AU2008252987 (A1); CN101679060 (A).

Inventor(s): BOERRIGTER HAROLD.

Assignee(s): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL].

3) CARBON DIOXIDE SEPARATION VIA PARTIAL PRESSURE SWING CYCLIC CHEMICAL REACTION

Publication number(s): US2009162268 (A1); EP2072111 (A2); US2010040520 (A1); JP2009149507 (A); CN101468790 (A); CA2646385 (A1).

Inventor(s): HUFTON JEFFREY RAYMOND; QUINN ROBERT; WHITE VINCENT; ALLAM RODNEY JOHN.

Assignee(s): AIR PRODUCTS AND CHEMICALS INC [US] .

4) PROCESS FOR THE SEQUESTRATION OF CO₂ BY REACTION WITH ALKALINE SOLID WASTES

Publication number(s): WO2009077358 (A1); EP2070578 (A1).

Inventor(s): MONTES HERNANDEZ GERMAN; PEREZ LOPEZ RAFAEL; RENARD FRANCOIS; CHARLET LAURENT; NIETO JOSE MIGUEL.

Assignee(s): UNIV. JOSEPH FOURIER [FR]; CENTRE NAT. RECH. SCIENT. [FR]; UNIV. HUELVA [ES].

5) INTEGRATED CHEMICAL PROCESS

Publication number(s): WO2008061305 (A1); US2009305378 (A1); MX2009005386 (A); KR20090102760 (A); EP2097164 (A1); CA2670299 (A1); AU2007324344 (A1).

Inventor(s): BRENT GEOFFREY FREDERICK.

Assignee(s): ORICA EXPLOSIVES TECHNOLOGIE PTY LTD [-/AU].

6) SYSTEM, APPARATUS AND METHOD FOR CARBON DIOXIDE SEQUESTRATION

Publication number(s): WO2008101293 (A1); US2010021362 (A1); KR20090125109 (A); EP2134449 (A1); CA2678800 (A1); AU2009250983 (A1).

Inventor(s): HUNWICK RICHARD J.

Assignee(s): HUNWICK RICHARD J.

7) A PROCESS FOR SEQUESTREATION OF CARBON DIOXIDE BY MINERAL CARBONATION

Publication number(s): WO2008142017 (A2) (A3); EP2158158 (A2); CA2687618 (A1); AU2008253068 (A1); US20070261947 (A1); CN101679059 (A).

Inventor(s): GEERLINGS JACOBUS JOHANNES CORNELIS; WESKER EVERT; BOERRIGTER HAROLD.

Assignee(s): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

8) PROCESS FOR SEQUESTRATION OF CARBON DIOXIDE

Publication number(s): WO2007071633 (A1); US2009010827 (A1); EP1966092 (A1); CN101331084 (A).

Inventor(s): GEERLINGS JACOBUS JOHANNES CORNELIS; VAN MOSSEL GERARDUS ANTONIUS F.; IN T VEEN BERNARDUS CORNELIS M.

Assignee(s): SHELL INT RESEARCH [NL].

9) APPARATUS AND METHOD FOR SEQUESTERING FLUE GAS CO₂

Publication number(s): WO2007081561 (A2) (A3); US2008267838 (A1).

Inventor(s): REDDY KATTA J.; ARGYLE MORRIS D.

Assignee(s): UNIVERSITY OF WYOMING [US/US].

10) METHOD FOR INDUSTRIAL MANUFACTURE OF PURE MgCO₃ FROM AN OLIVINE CONTAINING SPECIES OF ROCK

Publication number(s): WO2007069902 (A1); US2008299024 (A1); RU2008119911 (A); NO20082270 (A); EP1951622 (A1); CN101356118 (A).

Inventor(s): GORSET ODDVAR; JOHANSEN HARALD; KIHLE JAN; MUNZ INGRID ANNE; RAAHEIM ARNE.

Assignee(s): INSTITUTT FOR ENERGITEKNIKK [NO/NO].

11) PROCESS FOR PRODUCING CaCO₃ OR MgCO₃

Publication number(s): WO2006008242 (A1); CN1989073 (A); US2007202032 (A1).

Inventor(s): GEERLINGS JACOBUS J.C.; VAN MOSSEL GERARDUS ANTONIUS F.; IN T VEEN BERNARDUS C.M.

Assignee(s): SHELL OIL COMPANY.

12) HEAT TREATMENT PROCESS OF SERPENTINE AS RAW MATERIAL FOR MINERAL CARBONATION BY REMOVING ADSORBED WATER MOLECULES, HYDROXYL GROUP AND ORGANIC FRACTION IN UNTREATED SERPENTINE

Publication number(s): KR2006110119-A.

Inventor(s): LEE JAE KEUN; KIM KI HYUNG; KIM DONG WHA; CHOI WEON KYUNG; CHO TAE HWAN; MOON SEUNG HYUN; HAN SANG SIK; KONG KI HOON; HWANG OK JUNG; KIM KYONG HOON; YOUN CHANG HWA.

Assignee(s): KOREA ELECTRIC POWER CORPORATION.

13) METHOD FOR FIXING CARBON DIOXIDE

Publication number(s): JP 2005097072 (A).

Inventor(s): YOGO KATSUNORI; TOU EIKOU; YASHIMA TATEAKI.

Assignee(s): RESEARCH INSTITUTE OF INNOVATIVE TECHNOLOGY FOR THE EARTH.

14) METHOD FOR CARBON SEQUESTRATION IN THE FORM OF A MINERAL IN WHICH CARBON HAS A +3 DEGREE OF OXYDATION

Publication number(s): WO2005070521 (A1); FR2863911 (A1); US2008296146 (A1); RU2334547 (C2); PT1699545 (E); JP2007515283 (T).

Inventor(s): TOULHOAT HERVE; ROPITAL FRANCOIS; DUVAL SEBASTIEN.

Assignee(s): INST FRANCAIS DU PETROLE [FR].

15) CARBON DIOXIDE SEQUESTRATION USING ALKALINE EARTH METAL-BEARING MINERALS

Publication number(s): US2005180910 (A1).

Inventor(s): PARK AH-HYUNG.; FAN LIANG-SHIH.

Assignee(s): PARK AH-HYUNG; FAN LIANG-SHIH.

16) CARBON DIOXIDE CAPTURE AND MITIGATION OF CARBON DIOXIDE EMISSIONS

Publication number(s): WO2005108297 (A2) (A3); US2008031801 (A1); US2008138265 (AA); WO06009600 (A2) (A3).

Inventor(s): LACKNER KLAUS; GRIMES PATRICK; KREVOR SAMUEL; ZEMAN FRANK.

Assignee(s): COLUMBIA UNIVERSITY; THE TRUSTEES OF COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK.

17) PROCESS FOR REMOVAL AND CAPTURE OF CARBON DIOXIDE FROM FLUE GASES

Publication number(s): WO2004037391 (A1); US2004126293 (A1); JP2006503692 (T); DE60310594 (T2); CA2503096 (A1).

Inventor(s): GEERLINGS JACOBUS JOHANNES CORNELIS; WESKER EVERT.

Assignee(s): SHELL INTERNATIONALE REASEARCH MAATSCHAPPIJ B.V.

18) CARBONATION OF METAL SILICATES FOR LONG-TERM CO₂ SEQUESTRATION

Publication number(s): WO2004094043 (A2) (A3); US2004213705 (A1); US2008112868 (A1); EP1617933 (A2); CA2523135 (A1).

Inventor(s): BLENCOE JAMES G.; PALMER DONALD A.; ANOVITZ LAWRENCE M.; BEARD JAMES S.

Assignee(s): UT BATTELLE LLC [US].

19) PROCESS FOR SEQUESTERING CARBON DIOXIDE AND SULFUR DIOXIDE

Publication number(s): WO2004098740 (A2) (A3); US2005002847 (A1); US7604787 (B2).

Inventor(s): MAROTO-VALER M. MERCEDES; ZHANG YINZHI; KUCHTA MATTHEW E.; ANDRESEN JOHN M.; FAUTH DAN J.

Assignee(s): PENN. STATE RES. FOUND [US].

20) SEQUESTRATION OF CARBON DIOXIDE

Publication number(s): US2004219090 (A1); US7132090 (B2).

Inventor(s): DZIEDZIC DANIEL; GROSS KENNETH B.; GORSKI ROBERT A.; JOHNSON JOHN T.

Assignee(s): GENERAL MOTORS CORPORATION.

21) PROCESS FOR MINERAL CARBONATION WITH CARBON DIOXIDE

Publication number(s): WO02085788 (A1); US2004131531 (A1); NO20034678 (A); JP2004525062 (T); DE60209492 (T2); CA2444576 (A1).

Inventor(s): GEERLINGS JACOBUS JOHANNES CORNELIS; MESTERS CAROLUS MATTHIAS ANNA; OOSTERBEEK HEIKO.

Assignee(s): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

22) EXTRACTION OF SILICA AND MAGNESIUM COMPOUNDS FROM OLIVINE

Publication number(s): WO0248036 (A1); EP1373139 (A1); AU2554202 (A).

Inventor(s): HANSEN TORD; ZANDER BO.

Assignee(s): SILICA TECH ANS [NO].

23) METHOD OF MANUFACTURING CARBONATION CURED COMPACT

Publication number(s): JP2002201085 (A).

Inventor(s): INAGAKI KENJI; ISU NORIBUMI; TERAMURA TOSHIFUMI.

Assignee(s): CLION CO LTD; KENZAI GIJUTSU KENKYUSHO KK.

24) METHOD FOR EXTRACTING AND SEQUESTERING CARBON DIOXIDE

Publication number(s): US2001022952 (A1); US6890497 (B2); WO0010691 (A1); US7655193 (B1); AU5568099 (A).

Inventor(s): RAU GREGORY H.; CALDEIRA KENNETH G.

Assignee(s): RAU GREGORY H.; CALDEIRA KENNETH G.; THE UNITED STATES OF AMERICA AS REPRESENTED BY THE UNITED STATES DEPARTMENT OF ENERGY.

25) CARBON DIOXIDE SEQUESTRATION BY COBALT (II) COMPLEXES

Publication number(s): WO0198313 (A1); GB2365428 (A); AU7424901 (A).

Inventor(s): FREEMAN JONATHAN DUNCAN; WALTON PAUL HOWARD; PERUTZ ROBIN NOEL.

Assignee(s): LATTICE INTELLECTUAL PROPERTY.

26) TREATMENT OF HYDRATED CALCIUM SILICATE AND TREATING APPARATUS

Publication number(s): JP6279017 (A).

Inventor(s): AKIYAMA TADASHI; NOMURA MASARU.

Assignee(s): ASAHI CHEMICAL IND.