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Carbon dioxide sequestration by mineral carbonation

Literature Review

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Preface

This literature review is part of a PhD-programme 'CO_2 sequestration in alkaline solid wastes'. This programme began in January 2002 and will finish in December 2005. The research is performed within the Clean Fossil Fuels unit of the Energy research Centre of the Netherlands (ECN). The present report discusses literature that was published before January 2003.

Abstract

In order to prevent CO_2 concentrations in the atmosphere rising to unacceptable levels, carbon dioxide can be separated from the flue gas of, for example, a power plant and subsequently sequestrated. Various technologies for carbon dioxide sequestration have been proposed, such as storage in depleted gas fields, oceans and aquifers. An alternative sequestration route is the so-called "mineral CO_2 sequestration" route in which CO_2 is chemically stored in solid carbonates by the carbonation of minerals. As mineral feedstock, rocks that are rich in alkaline earth silicates can be used. Examples are olivine ($MgSiO_4$) and wollastonite ($CaSiO_3$). Mineral CO_2 sequestration has some fundamental advantages compared to other sequestration routes. The formed products are thermodynamically stable and therefore the sequestration of CO_2 is permanent and safe. Furthermore, the sequestration capacity is large because large suitable feedstock deposits are available worldwide. Finally, the carbonation reactions are exothermic and occur spontaneously in nature. The reaction rates of the process at atmospheric conditions, however, are much too slow for an industrial process. Therefore, research focuses on increasing the reaction rate in order to obtain an industrial viable process.

Optimisation of the process conditions is constrained by the thermodynamics of the process. Increasing the temperature and CO_2 pressure accelerates the reaction rate, but gaseous CO_2 is favoured over mineral carbonates at high temperatures. Using water or another solvent to extract the reactive component from the matrix accelerates the process. Pre-treatment of the mineral by size reduction and thermal or mechanical activation and optimisation of the solution chemistry result in major improvements of the reaction rate. During recent years, laboratory-scale experiments have shown major improvements of the conversion rates by developing various process routes and optimising process conditions. The most promising route available seems to be the direct aqueous route, for which reasonable reaction rates at feasible process conditions have been shown.

Important aspects of mineral CO_2 sequestration are the transport of the materials involved and the fate of the products. Transport costs can be minimised by transporting the carbon dioxide towards a mineral sequestration plant situated near the feedstock mine. The carbonated products can be used for mine reclamation and construction applications. Unfortunately, only few rough cost estimates have been published and detailed cost analyses of the most promising process routes are absent in the literature. Therefore, at present, there is insufficient knowledge to conclude whether a cost-effective and energetically acceptable process will be feasible. Mineral carbon sequestration is a longer-term option compared to other sequestration routes, but its fundamental advantages justify further research. Major issues that need to be resolved in order to enable large-scale implementation are the energy consumption of the process, the reaction rates and the environmental impact of mineral CO_2 sequestration. Finally, the use of alkaline solid wastes as an alternative feedstock for calcium or magnesium is acknowledged and warrants further research.

CONTENTS

1. INTRODUCTION

Since the beginning of the Industrial Age, the concentration of CO_2 in the atmosphere has increased by about 30% from 280 to 370ppm (Herzog *et al.*, 2000). Fifty percent of this increase has occurred during the last 40 years and is mainly due to human activities (Yegulalp *et al.*, 2001). The International Panel on Climate Control (IPCC) has set an upper limit target of 550ppm of CO_2 in order to prevent major climate changes (IPCC, 2001). The impacts of the increased CO_2 concentration are, among others, the greenhouse effect, the acidification of the surface of the ocean and the fertilization of ecosystems. The total amount of CO_2 annually released due to human activities worldwide is 7.0Gton of which 5.4Gton is caused by the use of fossil fuels (Liu *et al.*, 2000b). In the Netherlands the annual release of CO_2 has increased by about 8 percent since 1990 to 180Mton CO_2 (2001) and it has been predicted that it will reach 191±12Mton in 2010 (Wijngaart van den *et al.*, 2002).

Currently, about 60% of the emitted carbon is held in the atmosphere. The other 40% is converted into so-called 'carbon sinks' such as oceans, forests and rocks. Over geological times naturally occurring rock weathering is an important carbon sink. Carbonate rocks form the world's biggest carbon reservoir (see Table 1) (Liu *et al.*, 2000b).

Table 1 Distribution of carbon on earth (Dunsmore, 1992)

Source	Amount [10^{15} kg]	Relative amount [%]
Calcium carbonate	35,000	46.64
Ca-Mg-carbonate	25,000	33.31
Total carbonates	60,000	79.99
Sedimentary carbon (e.g. graphite)	15,000	19.99
Fossil fuels	4	0.0053
Other geological carbon	15,004	19.99
Total carbon in lithosphere ('dead' carbon[1])	75,004	99.94
Oceanic HCO_3^- and CO_3^{2-}	42	0.056
Dead surficial carbon (e.g. humus)	3	0.0040
Atmospheric CO_2	0.72	0.00095
All life	0.56	0.00074
Total non-geological carbon ('live' carbon)	46.28	0.06

Fossil fuels are still the main energy source and will probably continue to be so for the coming decades. Renewable fuels are still too expensive and the available fossil reserves are large enough to provide energy to the world during that time period. In order to reduce the amount of CO_2 emitted into the atmosphere, three main strategies are available: improvement of energy efficiency, use of renewable energy sources and carbon sequestration. The aim of carbon sequestration is to store the carbon dioxide released by the use of fossil fuels in order to prevent its emission to the atmosphere. Different approaches have been investigated (see Figure 1). The main ones are storage in the oceans, in depleted gas- and oil fields and in reforestation[2]. The CO_2 sequestration technologies can be divided in categories as shown in Table 2.

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[1] 'Live' versus 'dead' carbon: carbon being or not-being cycled within the atmosphere-hydrosphere-biosphere cycle.

[2] The various CO_2 sequestration technologies will not be discussed in detail in this report. An economic comparison of mineral CO_2 sequestration with the other CO_2 sequestration technologies is given in Section 8.2.

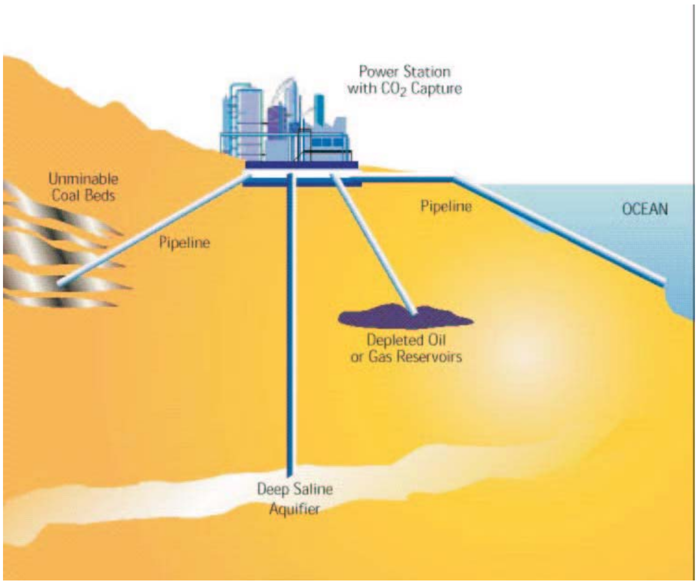

Figure 1 CO_2 sequestration options (IEA, 2001).

Table 2 Subdivision of CO_2 sequestration technologies.

	Utilisation	Storage
Chemical	Production of chemicals	*Mineral CO_2 sequestration*
Biological		Terrestrial biosphere (e.g. forestation)
Physical	Enhanced oil/gas recovery	Ocean storage
		Oil and gas reservoirs
		Deep saline formations

Of the mentioned sequestration technologies ocean sequestration has the greatest potential (see Table 3) (IEA, 2001).

Table 3 Estimated potential of CO_2 storage and utilization options (Kohlmann, 2001)[3]

Option	Estimated global capacity [GtC]
Mineral CO_2 sequestration	*Very large (more than the total release of oxidation of global fossil fuel reservoirs)*
Ocean disposal	>1,000[4]
Saline aquifers	>100
Depleted gas reservoirs	>140
Depleted oil reservoirs	>40
Improved forestry and reforestation	50-100
Enhanced oil recovery	65
Bio fixation	1.35
Chemicals	0.09

The main drawback of these techniques, besides the limited applicability of some, is the temporary character of the storage. CO_2 stored in the ocean, for example, will return to the atmosphere in about hundreds to thousands of years. Although it has been pointed out that the storage needs not necessarily be permanent (Seifritz, 1995), the question remains as to whether or not this not simply makes this problem the concern of future generations. Another drawback of ocean storage is the (local) change of pH of the water and the corresponding effects on the

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[3] For comparison: coal reserves worldwide: >10,000Gt, proven economic reserves: 1,000Gt. Lackner estimated the total carbon output during the coming century at 2,300 GtC (Lackner, 2002).

[4] Without adding alkalinity the maximum capacity in oceans is limited to about 300-600 GtC (Lackner, 2002).

environment. Storage of large amounts of non-converted concentrated CO_2 as in oil and gas reservoirs needs continuous monitoring for an infinite time. Apart from that, accidental releases of CO_2 can cause major health risks, as the Lake Nyos accident in 1987 proved (Kling *et al.*, 1987)[5]. An alternative technology to store carbon dioxide permanently and safely is carbon dioxide sequestration by mineral carbonation (or briefly: mineral CO_2 sequestration). This sequestration route is further discussed in Chapter 2.

All CO_2 sequestration technologies consist of two steps. First, the carbon dioxide is captured and separated from the flue gas or the air. Second, the CO_2 is stored. Separation of CO_2 from the captured flue gas is needed to avoid storing large amount of N_2. The separation is usually established using absorption with monoethanolamine (MEA) followed by stripping with steam. The absorption technology is energy-intensive and usually accounts for two-thirds to three-quarters of the total sequestration costs. Substantial research efforts are directed at cost-reduction of the separation step. Alternative technologies are, among others, adsorption, membranes, cryogenic separation and hydrate formation systems (Smith, 1999). Besides these, processes based on the use of the carbonation principle to capture CO_2 exist. These are discussed briefly in Annex A. In the main report only the storage of CO_2 is reviewed.

The structure of this report is as follows. First, the principle of mineral carbon dioxide sequestration is discussed in Chapter 2 and a selection of appropriate minerals is made in Chapter 3. Then, the thermodynamics of the processes are described in Chapter 4 and the various process routes in Chapter 5. The kinetics of carbonation processes are reviewed in Chapter 6, while Chapter 7 outlines the experimental results described in the literature to date. Chapter 8 discusses issues relevant to an industrial process layout (Section 8.1) and the economical and environmental aspects of the processes (Sections 8.2 and 8.3). The use of alkaline solid wastes as an alternative feedstock for mineral carbon sequestration is dealt with in Section 8.4. Finally, Chapter 9 contains the conclusions of this review.

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[5] In this (natural) accident about 1,700 people were killed by asphyxiation, when a $0.1 km^3$ CO_2 bubble emerged from a crater lake and went into the valley.

2. MINERAL CO_2 SEQUESTRATION

Carbon dioxide sequestration by mineral carbonation mimics the naturally occurring rock weathering which is known to have played an important role in the historical reduction of the CO_2 concentration in the atmosphere after the creation of the earth. This so-called 'mineral CO_2 sequestration' option was originally proposed by Seifritz (Seifritz, 1990). The first detailed study originates from Lackner *et al.* (Lackner *et al.*, 1995)[6]. The main advantage of the process is that the formed mineral carbonates are end products of geologic processes and are known to be stable over geological time periods (millions of years). Given the dominance of the lithosphere and the fact that the greater part of the carbon in the lithosphere is held in its oxidised form (Table 1), an enormous potential for carbon sequestration in solid carbonated form can be expected (Dunsmore, 1992) (see also Chapter 3). Besides, the reaction products are environmentally benign.

Rock weathering involves dissolution of atmospheric CO_2 into (rain) water and reaction with minerals. The weathering process can be viewed as an acid-base reaction in which an acid (H_2CO_3/CO_2) is neutralized by a solid base (mineral). As an example, the reaction for some minerals is given (Kojima *et al.*, 1997):

$$\begin{aligned}&CaSiO_3\ (s)\ \text{(wollastonite)} + 2CO_2\ (g) + H_2O\ (l) \rightarrow \\ &\qquad Ca^{2+}\ (aq) + 2HCO_3^-\ (aq) + SiO_2\ (s) \qquad \text{(eq. 1)}\end{aligned}$$

$$\begin{aligned}&Mg_3Si_4O_{10}(OH)_2\ (s)\ \text{(talc)} + 6CO_2\ (g) + 2H_2O\ (l) \rightarrow \\ &\qquad 3Mg^{2+}\ (aq) + 6HCO_3^-\ (aq) + 4SiO_2\ (s) \qquad \text{(eq. 2)}\end{aligned}$$

$$\begin{aligned}&2KAlSi_3O_8\ (s)\ \text{(orthoclase)} + 2CO_2\ (g) + 3H_2O\ (l) \rightarrow \\ &\qquad 2K^{2+}\ (aq) + 2HCO_3^-\ (aq) + 4SiO_2\ (s) + Al_2Si_2H_4O_9\ (s) \qquad \text{(eq. 3)}\end{aligned}$$

These reactions end with HCO_3^- in solution. If one CO_2 is consumed less, carbonates are formed. For example:

$$CaSiO_3\ (s)\ \text{(wollastonite)} + CO_2\ (g) \rightarrow CaCO_3\ (s) + SiO_2\ (s) \qquad \text{(eq. 4)}$$

Based on these principles, various approaches have been suggested. To define the scope of the review report a classification and selection of the approaches have to be made.

In his review on carbonate-based sequestration, Lackner distinguishes three carbonate disposal strategies: introduction of bicarbonate salts into the ocean, injection of (bi)carbonate brines into underground reservoirs and storage of solid carbonates on the surface or underground (mineral CO_2 sequestration) (Lackner, 2002). The focus of this report is storage in solid carbonates. Because carbonates are far less soluble than bicarbonates, carbon dioxide storage in carbonates is favoured in order to achieve permanent storage. The other two options are briefly discussed in Annex B.

Different process layouts have been suggested for mineral CO_2 sequestration. Three main types of processes can be distinguished:

1. In-situ: Underground mineral CO_2 sequestration combined with geological storage of CO_2.
2. Ex-situ: Above ground industrial process. A further subdivision can be made between:
    a) End-of-pipe technology.
    b) Integrated technology within the process.

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[6] The short period during which research has been conducted in this field is reflected by the available literature. A large part of the literature consists of conference papers and only few articles have appeared.

The carbonation reactions involved do not principally differ between the process layouts. Studies into in-situ mineral carbonation are mostly carried out as part of the research into the long-term consequences of geological carbon dioxide storage[7]. In this report only the ex-situ processes are discussed[8]. According to the ex-situ processes, the report describes only end-of-pipe technologies, simply because detailed reports of integrated processes are not available.

Besides this classification, another distinction for the ex-situ processes can be made. Most research is directed towards an industrial process. In this process CO_2 is artificially sequestrated in a controlled way. Another option is to spread out grinded reactive compounds and to allow it react with atmospheric carbon dioxide with the help of rain (Schuiling, 2002). A possible advantage of this approach could be lower sequestration costs, but important disadvantages are the slow reaction and the occupation of land. This report is concerned with industrial sequestration.

In summary, this report reviews industrial end-of-pipe processes in which CO_2 is converted into solid carbonates, which can be stored in order to sequestrate carbon dioxide. In Figure 2 an artist's impression of mineral CO_2 sequestration is given.

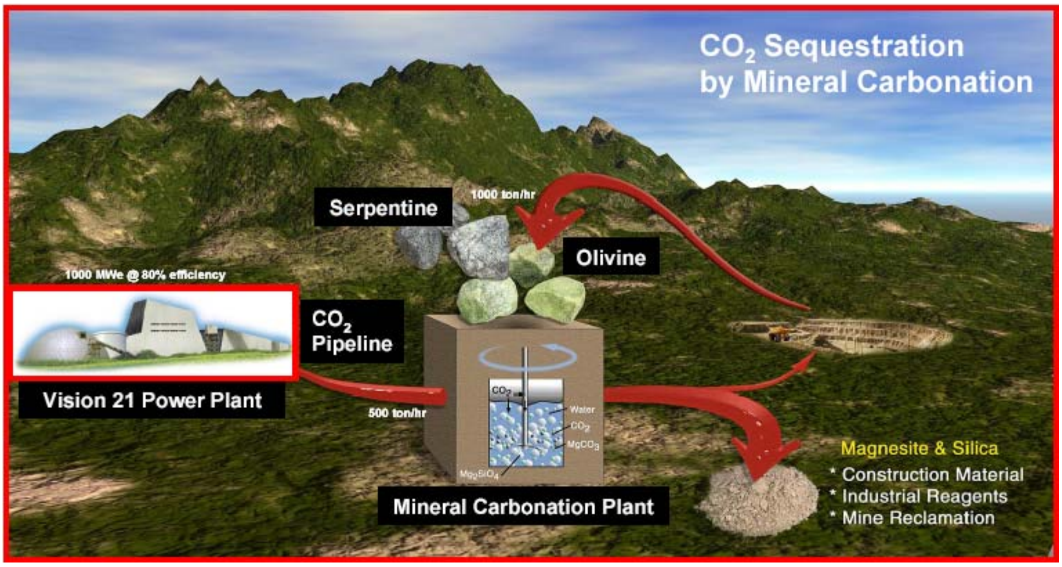

Figure 2 Artist's impression of mineral CO_2 sequestration (NETL, 2001).

Main players in this research field are the Japanese Research Institute for Innovative Technology for the Earth (RITE) and the United States National Energy Technology Laboratory (NETL). The latter institute co-ordinates a research programme of the United States Department of Energy (DOE), in which the Albany Research Centre, Los Alamos National Laboratory (LANL), Arizona State University and Science Applications International Corporation participate. This so-called 'mineral sequestration working group' aims at the design and construction of 10MW equivalent demonstration plant in 2008 (Goldberg *et al.*, 2002). LANL is also part of the Zero Emission Coal Alliance (ZECA), an international consortium of research institutes and private companies, which studies integrated concepts for efficient coal-based power generation and mineral carbon sequestration. Other research efforts are made by, for example, the Shell Research Centre Amsterdam, the Seikei University of Tokyo, the Columbia University and the Helsinki University of Technology.

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[7] Newall *et al.* concluded that in-situ mineral sequestration has more potential than ex-situ sequestration. This approach would avoid concerns about very slow reactions and the costly aboveground processing required (Newall *et al.*, 1999). However, monitoring is required for a long period because of possible accidental CO_2 release.

[8] For more information about in-situ carbonation see (Bachu *et al.*, 1994).

3. SELECTION OF MINERALS

Selection of element

Both alkali and alkaline earth metals can be carbonated. However, alkali carbonates are too soluble to form a stable product that can be stored aboveground and would have to be stored in salt caverns. Of the alkaline earth metals calcium and magnesium are by far the most common in nature. Magnesium and calcium comprise ~2.0 and 2.1mol% of the earth's crust (Goff *et al.*, 1998). Thus calcium and magnesium are generally selected for mineral CO_2 sequestration purposes. Although carbonation of calcium is easier (see Chapter 6), for mineral carbonation the use of magnesium-based minerals is favoured, because they are available worldwide in large amounts and in relatively high purity. Furthermore, the amount of oxide required to bind carbon dioxide from burning one ton of carbon also favours magnesium oxide at 3.3ton compared to 4.7ton calcium oxide. Therefore, most attention is paid to magnesium-containing minerals.

Of the non-alkali and non-alkaline earth metals, few metals can be carbonated (e.g. Mn, Fe, Co, Ni, Cu and Zn). However, most of these elements are too rare or too valuable. Iron is available in sufficient amounts, but forming iron carbonates implies consuming valuable iron ore.

Selection of mineral

In order to be able to react with acid CO_2, the mineral has to provide alkalinity. Not all alkali or alkaline earth metals containing minerals provide alkalinity. For example NaCl is not a source of alkalinity. Alkalinity is derived from oxides or hydroxide. This can be explained by showing the processes occurring during dissolution, e.g.:

$$CaO\ (s) + H_2O\ (l) \rightarrow Ca^{2+}\ (aq) + 2OH^-\ (aq) \tag{eq. 5}$$

$$Mg_3Si_2O_5(OH)_4\ (s) + H_2O\ (l) \rightarrow 3Mg^{2+}\ (aq) + 2SiO_2\ (s) + 6OH^-\ (aq) \tag{eq. 6}$$

Another (weaker) source of alkalinity is carbonates. This can be illustrated by the dissolution of calcite and the subsequent second dissociation step of carbonic acid.

$$CaCO_3\ (s) \rightarrow Ca^{2+}\ (aq) + CO_3^{2-}\ (aq) \tag{eq. 7}$$

$$CO_3^{2-}\ (aq) + H_2O\ (l) \rightleftharpoons HCO_3^-\ (aq) + OH^-\ (aq) \tag{eq. 8}$$

Although it is easier to convert carbonates into bicarbonates than to carbonate a silicate mineral (Lackner, 2002), oxides and hydroxides are preferred. Controlled storage is only possible for carbonates, because carbonates are almost insoluble in water while bicarbonates are fairly soluble[9]. Part of the sequestrated carbon dioxide would be released, if bicarbonates were dissolved in rainwater.

$$Ca(HCO_3)_2\ (s) \rightarrow Ca^{2+}\ (aq) + 2HCO_3^-\ (aq) \rightleftharpoons Ca^{2+}\ (aq) + 2CO_2\ (g) + 2OH^-\ (aq) \tag{eq. 9}$$

Calcium and magnesium rarely occur as binary oxides in nature. They are typically found in silicate minerals. These minerals are capable of being carbonated because carbonic acid is a

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[9] Although calcium and magnesium carbonates are almost insoluble, small amounts can dissolve in acid rainwater. Thus the sequestrated carbon leaches slowly from the storage and comes back into the carbon cycle. This has to be prevented to avoid a possible change of the atmospheric CO_2 concentration in the long-term. A potential option is to seal the mineral carbon dioxide sequestration storage (Newall *et al.*, 1999). The rate at which this occurs is probably very low, but needs to be studied.

stronger acid than silicic acid (H_4SiO_4). Thus silica present in the mineral is exchanged with carbonate and the mineral is carbonated.

Igneous rocks are particularly suitable for CO_2 fixation because they are essentially free of carbonates. The main candidate magnesium-rich ultramafic rocks are dunites, peridotites and serpentinites. The first two can be mined for olivine, a solid solution of forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). Ore grade olivine may contain alteration products, such as serpentine ($Mg_3Si_2O_5(OH)_4$) and talc ($Mg_3Si_4O_{10}(OH)_2$). Serpentine can take the form of antigorite, lizardite and chrysotile. The main calcium-containing candidate is wollastonite ($CaSiO_3$). The composition of various minerals and their specific CO_2 sequestration capacity are given in Table 4.

Table 4 Composition of various minerals and carbon dioxide sequestration characteristics. R_c = mass ratio of rock needed for CO_2 fixation to carbon burned. R_{CO2} = corresponding mass ratio of rock to CO_2 (Lackner *et al.*, 1995; Wu *et al.*, 2001).

Rock	MgO [wt%]	CaO [wt%]	R_C [kg/kg]	R_{CO2} [kg/kg]
Dunite (olivine)	49.5	0.3	6.8	1.8
Serpentine	~40	~0	~8.4	~2.3
Wollastonite	-	35	13.0	3.6
Talc	44	-	7.6	2.1
Basalt	6.2	9.4	26	7.1

Serpentine is found in large deposits worldwide, large reservoirs being known, for example, on both the East and West Coast of North America and in Scandinavia. The worldwide resources that can actually be mined are, however, unknown. Studies have been performed at individual peridotite/serpentinite bodies. Two selected reservoirs in the United States are Twin Sisters, Washington, and Wilbur Springs, California, which are capable of sequestering the globally emitted carbon dioxide for 2 and 5 years respectively (Goff *et al.*, 1998). Lackner indicated a deposit in Oman of 30,000km^3 magnesium silicates which alone would be able to store most of the CO_2 generated by combustion of the world's coal reserves (Lackner *et al.*, 1996; Lackner *et al.*, 2000). Basalt, which is rich in calcium, is ubiquitous, but it is difficult to extract the reactive components from the mineral matrix (Lackner, 2002).

In the DOE research programme olivine and serpentine are selected because of their large abundance in nature and the high molar ratio of the alkaline earth oxides within the minerals (Goff *et al.*, 1998). Other researchers, including Wu, concluded that talc and wollastonite would be the most appropriate minerals (Wu *et al.*, 2001).

Figure 3 Olivine (l) and serpentine (r) (NETL, 2001).

Alkaline solid wastes

Most available literature deals with mineral CO_2 sequestration using mineral rock as feedstock. An alternative source of alkalinity could be the use of solid alkaline waste materials, which are available in large amounts and are generally rich in calcium. Possible candidates are, among others, asbestos waste, iron and steel slag and coal fly ash (NETL, 2001). The carbonation of alkaline waste materials has two potential advantages: these materials constitute an inexpensive source of mineral matter for the sequestration of CO_2 and the environmental quality of the waste materials (i.e. the leaching of contaminants) can be improved by the resulting pH-neutralisation and mineral neoformation (see Section 8.4 for further discussion).

4. THERMODYNAMICS

Carbonate is the lowest energy-state of carbon. The carbonation reactions of magnesium and calcium oxide are strongly exothermic (Lackner *et al.*, 1995)[10]:

$$CaO\ (s) + CO_2\ (g)\ T\ CaCO_3\ (s)\ (\Delta H_r = -179 kJ/mol) \quad \text{(eq. 10)}$$
$$MgO\ (s) + CO_2\ (g)\ T\ MgCO_3\ (s)\ (\Delta H_r = -118 kJ/mol) \quad \text{(eq. 11)}$$

As mentioned before, magnesium and calcium occur typically as calcium and magnesium silicates. In general silicates react as (Goldberg *et al.*, 2001):

$$(Mg,Ca)_xSi_yO_{x+2y+z}H_{2z}\ (s) + xCO_2\ (g)\ T\ x(Mg,Ca)CO_3\ (s) + ySiO_2\ (s) + zH_2O\ (l/g) \quad \text{(eq. 12)}$$

These reactions are still exothermic, but to a lesser extent than the carbonation of pure oxides. For example (Goldberg *et al.*, 2001; Kojima *et al.*, 1997):

$$Mg_3Si_2O_5(OH)_4\ \text{(serpentine)}\ (s) + 3CO_2\ (g)\ T\ 3MgCO_3\ (s) + 2SiO_2\ (s) + 2H_2O\ (l)$$
$$(\Delta H_r = -64 kJ/mol) \quad \text{(eq. 13)}$$
$$Mg_2SiO_4\ (s)\ \text{(olivine)} + 2CO_2\ (g)\ T\ 2MgCO_3\ (s) + SiO_2\ (s) \quad (\Delta H_r = -90 kJ/mol) \quad \text{(eq. 14)}$$

The carbonation reaction with gaseous CO_2 proceeds very slowly at room temperature and pressure (see Chapter 6). Increasing the temperature increases the reaction rate. However, because of entropy effects the chemical equilibrium favours gaseous CO_2 over solid-bound CO_2 at high temperatures (calcination reaction). The highest temperature at which the carbonation occurs spontaneously depends on the CO_2 pressure and the type of mineral. Some examples are given below.

Table 5 Maximum allowable reaction temperature at corresponding pressure for different materials (Lackner *et al.*, 1995).

Mineral	T_{max} [K]	p_{CO2} [bar]
Calcium oxide (CaO)	1161	1
	1670	200
Magnesium oxide (MgO)	680	1
	930	200
Calcium hydroxide ($Ca(OH)_2$)	1161 (T_{deh}=791K)[11]	1
Magnesium hydroxide ($Mg(OH)_2$)	680 (T_{deh}=538K)	1
Wollastonite ($CaSiO_3$)	554	1
Forsterite (olivine) (Mg_2SiO_4)	515	1
Chrysotile (serpentine) ($Mg_3Si_2O_5(OH)_4$)	680 (T_{deh}=808K)	1
Anorthite (feldspar) ($CaAl_2Si_2O_8$)	438	1

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[10] For comparison: $C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$ ($\Delta H_r = -394 kJ/mol$) (Lackner *et al.*, 1995).

[11] T_{deh} is the temperature at which $p_{H2O} = 1$ atm and the mineral dehydrates.

5. PROCESS ROUTES

Different process routes for mineral CO_2 sequestration have been postulated in the literature. Most of them are a combination of a pre-treatment and a sequestration process. The pre-treatment options are discussed first (Section 5.1), followed by a description of the sequestration routes. Two main types of routes can be distinguished:

1. Direct routes in which the mineral is carbonated in one step (Section 5.2).
2. Indirect routes in which the reactive components are first extracted from the mineral matrix and then carbonated in a separate step (Section 5.3).

Finally, in Section 5.4 the process routes are compared with each other.

5.1 Pre-treatment

A variety of pre-treatment options exist. The main ones are: size reduction, magnetic separation and thermal treatment. Their common goal is to increase to reaction rate by increasing the reactive surface available for carbonation.

Size reduction

In order to achieve a reasonable reaction rate the minerals have to be grinded. The reaction rate increases with the surface area. Among others, O'Connor *et al.* examined the influence of the particle size on the conversion. These authors found that a reduction from 106-150μm to <37μm increased the conversion in their experiments from 10% to 90% (O'Connor *et al.*, 2000b).

High-energy attrition grinding[12] induces imperfections into the crystal lattice (Gerdemann *et al.*, 2002). This results in a higher conversion than size reduction to the same diameter using 'normal' grinding. Attrition grinding, however, is energy intensive and difficult to conduct on a large scale.

Magnetic separation

The oxidation of iron (magnetite) slows down the carbonation of serpentine due to the formation of a layer of hematite on the mineral surface (Fauth *et al.*, 2000). To execute the process in a non-oxidising atmosphere complicates the process and increases the costs significantly. Magnetic separation of the iron compounds prior to the carbonation process resolves this complication (NETL, 2001). Furthermore, a potentially marketable iron ore by-product is formed (O'Connor *et al.*, 2001a). When a combination of magnetic separation and thermal treatment is used, it is more effective first to conduct the magnetic treatment step (O'Connor *et al.*, 2000a).

Thermal treatment

Serpentine contains up to 13wt% chemically-bound water. By heating the serpentine to 600-650°C the water is removed and an open structure is created (O'Connor *et al.*, 2000b). This significantly improves the reaction kinetics owing to the increase reactive surface. For example heat-treatment of antigorite increased the surface areas from 8.5m^2/g to 18.7m^2/g (NETL, 2001).

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[12] During attrition grinding small balls mixed with the sample are stirred in a chamber.

The heating process can be further extended to higher temperatures in order to separate, for example, MgO from its matrix. Temperatures above 900°C are needed for serpentine and even higher values for olivine (Zevenhoven *et al.*, 2002):

$$xMgO{\cdot}ySiO_2{\cdot}zH_2O\ (s) \rightarrow xMgO\ (s) + ySiO_2\ (s) + zH_2O\ (g) \tag{eq. 15}$$

The mineral porosity can also be increased by treatment with steam (NETL, 2001) or supercritical water (T=385°C, p=272atm) (O'Connor *et al.*, 2000b).

Other pre-treatment options

O'Connor *et al.* have tried ultrasonic pre-treatment of olivine, but it failed to activate the mineral (O'Connor *et al.*, 2001a). Furthermore, these authors have used chemical pre-treatment steps combined with size reduction. Wet grinding in a caustic solution (1M NaOH, 1M NaCl) was found to be most effective, but still insufficient to achieve a reasonable reaction rate (O'Connor *et al.*, 2001a).

Conclusion

Pre-treatment seems necessary in order to obtain a reasonable reaction rate in direct carbonation processes (see Chapter 7). This benefit should be balanced by the extra costs and energy consumption of the pre-treatment step. Thermal treatment in particular is very energy-consuming and should, if possible, be avoided (Section 8.3).

Special attention should be paid to avoiding undesirable effects during pre-treatment. Gerdemann *et al.* reported surface oxidation when ground ore was allowed to stand in water after wet grinding resulting in an initiation period for carbonation of olivine of about 3 hours (Gerdemann *et al.*, 2002).

5.2 Direct carbonation

Direct carbonation of a mineral can be conducted in two ways: as a direct dry gas-solid reaction or in an aqueous solution.

Direct gas-solid carbonation with CO_2

The most straightforward process route is the direct gas-solid carbonation. This was first studied by Lackner (Lackner *et al.*, 1997b). Various reactions depending on the feedstock are possible. As an example, the direct gas-solid reaction of olivine is given:

$$Mg_2SiO_4\ (s) + 2CO_2\ (g) \rightarrow 2MgCO_3\ (s) + SiO_2\ (s) \tag{eq. 16}$$

High CO_2 pressures are necessary in order to obtain reasonable reaction rates. The reaction rate can further be improved by the use of supercritical CO_2 (Zevenhoven *et al.*, 2002). The produced water dissolves in supercritical CO_2. For serpentine this gives:

$$Mg_3Si_2O_5(OH)_4\ (s) + 3CO_2\ (sc) \rightarrow 3MgCO_3\ (s) + 2SiO_2\ (s) + 2H_2O\ (l/g) \tag{eq. 17}$$

Aqueous scheme

From natural rock weathering it is known that water greatly improves the reaction rate. A process developed on the basis of this principle is the carbonic acid route (O'Connor *et al.*, 1999; O'Connor *et al.*, 2000b), in which CO_2 reacts at high pressure in an aqueous suspension of forsterite or serpentine. First, CO_2 dissolves in the water and dissociates to bicarbonate and H^+ resulting in a pH of about 5.0 to 5.5 at high CO_2 pressure:

$$CO_2\ (g) + H_2O\ (l)\ T\ H_2CO_3\ (aq)\ T\ H^+\ (aq) + HCO_3^-\ (aq) \qquad \text{(eq. 18)}$$

Then the Mg^{2+} is liberated from the mineral matrix by H^+:

$$Mg_2SiO_4\ (s) + 4H^+\ (aq)\ T\ 2Mg^{2+}\ (aq) + SiO_2\ (s) + 2H_2O\ (l) \qquad \text{(eq. 19)}$$

Finally, the Mg^{2+} reacts with bicarbonate and precipitates as magnesite:

$$Mg^{2+}\ (aq) + HCO_3^-\ (aq)\ T\ MgCO_3\ (s) + H^+\ (aq) \qquad \text{(eq. 20)}$$

A bicarbonate/salt mixture ($NaHCO_3$/NaCl) can be used to accelerate the reaction (O'Connor *et al.*, 2000b). The sodium bicarbonate increases the HCO_3^- concentration and thus accelerates the carbonation reaction. An increase of 0.5-1.0g/l CO_2 in distilled water to 20g/l CO_2 in a $NaHCO_3$/NaCl-solution has been reported (Fauth *et al.*, 2000). The reaction can take place at a lower pressure. Used concentrations are about 1M NaCl and 0.5-0.64M $NaHCO_3$ and a 15% containing slurry solids is used[13]. The solution is buffered at pH 7.7 to 8.0 (O'Connor *et al.*, 2001a). At this pH-values the reaction sequence modifies to:

$$Mg_2SiO_4\ (s) + 2HCO_3^-\ (aq)\ T\ 2MgCO_3\ (s) + SiO_2\ (s) + 2OH^-\ (aq) \qquad \text{(eq. 21)}$$

The bicarbonate is almost immediately regenerated by reaction of the hydroxyl ion with gaseous carbon dioxide:

$$OH^-\ (aq) + CO_2\ (g)\ T\ HCO_3^-\ (aq) \qquad \text{(eq. 22)}$$

Thus the HCO_3^- concentrations and pH of the solution are kept constant and the process does not consume $NaHCO_3$.

Alternatively the reaction scheme can be written as (Fauth *et al.*, 2000):

$$\begin{aligned} &Mg_2SiO_4\ (s) + 4NaHCO_3\ (aq) && \text{(eq. 23)}\\ &\qquad T\ 2MgCO_3\ (s) + 2Na_2CO_3\ (aq) + SiO_2\ (s) + 2H_2O\ (l) &&\\ &2Na_2CO_3\ (aq) + 2H_2CO_3\ (aq)\ T\ 4NaHCO_3\ (aq) && \text{(eq. 24)} \end{aligned}$$

Addition of NaCl increases the release of Mg^{2+} ions from the silicate by creating soluble complexes and thus lowering the magnesium activity in solution (Fauth *et al.*, 2001):

$$Mg^{2+}\ (aq) + 2Cl^-\ (aq)\ TMgCl_2,\ MgCl_3^-,\ MgCl_4^{2-}\ (aq)\ \text{etc.} \qquad \text{(eq. 25)}$$

The solution chemistry can be further improved by adding alkali metal hydroxides. Thus the pH of the solution is elevated and the absorption of CO_2 is further improved (reaction 22). The hydroxide is also not consumed. Both HCO_3^- and OH^- act as a catalyst. Probably an optimum pH-value exists, depending on which route is preferred: reaction of magnesium with bicarbonate or carbonate ions. Another option that could improve the dissolution of serpentine and simultaneously elevate the pH is the addition of Na_2CO_3.

A process flow diagram of the aqueous carbonation process route is given in Figure 4.

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[13] In the experiments a 0.64mol/l $NaHCO_3$ and 0.54mol/l (15wt%) serpentine containing slurry is used. This reacts with 1.628 mol/l CO_2.. This means that a large fraction of CO_2 stored originates from the $NaHCO_3$.

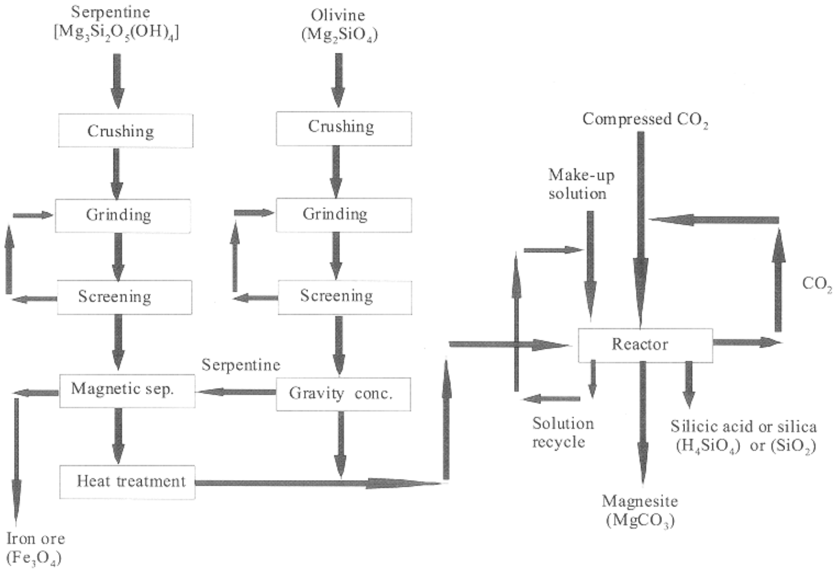

Figure 4 Process flow diagram of the aqueous direct carbonation route using serpentine and olivine (O'Connor *et al.*, 2000a).

5.3 Indirect carbonation

In order to improve the reaction an extra step can be introduced in which the reactive compound is extracted from the matrix. The reactive compound can relatively easily be carbonated in a separate step. Many indirect carbonation routes using various minerals have been proposed.

HCl extraction route

To extract the magnesium from the mineral matrix hydrochloric acid can be used (Lackner *et al.*, 1995; Lackner *et al.*, 1997b). The process was originally developed during World War II as an alternative route producing magnesium. As an example, the process steps using serpentine as feedstock are given.

First, the magnesium is extracted from the mineral with the help of HCl. The use of an excess HCl results in an acid solution in which the magnesium dissolves as $MgCl_2 \cdot 6H_2O$.

$$Mg_3Si_2O_5(OH)_4\ (s) + 6HCl\ (l) + H_2O\ (l)\ \mathrm{T}$$
$$3MgCl_2 \cdot 6H_2O\ (aq) + 2SiO_2\ (s)\ (T=100°C, \text{residence time}=\pm 1h) \quad \text{(eq. 26)}$$

The HCl is recovered by heating the solution from 100 to ±250°C. During this temperature increase, the $MgCl_2 \cdot 6H_2O$ first loses its associated water, resulting in $MgCl_2 \cdot H_2O$ and, finally, HCl separates instead of further water release. Overall, the process step can be given as:

$$MgCl_2 \cdot 6H_2O\ (aq/l)\ \mathrm{T}\ MgCl(OH)\ (l) + HCl\ (l) + 5H_2O\ (l) \quad \text{(eq. 27)}$$

The MgCl(OH) reforms to magnesium hydroxide when water is reintroduced.

$$2MgCl(OH)\ (l)\ \mathrm{T}\ Mg(OH)_2\ (s) + MgCl_2\ (l/s) \quad \text{(eq. 28)}$$

Finally, the $Mg(OH)_2$ is carbonated:

$$Mg(OH)_2\ (s) + CO_2\ (g)\ \mathrm{T}\ MgCO_3\ (s) + H_2O\ (l/g) \quad \text{(eq. 29)}$$

The process scheme is given in Figure 5.

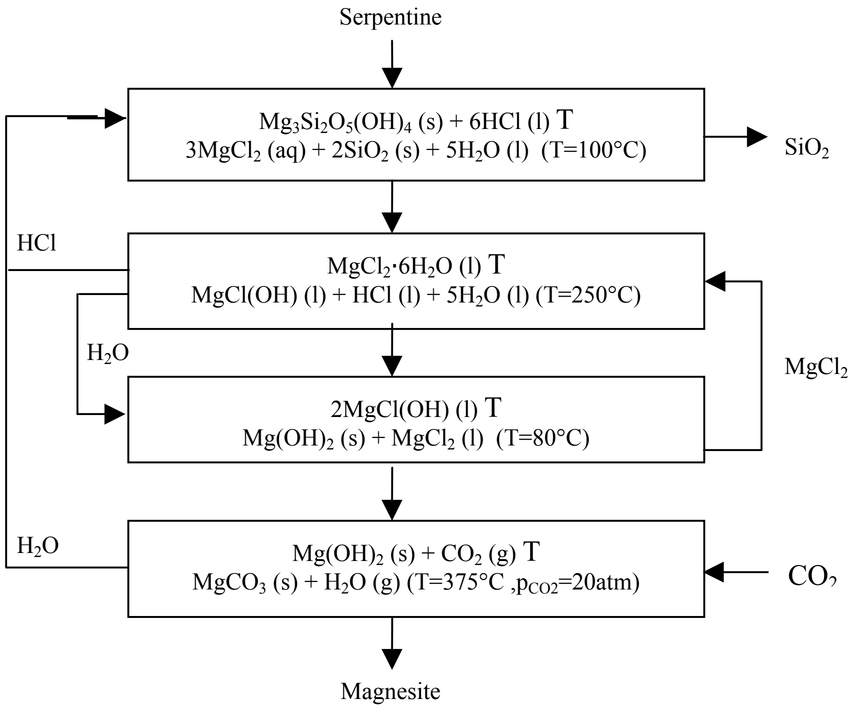

Figure 5 Process flow diagram based on (Newall *et al.*, 1999)

In order to recover successfully the HCl, the formation of soluble chloride has to be avoided. Alkali metal chlorides are soluble and alkali metals should therefore be absent in the feedstock. The serpentine feedstock should preferably contain far less than 1wt% alkali metals. Because solid wastes in general contain more alkali metals, this route seems not to be useful for alkaline solid waste mineral sequestration. The loss of hydrochloric acid would be too great. Another undesirable side-reaction could be the extraction of iron from the feedstock that is present in significant amounts in serpentine. In the process, iron is extracted when HCl is used, but precipitates simultaneously with the silica when the pH of the solution is raised.

The thermodynamics of the process have been studied in detail by Wendt *et al.* (Wendt *et al.*, 1998a). The third step of the process in which $Mg(OH)_2$ is formed has a positive Gibbs energy change and therefore the energy consumption of the process is considerable (see Figure 6). Changing the extraction medium can lower energy consumption (dashed line).

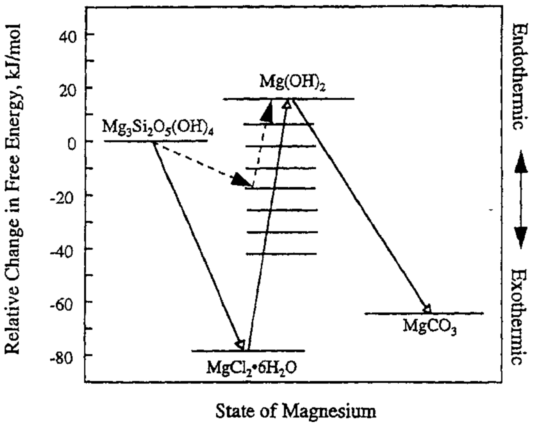

Figure 6 Free energy at main stages in the HCl extraction route (Butt *et al.*, 1998).

Molten salt process

A first approach towards lowering energy consumption is the use of a molten salt ($MgCl_2 \cdot 3.5H_2O$) as an alternative extraction agent (Wendt *et al.*, 1998b; Wendt *et al.*, 1998b). The salt is recycled within the process. There are two options. In the first process, $Mg(OH)_2$ is produced and carbonated separately. In the second process, the steps are integrated into one step[14].

Option A: $MgCl_2 \cdot 3.5H_2O$ is used as solvent to produce $Mg(OH)_2$.

First, the serpentine is dissolved in the molten salt (T=±200°C):

$$\begin{aligned} &Mg_3Si_2O_5(OH)_4\ (s) + 3MgCl_2 \cdot 3.5H_2O\ (l)\ \mathrm{T} \\ &\qquad 6Mg(OH)Cl\ (l) + 2SiO_2\ (aq) + 9.5H_2O\ (l) \end{aligned} \tag{eq. 30}$$

Then the silica is precipitated (T=±150°C), water is added and $Mg(OH)_2$ precipitates:

$$2Mg(OH)Cl\ (l) + nH_2O\ (l)\ \mathrm{T}\ MgCl_2 \cdot nH_2O\ (l) + Mg(OH)_2\ (s) \tag{eq. 31}$$

The $MgCl_2$ is partially dehydrated in order to recover the solvent (T=±110-250°C):

$$MgCl_2 \cdot nH_2O\ (l)\ \mathrm{T}\ MgCl_2 \cdot 3.5H_2O\ (l) + (n-3.5)H_2O\ (l) \tag{eq. 32}$$

The magnesium hydroxide is separated and carbonated:

$$Mg(OH)_2\ (s) + CO_2\ (g)\ \mathrm{T}\ MgCO_3\ (s) + H_2O\ (g) \tag{eq. 33}$$

Option B: The carbonation takes place directly in $MgCl_2 \cdot 3.5H_2O(l)$. The overall reaction is:

$$Mg_3Si_2O_5(OH)_4\ (s) + 3CO_2\ (g)\ \mathrm{T}\ 3MgCO_3\ (s) + 2SiO_2\ (s) + 2H_2O\ (l) \tag{eq. 34}$$

The CO_2 pressure is about 30 bar (Newall *et al.*, 1999).

Important drawback of this route is the corrosive nature of the solvent. This causes construction and operational difficulties. Furthermore, in spite of recycling, make-up $MgCl_2 \cdot 3.5H_2O$ is needed. Based on a detailed assessment, Newall *et al.* concluded that a commercial supply of $MgCl_2$ of this scale is probably unrealistic and if at all possible, unaffordable (Newall *et al.*, 1999).

Route via calcium hydroxide from calcium-rich silicate rock

The same principle as used in the HCl extraction route can be used with $CaSiO_3$ as feedstock (Haywood *et al.*, 2001). The process remains principally the same. First, calcium is extracted from the wollastonite rock and $CaCl_2$ is formed.

$$CaSiO_3\ (s) + 2HCl\ (l)\ \mathrm{T}\ CaCl_2\ (aq) + SiO_2\ (s) + H_2O\ (l) \tag{eq. 35}$$

The $CaCl_2$ is converted to $Ca(OH)_2$ by precipitating $Ca(OH)_2$, being less soluble than $CaCl_2$, and separating the HCl by heating the solution.

$$CaCl_2\ (aq) + 2H_2O\ (l)\ \mathrm{T}\ Ca(OH)_2\ (s) + 2HCl\ (g) \tag{eq. 36}$$

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[14] Strictly speaking this means that option B is a direct carbonation process and should be dealt with in Section 5.2. Because of the use of a chloride containing compounds, however, it is discussed in this chapter.

The solid calcium hydroxide is carbonated:

$$Ca(OH)_2\ (s) + CO_2\ (g)\ T\ CaCO_3\ (s) + H_2O\ (l) \qquad \text{(eq. 37)}$$

Wollastonite carbonation using acetic acid

A second approach towards the reduction of energy consumption is the use of other acids than HCl. Kakizwawa *et al.* selected acetic acid to extract calcium ions from wollastonite (Kakizawa *et al.*, 2001). The route consists of two steps. First, wollastonite is treated with acetic acid.

$$CaSiO_3\ (s) + 2CH_3COOH\ (l)\ T\ Ca^{2+}\ (aq) + 2CH_3COO^-\ (aq) + H_2O\ (l) + SiO_2\ (s) \qquad \text{(eq. 38)}$$

Then the calcium is carbonated and the acetic acid recovered in a combined step:

$$Ca^{2+}\ (aq) + 2CH_3COO^-\ (aq) + CO_2\ (g) + H_2O\ (l)\ T\ CaCO_3\ (s)\downarrow + 2CH_3COOH\ (l) \qquad \text{(eq. 39)}$$

In Figure 7 a schematic drawing of the process is given.

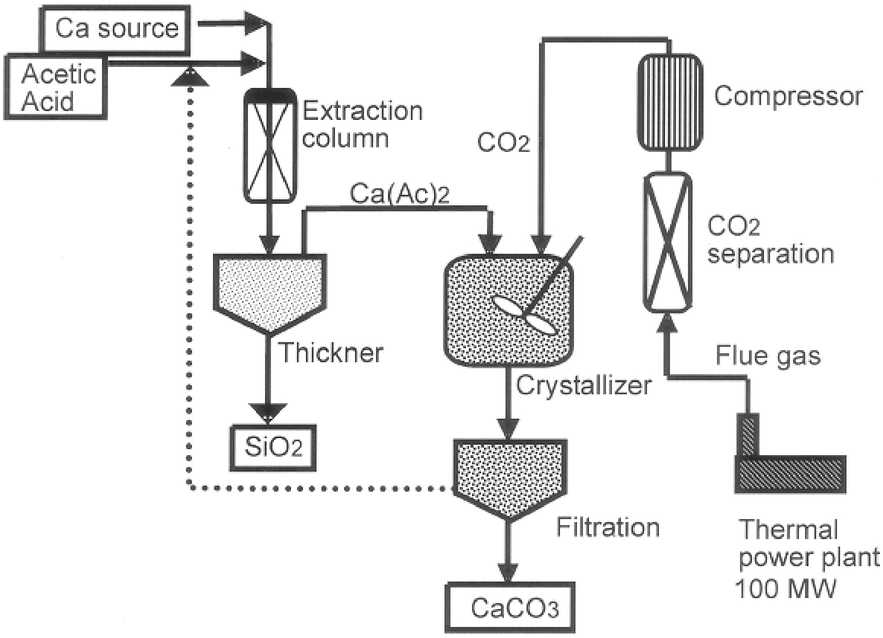

Figure 7 Process scheme of acetic acid route (Kakizawa *et al.*, 2001).

So far, this route has not received much attention in the literature. The main advantage of the route is the ability to speed up the carbonation process by extracting reactive compounds from the matrix without using hydrochloric acid.

Dual alkali approach

The dual alkali approach is based on the Solvay process in which sodium carbonate is produced from sodium chloride using ammonia as a catalyst (Huang *et al.*, 2001). The process is given below.

$$NaCl\ (s) + NH_3\ (g) + CO_2\ (g) + H_2O\ (l)\ T\ NaHCO_3\ (s)\downarrow + NH_4Cl\ (s) \qquad \text{(eq. 40)}$$

Ammonia is recovered according to:

$$2NH_4Cl\ (s) + Ca(OH)_2\ (s)\ T\ 2NH_3\ (g) + CaCl_2\ (s) + 2H_2O\ (l) \qquad \text{(eq. 41)}$$

Overall, the process is:

$$2NaCl\ (s) + Ca(OH)_2\ (s) + 2CO_2\ (g) \rightarrow CaCl_2\ (s) + 2NaHCO_3\ (s) \qquad \text{(eq. 42)}$$

Finally, if desired the bicarbonate can be converted to a carbonate.

$$2NaHCO_3\ (s) \rightarrow Na_2CO_3\ (s) + H_2O\ (g) + CO_2\ (g) \qquad \text{(eq. 43)}$$

For two reasons the Solvay process is ineffective in sequestrating carbon dioxide. The first is that large amounts of energy are consumed. The second is that one mole CO_2 is produced for every two moles sequestrated because $Ca(OH)_2$ is used to recycle the ammonia. Slaked lime ($Ca(OH)_2$) is produced by calcination of limestone:

$$CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2\ (g) \qquad \text{(eq. 44)}$$
$$CaO\ (s) + H_2O\ (l) \rightarrow Ca(OH)_2\ (s) \qquad \text{(eq. 45)}$$

Thus for every mole CO_2 sequestrated by the Solvay process, one mole is indirectly produced.

In order to improve energy efficiency, research on the modification of the process has been done. In the modified process $HOCH_2CH_2(CH_3)NH$ is used instead of ammonia *(Huang et al., 2001)*.

The undesirability of carbon dioxide storage in sodium compounds has been discussed in Chapter 3 and this process route is therefore excluded from further consideration. It is, however, unclear if this route can be used for the storage in calcium of magnesium compounds.

5.4 Comparison of process routes

When the two groups of process routes are compared some differences appear. The main advantage of the direct routes is their straightforward design and the absence of a non-aqueous solvent. The reaction rate, however, is lower and the CO_2 pressure needed is higher than in the indirect process routes.

Within the group of direct processes the dry and wet processes differ on certain aspects. The reactions in an aqueous environment are faster, but, because of the high degree of dilution and the lower reaction temperature, the heat of the reaction is not suitable for practical purposes (Goff *et al.*, 1998). In the dry process design the heat of reaction is available at high temperatures and can therefore be applied usefully. The reaction kinetics, however, are too slow at thermodynamically allowed temperatures. A possible disadvantage of the aqueous route with modified solution chemistry is the need for additional chemicals. Using seawater as solvent can partly provide these, but extra chemicals will be needed to create the optimal concentration. Thus the costs of the process and the environmental consequences will increase. Furthermore, the products have to be de-watered and perhaps even dried. Difficulties arise due to the fine nature of the precipitate.

The main indirect routes are extraction with hydrochloric acid and acetic acid. Advantages of the acetic acid extraction route compared with the HCl using route are the lower energy consumption and the use of a less severe extraction medium. The use of hydrochloric acid restricts the selection of materials due to corrosiveness. The HCl extraction route, however, consists for most part of proven technology and much knowledge on this route has been collected.

As has been mentioned above, the use of other extractants than HCl to extract to active compounds can be promising. Possible extraction agents are weak acids, NH_4Cl and EDTA (Goldberg *et al.*, 2002). At the moment research is being carried out on the use of citrate acid and EDTA to dissolve crysotile ($Mg_3Si_2O_5(OH)_4$).

Overall, the most promising route at this moment seems to be the direct aqueous carbonation. In this route the dissolution and carbonation reactions are combined in a single unit operation. This route has reasonable process rates and avoids the use of chlorine. Disadvantages are its lack of potential heat integration and the possible need for extra chemicals. Indirect routes using less severe acids, e.g. acetic acid, also look promising and have to be examined further.

In the only known detailed study available in literature in which various process routes are compared, it was concluded that the $MgCl_2$ route of Wendt is the most promising route (Newall *et al.*, 1999). However, in their comparison the aqueous route and the acetic acid extraction route were not taken into account.

6. KINETICS

As outlined before, the process rate is the limiting aspect for a successful implementation of mineral carbon sequestration. Furthermore, for an effective design and scale-up of a mineral carbonation reactor, determination of the rate-limiting step is essential (Ityokumbul *et al.*, 2001) The processes as described in Chapter 5 can be subdivided by the nature of the carbonation step within the process.

Dry carbonation

Research focuses on the dry carbonation of calcium and magnesium oxides and hydroxides. The carbonation of CaO and $Ca(OH)_2$ progresses very rapidly and proceeds towards completion in several minutes at elevated temperature and pressure (Lackner *et al.*, 1997b). The advantage of a fast reaction of calcium minerals, however, is counterbalanced by their low concentrations in naturally occurring ores, which makes them less suitable as feedstock. The concentrations of magnesium in ores are generally higher, but the carbonation rate of MgO is slow. The reaction of $Mg(OH)_2$ can be fast enough for an industrial process (Lackner *et al.*, 1997b).

The kinetics of the carbonation of $Mg(OH)_2$ have been investigated in detail by McKelvy *et al.* (McKelvy *et al.*, 2001a; McKelvy *et al.*, 2001b). The mechanism consists of a two-step process:

$Mg(OH)_2$ (s) T MgO (s) + H_2O (g) (dehydroxylation) (eq. 46)
MgO (s) + CO_2 (g) T $MgCO_3$ (s) (carbonation) (eq. 47)

The first step is an equilibrium reaction and can also proceed backwards:
MgO (s) + H_2O (g) T $Mg(OH)_2$ (s) (rehydroxylation) (eq. 48)

The activation energy of the dehydroxylation of magnesium hydroxide is 146 kJ/mol and the reaction can be described using a contracting sphere model (Butt *et al.*, 1996). In this model the solid is assumed to be a round with a uniform product layer on it (see Figure 8). The gas (CO_2) diffuses through the product layer to the unreacted core. Thus the product layer increases and the unreacted core shrinks[15].

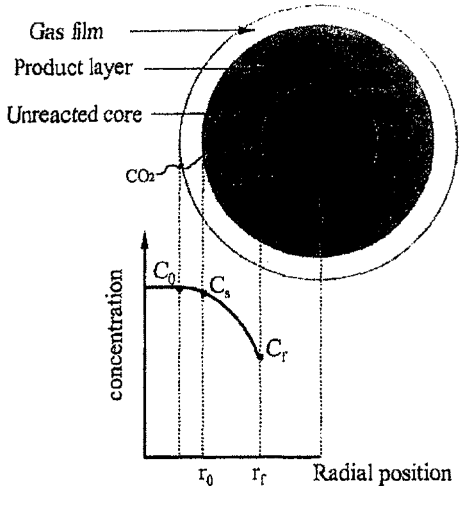

Figure 8 Shrinking core model (Liu *et al.*, 2000a).

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[15] For more details see (Qui *et al.*, 2000).

The net activation energy of the combined carbonation and dehydroxylation is 304 kJ/mol. The contribution of the carbonation reaction could not be determined separately because the reaction occurs simultaneously with the dehydroxylation. The optimum temperature is 375°C. At this temperature the reaction proceeds quickly and the carbonated product is thermodynamically favoured (Butt *et al.*, 1996). More complicated magnesium minerals such as lizardite ($Mg_3Si_2O_5(OH)_4$) have been studied more recently by Chizmeshya (Chizmeshya *et al.*, 2002).

During the reactions a thin layer of the carbonate product is formed. This acts as a diffusion barrier to both the outward diffusion of H_2O and the inward diffusion of CO_2. Thus both dehydroxylation and carbonation are hindered resulting in a reduction of the reaction speed (Butt *et al.*, 1998). A possible positive effect is crack forming in the grain. When, for example, CaO in a matrix is carbonated, the resulting $CaCO_3$ needs more space than the original CaO. Thus strength is imposed on the matrix, which can lead to cracks and an increase of the reactive surface and reaction speed.

Aqueous carbonation

In an aqueous process the magnesium or calcium first has to dissolve from the matrix into the water. For example:

$$MgO\ (s) + H_2O\ (l)\ T\ Mg^{2+}\ (aq) + 2OH^-\ (aq) \qquad \text{(eq. 49)}$$

Two possible routes of the carbonation reaction are (1) a direct conversion of Mg^{2+} into magnesium carbonate

$$Mg^{2+}\ (aq) + CO_3^{2-}\ (aq)\ T\ MgCO_3\ (s) \qquad \text{(eq. 50)}$$
$$\text{or } Mg^{2+}\ (aq) + HCO_3^-\ (aq)\ T\ MgCO_3\ (s) + H^+\ (aq) \qquad \text{(eq. 51)}$$

and (2) an indirect route via hydromagnesite (NETL, 2001).

$$5Mg^{2+}\ (aq) + 4CO_3^{2-}\ (aq) + 2OH^-\ (aq) + 4H_2O\ (l)\ T\ Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O\ (s) \qquad \text{(eq. 52)}$$
$$Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O\ (s) + CO_3^{2-}\ (aq)\ T\ 5MgCO_3\ (s) + 2OH^-\ (aq) + 4H_2O\ (l) \qquad \text{(eq. 53)}$$

A detailed analysis of the rates of the various aqueous route process steps was made by Guthrie *et al.* (Guthrie *et al.*, 2001). These authors concluded that the dissolution of the magnesium silicate is an important step that probably determines the reaction rate. The dissolution rate differs for the various minerals. Olivine, for example, dissolves faster than lizardite. Thermal pre-treatment is known to increase the dissolution rate of serpentine (see Section 5.1). Another important factor is the role of silica. On the dissolving particles a silica-enriched layer may develop that changes the rate and mechanism of dissolution. This layer is formed by incongruent dissolution (Guthrie *et al.*, 2001). In this process calcium and magnesium dissolve into the solution, while other parts of the matrix (e.g. Si) remain in the solid form. This is the subject of further studies.

Wu *et al.* concluded that the rate-determining steps for the carbonation of wollastonite are the dissolution of calcium from the matrix and the carbonation in aqueous solution (Wu *et al.*, 2001). These authors also suggested that the slow reaction rate might result from the development of a thin product layer on the surface.

For the aqueous routes an optimum concentration range can be expected. On the one hand the precipitation reactions need high ionic concentration, on the other the dilution steps prefer low ionic concentration.

In a dry carbonation route increasing the temperature within thermodynamic limits increases the reaction rate. For the aqueous route this effect is counteracted by a decreasing solubility of carbon dioxide in the water phase, thereby resulting in an optimum temperature. Gerdemann *et al.* found an optimum temperature for olivine at 185°C and 155°C for serpentine (Gerdemann *et al.*, 2002).

Fernandez *et al.* found that the kinetics of the carbonation of MgO at atmospheric pressure can be described by a shrinking reaction core model (Fernandez *et al.*, 1999). The activation energy these authors found is 29.1 kJ/mol. The rate-determining step seems to be the reaction between the precipitated magnesium carbonate on the surface and the CO_2 to form bicarbonate. This looks contradictory to remarks made by Lackner (Lackner, 2002) (see Chapter 3). However, the formed magnesium carbonate precipitates on the surface and thus hinders further carbonation. If bicarbonate is formed the magnesium dissolves and new magnesium oxide can react.

Catalysis

By optimisation of the process conditions (e.g. increasing the pressure and temperature) the process rate can be increased. This has, however, undesirable side effects. It would be more efficient to increase the reaction rate itself. Catalysis could be an effective way of realising this. Therefore it is necessary to determine which reaction step is rate determining. Few studies have been conducted in this field. Medina *et al.* found that, except at high pH, hydration of CO_2 is essential for the reaction rate (Medina *et al.*, 2000). Carbonic anhydrase is a possible enzymatic catalyst for this step (so-called bio mimetic approach) (Simsek-Ege *et al.*, 2001). This enzyme has played an important role in the reduction of atmospheric CO_2 concentrations of the early earth through the photosynthetic action of cyanobacteria (Simsek-Ege *et al.*, 2001).

Besides the role of $NaHCO_3$ in the aqueous route and as far as is known, this is the only catalyst described in public literature useful in accelerating the mineral CO_2 sequestration process. It would be useful to investigate further possibilities for enhancing the dissolution of reactive compounds from the matrix and the precipitation of carbonates from the solution.

7. EXPERIMENTAL RESULTS

The experiments on mineral CO_2 sequestration reported in the literature have generally passed the proof-of-principle stage and are at the laboratory-scale stage. A typical experimental scale is a 2-litre autoclave as used by Dahlin *et al.* (Dahlin *et al.*, 2000). As far as can be known, no pilot-plant scale experiments have been performed so far.

Owing to optimisation of the reaction conditions, the realised conversion has increased over time. In 1998 the aqueous sequestration route took nearly 50 hours to get 50% conversion, decreasing to an hour for 80% conversion in 2001 (Goldberg *et al.*, 2001). Apart from the reaction time, also the carbon dioxide pressure decreased considerably. First direct gas-solid carbonation experiments were conducted at 340bar (Lackner *et al.*, 1995). In 2001 reasonable conversion could be obtained within an hour at 10bar CO_2 (O'Connor *et al.*, 2001a). A selection of results reported in the literature is given per route in Table 6, as are important process parameters such as the temperature, CO_2 pressure and particle size.

From the experimental results shown in Table 6, the following conclusions can be drawn:
- The carbonation of serpentine is more difficult than that of olivine, owing to its more complex structure with its chemically bound water. Heat treatment of the serpentine is necessary in order to realise the same order of the reaction rate as for olivine.
- The acetic acid route is far from optimised, the realised conversion being too low for industrial purposes.
- The addition of a $NaHCO_3$/NaCl solution increases the achieved conversion for the aqueous process routes.
- The HCl-extraction route results in the fastest carbonation reaction. Both pressure and time needed have been decreased significantly compared to other routes.
- The use of a pre-treatment step can greatly enhance the process. As mentioned, the main factor is the increase in the available reactive surface. However, Jia *et al.* found that the differences in the carbonation rate in their experiment could not be explained only by a BET-surface area increase (Jia *et al.*, 2002). A more detailed examination of the effect of the pre-treatment options seems essential.

Table 6 Experimental results.

Process route	CO_2[16]	Starting material	Pre-treatment	T [°C] [17]	p_{CO2} [bar]	d [μm]	τ[18] [min]	ζ[19] [%]	Remarks	Source
Direct carbonation	sc	$Mg(OH)_2$		500	340	20	< 120	100		(Lackner *et al.*, 1997b)
Direct carbonation	sc	Serpentine		(140-300)	340	(50-100)	N.A. [20]	30	Packed bed gas-solid reactor.	(Lackner *et al.*, 1997b)
Aqueous route	sc	Olivine		185	116	<37	1440	91		(O'Connor *et al.*, 2001b)
Aqueous route and addition of $0.64MNaHCO_3/1MNaCl$	sc	Olivine		150-250	85-125	N.A. (<37)	60 180	65 83		(Goldberg *et al.*, 2001)
Aqueous route	sc	Antigorite		185	116	<37	1440	34		(O'Connor *et al.*, 2001b)
Aqueous route and addition of $0.64MNaHCO_3/1MNaCl$	sc	Antigorite	Heat treatment	155 (155-200)	187 (152-223)	<37	30 60	78 82		(Dahlin *et al.*, 2000)
Aqueous route and addition of $0.64MNaHCO_3/1MNaCl$	sc	Lizardite	Heat treatment	155	152	N.A. (<37)	180	~52		(NETL, 2001)
Aqueous route	g	Serpentine	Attrition	24	10	<75	60	66		(O'Connor *et al.*, 2001a)
HCl extraction	g	Mg-rich minerals		550	50	N.A.	30	90	Carbonation of $Mg(OH)_2$ via aqueous route.	(Kohlmann *et al.*, 2001)
Acetic acid extraction route	g	Wollastonite		60 (40-80)	30 (5-50)	N.R.[21]	60	20	Crystallisation step	(Kakizawa *et al.*, 2001)

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[16] l = liquid, g = gas and sc = supercritical

[17] The temperature and pressure ranges in which experiments have been conducted are given between brackets.

[18] Residence time.

[19] Conversion.

[20] N.A. = not available

[21] N.R. = not relevant

8. PROCESS ANALYSIS

8.1 Process lay-out

Because the development of mineral CO_2 sequestration is still in a lab-scale phase, only a limited number of process studies have been published. Most postulated processes are end-of-pipe technologies in which the CO_2 is captured first from a flue gas and subsequently reacted with alkaline minerals. Because of costs and reasons of efficiency, integrated process layouts have a greater perspective. Complications arise, however, from the low CO_2 concentration and consequently slow reaction rate.

One aspect of industrial-scale sequestration processes that has received much attention in the literature is the calculation of the magnitude of the product and by-product streams. The amount of carbonate and silica produced by mineral CO_2 sequestration is given for various minerals in Table 7 (Haywood *et al.*, 2001).

Table 7 Amount of products and by-products[22].

Rock	R_C [kg/kg]	R_{CO2} [kg/kg]	$(Ca,Mg)CO_3/CO_2$ [kg/kg]	SiO_2/CO_2 [kg/kg]
Serpentine ($Mg_3SiO_5(OH)_4$)	7.7	2.1	1.9 ($MgCO_3$)	0.9
Olivine ($MgSiO_3$)	8.4	2.3	1.9 ($MgCO_3$)	1.4
Forsterite (Mg_2SiO_4)	5.9	1.6	1.9 ($MgCO_3$)	0.7
Wollastonite ($CaSiO_3$)	9.9	2.7	2.3 (CaO_3)	1.4

The large amount of materials required for mineral carbonation causes practical concerns. First, the scale of the mining needed is great and even greater than that of coal, because more serpentine is needed to sequester the carbon dioxide resulting from the combustion of an equal amount of coal. In addition, transportation is an important factor. In order to avoid the transport of large quantities of rock, transportation of the carbon dioxide is preferable. This implies that the sequestration facilities have to be placed near the mining locations, which imposes geographical constraints on the mineral sequestration option.

With research moving towards process development, the selection of a specific reactor type comes in focus. Ityokumbul *et al.* performed a systematic analysis of reactor design (Ityokumbul *et al.*, 2001). The necessary long residence time complicates the selection of an appropriate reactor for an industrial process. The conventional reactor is a continuous-flow leach-type autoclave and exists of a multi-chamber layout of a stirred tank reactor. Another option is a pipeline reactor, which consists of a bent sequence of static mixers and 'empty' pipe reactors (NETL, 2001).

8.2 Economic considerations

Mineral CO_2 sequestration is in general more expensive than other sequestration routes because of the additional equipment and the more complicated nature of the process needed. However,

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[22] Rc = mass ratio of rock needed for CO_2 fixation to carbon burned. R_{CO2} = mass ratio of rock needed for CO_2 fixation to carbon dioxide sequestrated. $(Ca,Mg)CO_3/CO_2$ = mass ratio of carbonate produced to CO_2 sequestrated. SiO_2/CO_2 = mass ratio of SiO2 produced to carbon dioxide sequestrated.

many authors have acknowledged the economical viability of mineral CO_2 sequestration, e.g. (Goldberg *et al.*, 2001; Lackner *et al.*, 1996). Potentially, costs can be limited by the exothermic nature of the reactions. Furthermore, mining for mineral sequestration can create valuable by-products, such as magnesium, silicon, chromium, nickel and manganese. Finally, re-use of the resulting products could improve the economic returns of the process.

Costs can be divided in two ways. First, costs can be allocated to the various stages in the sequestration process: (1) CO_2 capture and separation from the flue gas, (2) compression and transport and (3) sequestration. For mineral CO_2 sequestration the sequestration costs can be further divided into costs for the pre-treatment of minerals and for the sequestration process itself. Second, costs can be split up in fixed (investment costs) and variable costs (energy consumption, raw materials needed, etc.). The costs of the sequestration process without capture and transport of the CO_2 are discussed first.

Very few detailed cost analyses of mineral CO_2 sequestration are available. As an indication, scale-up of current laboratory practices leads to costs of about 70€/ton. A major part of the costs comes from the heat treatment step. If this problem can be overcome, costs of about 20-30€/ton seem a realistic target (Lackner, 2002).

Estimated costs of the different process routes of mineral CO_2 sequestration are summarised in Table 8. For a comparison, a few cost estimates of other carbon dioxide sequestration technologies are also given. The comparison is complicated by the different assumptions and starting-points of the various cost analyses. The results also depend on the source of the carbon dioxide. In general mineral carbon dioxide sequestration is more expensive than sequestration technologies based on physical storage. The (extra) costs have to be weighed against factors such as the technical feasibility, environmental benefits and public acceptance.

Table 8 Cost comparison of different mineral CO_2 sequestration process routes and other CO_2 sequestration options without CO_2 capture (US conditions).

CO_2 sequestration method	Fixed cost [€/tonCO_2]	Variable costs [€/tonCO_2]	Total costs [€/tonCO_2]	Source
Acetic acid extraction route	9	54[23]	63	(Kakizawa *et al.*, 2001)
HCl extraction route[24]			30[25]	(Lackner *et al.*, 1996)[26]
			233[27]	(Newall *et al.*, 1999)
Molten salt process	±11	±52	63[28]	(Newall *et al.*, 1999)
Underground storage			1-2	(Smith, 1999)
Ocean storage			1-15[29]	(Smith, 1999)
Ocean nourishment			6-12[30]	(Smith, 1999)

In general the variable costs are more important than the investment costs. The main source of variable costs seems to be the energy consumption of the process. The mining costs for mineral

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[23] Only energy costs.

[24] Cost estimate based on comparison with existing industrial processes such as copper mining and magnesium production.

[25] Coal fired electric power plants. 30€/ton CO_2 is formulated as the costs objective for mineral CO_2 sequestration. Based on comparisons with the magnesium oxide producing industry, Lackner *et al.* concluded that such costs might be feasible (Lackner *et al.*, 1996). However, his estimates seem to be too low because little energy consumption is assumed which is probably too optimistic (see Section 5.3).

[26] Based on data from copper mining, the mining and milling costs for mineral CO_2 sequestration feedstock are estimated to be 10€/ton CO_2 sequestrated (Lackner *et al.*, 1997a).

[27] Assumed: 10% discount rate. Cost estimate based on process flow sheet and general design of equipment. Main costs are the energy consumption related to the dehydration steps and need for make-up chemicals.

[28] Assumed: 10% discount rate.

[29] Depending on depth.

[30] Without a value for the extra fish produced.

CO_2 sequestration are small and are estimated at 3-5€/ton (NETL, 2001)[31]. The HCl extraction route seems to be too expensive. The use of HCl as an extraction agent causes the need for extra chemicals and the use of large amounts of energy to recover the solvent.

To estimate the total sequestration costs, the costs of CO_2 capture have be taken into account. As an indication, the costs for extraction, concentration and transport of CO_2 are estimated at 31€/tonCO_2 (NETL, 2001). The specific costs depend on the type of power plant and capture technology used. Of the many studies that have been performed on this subject the results of one study are given as an example. The cost of carbon dioxide capture are 27€/tonCO_2 for Integrated Gasification Combined Cycles (IGCC) plants, 52€/tonCO_2 for Pulverised Coal Power Cycles (PC) plants and 51€/tonCO_2 for natural Gas Combined Cycle (NGCC) plants (David, 2000).

It can be concluded that the costs of mineral sequestration and capture of CO_2 are of the same order and that total costs are about 90-120 €/tonCO_2. The cost increase of the generated electricity varies with the type and efficiency of the power plant. As a rough estimate the total mineral CO_2 sequestration costs correspond to 0.09-0.12 €/kWh. These costs are too high for large-scale mineral CO_2 sequestration and substantial cost reduction is needed in order to allow successful implementation.

8.3 Environmental considerations

As mentioned before, the amounts of minerals needed as feedstock for mineral CO_2 sequestration and the produced (by)-products are very large, which leads to environmental concerns. Dahlin and co-workers give a good example of the scale of operation (Dahlin *et al.*, 2000). A single 500 MW power plant generates about 10,000 ton CO_2/day. To sequester this amount of CO_2 via the mineral route would require approximately 23,000 ton/day of magnesium silicate ore. Feedstock minerals are produced as by-products at several existing mines, but a massive increase in mining activities would be necessary to facilitate large-scale mineral CO_2 sequestration. Mining can also have serious environmental consequences. Ultramafic rocks have a low content of potassium and phosphorus and are relatively rich in magnesium and iron. Therefore, they sustain a unique flora and fauna. Large-scale mining of these rocks can have serious impacts on this ecosystem (Goff *et al.*, 1998).

The carbonate products can be returned to the mines in order to restore the landscape. Because of the increased volume of the carbonated minerals, part of the material cannot be used for mine reclamation, but has to be disposed of or re-used otherwise. The impact of such storage would be limited on a global scale, but could have serious consequences on a local scale because of environmental or land-use constraints.

In addition to these considerations, mineral CO_2 sequestration technologies involve other environmental impacts such as the consumption of extra energy. Assuming that the required energy is provided by fossil fuels, mineral sequestration would enhance the use of fossil fuels. When mineral sequestration is applied at a power plant, the extra energy consumption would consequently decrease its efficiency. Kakizawa calculated a decrease from 40% to 32% for a thermal power plant (Kakizawa *et al.*, 2001).

A large part of the energy consumption comes from the pre-treatment of the feedstock. Heat treatment of 1 ton of serpentine to remove chemically bound water requires 200-250kWh of energy (O'Connor *et al.*, 2001a). In addition, Kojima and co-workers estimated that an extra 18.7kg CO_2 has to be sequestrated to crush 1 ton of wollastonite from 0.2m to 75µm (Kojima *et al.*, 1997)[32].

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[31] In this report all costs are given in € (with 1$=1€).

[32] 1ton $CaSiO_3$ can sequestrate 278kg CO_2.

The energy consumption for different process routes is given in Table 9.

Table 9 The energy consumption of the CO_2 sequestration technology for a 100 MW power plant without capture.

Process route	Energy consumption [MW]		CO_2 [t/hr]	Source
Extraction by acetic acid	CO_2 compression	4.65	63	(Kakizawa *et al.*, 2001)
	Pulverization	5.29		
	Extraction	1.27		
	Crystallization	2.60		
	$CaCO_3$ separation	1.01		
	Total	14.8		
HCl extraction	40		100	(Kohlmann *et al.*, 2001)
HCl extraction	441[33]		70	(Newall *et al.*, 1999)
$MgCl_2$ process	30		70	(Newall *et al.*, 1999)

To determine the overall energy consumption, the capture of CO_2 also has to be taken into account. As an indication the amount of energy needed for separation and compression of CO_2 from power plants has been calculated at the Massachusetts Institute of Technology (David, 2000). The energy costs for CO_2 capture are 0.147 MW for the IGCC, 0.256 MW for the PC and 0.138 MW for the NGCC power plant per net megawatt power output of the power plant. Kakizawa and co-workers have estimated an energy consumption of 0.07MW per MW produced by a thermal power plant (Kakizawa *et al.*, 2001). The overall energy consumption of mineral carbon sequestration would be 25-50 MW for a 100MW power plant. Further research should aim at a reduction of the energy consumption.

Finally, the use of hydrochloric acid as solvent in the HCl extraction route needs to be examined. In the process the acid is recycled. However, some hydrochloric acid probably escapes from the process and ends up in the (by-)products or the environment. This causes environmental concerns and extra HCl has to be produced with additional energy costs. Therefore, process routes using large amounts of hydrochloric acid are less attractive.

Haywood *et al.* compared six mineral carbon sequestration routes and concluded that all routes are environmentally unacceptable (Haywood *et al.*, 2001). Newall *et al.* came to the same conclusions based both on environmental and cost analyses of various mineral sequestration technologies (Newall *et al.*, 1999). However, in both reports the most promising process routes were not studied (see Section 5.4).

Besides a reduction of the greenhouse effect, mineral sequestration also has positive environmental effects. First, the same techniques can be used with ‘white’ asbestos (chrysotile) as feedstock (Goff *et al.*, 1998). Chrysotile forms the bulk of asbestos-contaminated waste resulting from demolition activities. Waste chrysotile asbestos could be used as feedstock in CO_2 sequestration if it is relatively uncontaminated by other materials. Also, other wastes could be used as feedstock. Carbonation is known to reduce the leaching of contaminants from solid wastes (e.g. (Meima *et al.*, 2002)). Using alkaline solid waste as feed material can cause a decrease of the contamination of soil and groundwater and an enhanced re-use of materials (see Section 8.4). It would also contribute towards reducing the mining of primary minerals. Furthermore, some metal oxides are known to be able to bind acid gases such as SO_2 in a

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[33] The energy consumption is higher than energy production of the power station without carbon dioxide sequestration. Thus more CO_2 is produced than sequestrated.

process similar to mineral carbonation (see Annex A.2). Thus a combined flue gas treatment might be possible (Robertson, 1995).

8.4 Alkaline solid wastes

As mentioned before, alkaline solid waste materials are worth considering as a potential alternative feedstock for mineral CO_2 sequestration. Applying the technology to wastes can improve the economic return of the process. Carbonation can improve the environmental quality of alkaline waste materials and facilitate their re-use.

In alkaline solid wastes calcium minerals are the prominent alkaline compounds. Thus it can be expected that the carbonation of wastes is a faster process than that of predominantly magnesium-containing minerals. In addition, owing to its relatively open structure the reactive surface area of, for example, municipal solid waste incinerator bottom ash is probably larger than that of primary minerals.

Indirect routes do not seem attractive for carbon dioxide sequestration in alkaline solid wastes. First of all, the recovery of the solvent is probably poor due to the heterogeneous composition of alkaline solid wastes and corresponding side-reactions. Secondly, the environmental quality of the produced materials would very likely be less than those produced by the direct route. By extracting the calcium and magnesium, the solid matrix that retains contaminants is largely destroyed, which in turn would lead to enhanced leaching of heavy metals.

The alkaline solid waste option has been acknowledged and has passed the proof-of-principle stage. One study compares alkaline solid wastes carbonation with mineral carbonation. Coal fly ash, for example, was carbonated for 80% using the aqueous route with a Na_2CO_3/$NaHCO_3$/NaCl-solution. Under the same conditions the conversion of olivine was 70% and that of serpentine only 12% (NETL, 2001). More information is available about CO_2 sequestration using solid residues in general (Fauth *et al.*, 2002; Johnson, 2000), MSWI bottom ash (Devoldere *et al.*, 2000) and waste concrete (Fujii *et al.*, 2001). The carbon sequestration in alkaline solid wastes and the effect of carbonation on (leaching) properties of waste materials is further discussed in an internal ECN literature review.

9. DISCUSSION & CONCLUSION

Of the main candidate minerals for the sequestration of CO_2, wollastonite and olivine have been shown to react faster than serpentine. However, their worldwide availability is lower. Some researchers have concluded that the wollastonite resources are too small to be of practical interest (Lackner, 2002). If a large fraction of the future emissions of carbon dioxide are sequestrated using the mineral route, the use of serpentine indeed seems to be the only option. However, on a smaller scale wollastonite and olivine are more promising because their use as feedstock probably facilitates the realisation of an industrial process. The most promising route at the moment is the direct aqueous route.

It can be concluded that the mineral CO_2 sequestration technology seems to be an attractive and achievable option for carbon dioxide storage. The development of the reaction rate and process conditions during optimisation is promising, but the reaction rates are still too low. In spite of the exothermic character of the carbonation reaction, the process (still) consumes a lot of energy. Furthermore, the overall environmental consequences require further study and detailed cost analyses have to be made available. The optimum process parameters should be determined in a detailed process design by balancing the reaction rate and the extra energy consumption. The desired physical properties of the reaction products may also require adjustment of process parameters.

Compared to the other sequestration options mineral carbonation is a longer-term option. It has some fundamental advantages such as the permanent nature of the carbon dioxide storage and its theoretically vast capacity, but at this moment there is insufficient knowledge to conclude whether a cost-effective and energetically acceptable process will be feasible.

Future work

In this report a number of issues have been discussed that need to be resolved before mineral carbon sequestration can be implemented on a large scale. The main aspects in the further development of the route are:

- Increase of the reaction rate of the process and optimisation of process conditions.
- Reduction of energy consumption and other costs of the process (energy input during pre-treatment and recycling of solvents, costs of feedstock and re-use or disposal of reaction products, etc.). As discussed earlier, the sequestration of CO_2 in alkaline solid waste materials can potentially improve this aspect.
- Assessment of disposal and re-use options of the carbonated products. Analysis of environmental impacts.
- Investigation of sequestration potential and feasibility of various ores.
- Design of a large-scale carbonation reactor and process development including transport of feedstock and CO_2.

10. REFERENCES

Abanades, J. C. (2002) *The maximum capture efficiency of CO_2 using a carbonation/calcination cycle of $CaO/CaCO_3$,* Chemical Engineering Journal 90/3, pp. 303-306.

Abanades, J. C.; Oakey, J. E.; Alvarez, D. & Hämäläinen, J. (2002) *Novel combustion cycles incorporating capture of CO_2 with CaO*, Proceedings of the 6th international conference on greenhouse gas control technologies, Kyoto, Japan.

Bachu, S.; Gunter, W. D. & Perkins, E. H. (1994) *Aquifer disposal of CO_2: hydrodynamic and mineral trapping,* Energy Conversion and Management 35, pp. 269-279.

Butt, D. P.; Lackner, K. S. & Wendt, C. H. (1998) *The kinetics of binding carbon dioxide in magnesium carbonate*, Proceedings of the 23th international conference on coal utilization and fuel systems, Clearwater, Florida, USA.

Butt, D. P.; Lackner, K. S.; Wendt, C. H.; Conzone, S. D.; Kung, H.; Lu, Y.-C. & Bremser, J. K. (1996) *Kinetics of thermal dehydroxylation and carbonation of magnesium hydroxide,* Journal of American Ceramic Society 79/7, pp. 1892-1898.

Chizmeshya, A. V. G.; Sankey, O. F.; McKelvy, M. J.; Sharma, R.; Carpenter, R. W.; Wolf, G. H.; Bearat, H. & Diefenbacher, J. (2002) *Atomic-level understanding of CO_2 mineral carbonation mechanisms from advanced computational modelling*, 27th international technical conference on coal utilization and fuel systems, Coal Technology Association, Clearwater, USA.

Dahlin, D. C.; O'Connor, W. K.; Nilsen, D. N.; Rush, G. E.; Walters, R. P. & Turner, P. C. (2000) *A method for permanent CO_2 sequestration: supercritical CO_2 mineral carbonation*, Proceedings of the 17th annual international Pittsburgh coal conference, Pittsburgh, PA.

David, J. (2000) *Economic evaluation of leading technology options for sequestration of carbon dioxide*, Massachusetts Institute of Technology.

Devoldere, K.; Weyten, H.; Vrancken, K. & Ginneken van, L. (2000) *Accelerated weathering of MSWI bottom ash by means of liquid and supercritical CO_2*, Proceedings of the 7th meeting on supercritical fluids.

Dunsmore, H. E. (1992) *A geological perspective on global warming and the possibility of carbon dioxide removal as calcium carbonate mineral,* Energy Conversion and Management/33, pp. 565-572.

Fauth, D. J.; Baltrus, J. P.; Knoer, J. P.; Soong, Y.; Howard, B. H.; Graham, W. J.; Maroto-Valer, M. M. & Andresen, J. M. (2001) *Conversion of silicate minerals with carbon dioxide producing environmentally benign and stable carbonates,* Preprints of papers, Division of Fuel Chemistry, American Chemical Society 46/1, pp. 278-279.

Fauth, D. J.; Goldberg, P. M.; Knoer, J. P.; Soong, Y.; O'Connor, W. K.; Dahlin, D. C.; Nilsen, D. N.; Walters, R. P.; Lackner, K. S.; Ziock, H.-J.; McKelvy, M. J. & Chen, Z.-Y. (2000) *Carbon dioxide storage as mineral carbonates*, Preprints of symposia - American Chemical Society, Division Fuel Chemistry, pp. 708-712.

Fauth, D. J.; Soong, Y. & White, C. M. (2002) *Carbon sequestration utilizing industrial solid residues*, Preprints Symposium, American Chemical Society, Division Fuel Chemistry, pp. 37-38.

Fernandez, A. I.; Chimenos, J. M.; Segarra, M.; Fernandez, M. A. & Espiell, F. (1999) *Kinetic study of carbonation of MgO slurries,* Hydrometallurgy 53/2, pp. 155-167.

Freeman, J. D.; Walton, P. H. & Perutz, R. N. (2001) *Carbon dioxide sequestration by novel cobalt (II) complexes*, Anon., patent number WO 01/98313 A1.

Fujii, M.; Yamasaki, A.; Kakizawa, M. & Yanagisawa, Y. (2001) *Reduction of CO_2 emission by treatment of waste concrete via an artificial process,* Symposium - American Chemical Society, Division Fuel Chemistry 46/1, pp. 75-77.

Gerdemann, S. J.; Dahlin, D. C. & O'Connor, W. K. (2002) *Carbon dioxide sequestration by aqueous mineral carbonation of magnesium silicate minerals*, Proceedings of the 6th international conference on greenhouse gas control technologies, Kyoto, Japan.

Goff, F.; Lackner, K. S. (1998) *Carbon dioxide sequestering using ultramafic rocks,* Environmental Geosciences/5, pp. 89-101.

Goldberg, P.; Walters, R. (2002) *A program to develop CO_2 sequestration via mineral carbonation*, Proceedings of the 6th international conference on greenhouse gas control technologies, Kyoto, Japan.

Goldberg, P.; Zhong-Ying, C.; O'Connor, W. K. & Walters, R. P. (2001) *CO_2 mineral sequestration studies in U.S.*, Proceedings of the first national conference on carbon sequestration, Washington, DC.

Golomb, D.; Angelopoulos, A. (2000) *A benign form of CO_2 sequestration in the ocean*, 5th international conference on greenhouse gas technologies, Cairns, Australia.

Golomb, D. S. (2002) *Carbon dioxide/limestone/water emulsion for ocean and geologic sequestration of CO_2*, Proceedings of the 6th international conference on greenhouse gas control technologies, Kyoto, Japan.

Green, D. A.; Turk, B. S.; Gupta, R. P.; Portzer, J. W.; McMichael, W. J. & Harrison, D. P. (2002) *Capture of carbon dioxide from flue gas using solid regenerable sorbents*, Nineteenth annual international Pittsburgh coal conference, Pittsburgh, USA.

Guthrie, G. D.; Carey, J. W.; Bergfeld, D.; Byler, D.; Chipera, S.; Ziock, H. J. & Lackner, K. S. (2001) *Geochemical aspects of the carbonation of magnesium silicates in an aqueous medium*, NETL Conference on Carbon Sequestration.

Haywood, H. M.; Eyre, J. M. & Scholes, H. (2001) *Carbon dioxide sequestration as stable carbonate minerals - environmental barriers,* Environmental Geology 41, pp. 11-16.

Herzog, H. J.; Eliasson, B. & Kaarstad, O. (2000) *Capturing greenhouse gases,* Scientific American 282/2, pp. 54-61.

Huang, H. P.; Shi, Y.; Li, W. & Chang, S. G. (2001) *Dual alkali approaches for the capture and separation of CO_2,* Energy and Fuels/15, pp. 263-268.

IEA (2001) *Putting carbon back into the ground.*

IPCC (2001) *Synthesis report 2001. Summary.*

Ityokumbul, M. T.; Chander, S.; O'Connor, W. K.; Dahlin, D. C. & Gerdemann, S. J. (2001) *Reactor design considerations in mineral sequestration of carbon dioxide*, 18th annual international Pittsburgh coal conference, Newcastle, Australia.

Jia, L.; Anthony, E. J. (2002) *Mineral carbonation and ZECA*, Proceedings of the 6th international conference on greenhouse gas control technologies, Kyoto, Japan.

Johnson, D. C. (2000) *Accelerated carbonation of waste calcium silicate materials,* SCI Lecture Paper Series/108, pp. 1-10.

Kakizawa, M.; Yamasaki, A. & Yanagisawa, Y. (2001) *A new CO_2 disposal process using artificial rock weathering of calcium silicate accelerated by acetic acid,* Energy/26, pp. 341-354.

Kaljuvee, T.; Trikkel, A. & Kuusik, R. (2001) *Decarbonization of natural lime-containing materials and reactivity of calcined product towards SO_2 and CO_2.,* Journal of Thermal Analysis and Calorimetry 64/3, pp. 1229-1240.

Kato, M.; Yoshikawa, S. & Nakagawa, K. (2002) *Carbon dioxide absorption by lithium orthosilicate in a wide range of temperature and carbon dioxide concentrations,* Journal of Materials Science Letters 21/6, pp. 485-487.

Kim, H.-T.; Jung, W.-G.; Kim, S.-H. & Kang, M.-C. (2001) *Evaluation of CaO-added gasification process incorporating CO2 removal*, Eighteenth annual international Pittsburgh coal conference, Newcastle, Australia.

Kling, G. W.; Clark, M. A.; Compton, H. R.; Devine, J. D.; Evans, W. C.; Humphrey, A. M.; Koenigsberg, E. J.; Lockwood, J. P.; Tuttle, M. L. & Wagner, G. N. (1987) *The 1986 lake Nyos gas disaster in Cameroon, West Africa,* Science/236, pp. 169-175.

Kohlmann, J. (2001) *Removal of CO_2 from flue gases using magnesium silicates in Finland*, Helsinki university of technology department of mechanical engineering, Espoo, TKK-ENY-3.

Kohlmann, J.; Zevenhoven, R. (2001) *The removal of CO_2 from flue gases using magnesium silicates, in Finland*, Proceedings of the 11th international conference on coal sciences (ICCS-11), San Fransisco, California, USA.

Kojima, T.; Nagamine, A.; Ueno, N. & Uemiya, S. (1997) *Absorption and fixation of carbon dioxide by rock weathering,* Energy Conversion and Management 38, S461-S466.

Lackner, K. S. (2002) *Carbonate chemistry for sequestering fossil carbon,* Annual review of energy and the environment 27, pp. 193-232.

Lackner, K. S.; Butt, D. P. & Wendt, C. H. (1997a) *Magnesite disposal of carbon dioxide*, Proceedings of the 22th international conference on coal utilization and fuel systems, Clearwater, Florida, USA.

Lackner, K. S.; Butt, D. P. & Wendt, C. H. (1997b) *Progress on binding CO_2 in mineral substrates,* Energy Conversion and Management/38, S259-S264.

Lackner, K. S.; Butt, D. P.; Wendt, C. H. & Sharp, D. H. (1996) *Carbon dioxide disposal in solid form*, Proceedings 21st international conference on coal utilization and fuel systems, Clearwater, Florida.

Lackner, K. S.; Wendt, C. H.; Butt, D. P.; Joyce, E. L. & Sharp, D. H. (1995) *Carbon dioxide disposal in carbonate minerals,* Energy/20, pp. 1153-1170.

Lackner, K. S.; Ziock, H. J. (2000) *From low to no emissions,* Modern Power Systems 20/3, pp. 31-32.

Liu, H.; Katagiri, S.; Kaneko, U. & Okazaki, K. (2000a) *Sulfation behavior of limestone under high CO_2 concentration in O2/CO2 coal combustion,* Fuel 79/8, pp. 945-953.

Liu, Z.; Zhao, J. (2000b) *Contribution of carbonate rock weathering to the atmospheric CO_2 sink,* Environmental Geology 39/9, 1053.

McKelvy, M. J.; Chizmeshya, A. V. G.; Bearat, H.; Sharma, R. & Carpenter, R. W. (2001a) *Developing a mechanistic understanding of lamellar hydroxide mineral carbonation reaction processes to reduce CO_2 mineral sequestration process cost*, NETL Conference on Carbon Sequestration.

McKelvy, M. J.; Sharma, R.; Chizmeshya, A. V. G.; Carpenter, R. W. & Streib, K. (2001b) *Magnesium hydroxide dehydroxylation: in situ nanoscale observations lamellar nucleation and growth,* Chemistry of Materials 13/3, pp. 921-926.

Medina, M.-G.; Bond, G. M. & Rogelj, S. (2000) *Comparison of carbonic anhydrase isozymes for use as catalyst in carbon dioxide sequestration process*, Proceedings of the air & waste management association's 93rd annual conference & exhibition, Air & waste management association, Pittsburgh, PA, pp. 5996-6013.

Meima, J. A.; Weijden van der, R. D.; Eighmy, T. T. & Comans, R. N. J. (2002) *Carbonation processes in municipal solid waste incinerator bottom ash and their effect on the leaching of copper and molybdenum,* Applied Geochemistry 17, pp. 1503-1513.

NETL (2001) *Proceedings of Workshop NETL Mineral CO_2 Sequestration.*

Newall, P. S.; Clarke, S. J.; Haywood, H. M.; Scholes, H.; Clarke, N. R. & King, P. A. (1999) *CO_2 storage as carbonate minerals*, IEA, Cheltenham, UK.

O'Connor, W. K.; Dahlin, D. C.; Nilsen, D. N.; Gerdemann, S. J.; Rush, G. E.; Walters, R. P. & Turner, P. C. (2001a) *Research status on the sequestration of carbon dioxide by direct aqueous mineral carbonation*, 18th annual international Pittsburgh coal conference, Newcastle, Australia.

O'Connor, W. K.; Dahlin, D. C.; Nilsen, D. N.; Rush, G. E.; Walters, R. P. & Turner, P. C. (2000a) *CO_2 storage in solid form: a study of direct mineral carbonation*, 5th international conference on greenhouse gas technologies, Cairns, Australia.

O'Connor, W. K.; Dahlin, D. C.; Nilsen, D. N.; Rush, G. E.; Walters, R. P. & Turner, P. C. (2001b) *Carbon dioxide sequestration by direct mineral carbonation: results from recent studies and current status*.

O'Connor, W. K.; Dahlin, D. C.; Nilsen, D. N.; Walters, R. P. & Turner, P. C. (2000b) *Carbon dioxide sequestration by direct mineral carbonation with carbonic acid*, Proceedings, 25th international technical conference on coal utilization and fuel systems, Clearwater, Florida.

O'Connor, W. K.; Dahlin, D. C.; Turner, P. C. & Walters, R. (1999) *Carbon dioxide sequestration by ex-situ mineral carbonation*, Second Dixy Lee Memorial Symposium: Utilization of fossil fuel-generated carbon dioxide in agriculture and industry, Washington DC.

Qui, K.; Lindqvist, O. (2000) *Direct sulfation of limestone at elevated pressures,* Chemical Engineering Science 55/16, pp. 3091-3100.

Robertson, D. (1995) *Old is new,* The chemical engineer/October, pp. 40-43.

Schuiling, R. D. (2002) *Versnelde verwering. De natuurlijkste manier om kooldioxide te binden.* Natuur & Techniek: pp. 55-57 (in Dutch).

Seifritz, W. (1990) *CO_2 disposal by means of silicates,* Nature/345, 486.

Seifritz, W. (1995) *Optimum CO_2 management of the atmosphere,* International Journal of Hydrogen Energy 20/6, 501.

Shimizu, T.; Peglow, M.; Yamagiwa, K.; Tanaka, M.; Sakuno, S.; Misawa, N.; Suzuki, N.; Ueda, H.; Sasatsu, H. & Gotou, H. (2002) *A simplified model of SO_2 capture by limestone in 71 MWe pressurized fluidized bed combustor,* Chemical Engineering Science 57, pp. 4117-4128.

Simsek-Ege, F. A.; Bond, G. M. & Stringer, J. (2001) *A biomimetic route to environmentally friendly CO_2: catalyst immobilization*, Proceedings Electrochemical Society, 2000-20 (Global Climate Change), pp. 162-170.

Smith, I. M. (1999) *CO_2 reduction - prospects for coal*, IEA Coal Research.

Wendt, C. H.; Butt, D. P.; Lackner, K. S. & Ziock, H.-J. (1998a) *Thermodynamic calculations for acid decomposition of serpentine and olivine in $MgCl_2$ melts I*, Los Alamos National Laboratory, Los Alamos, New Mexico, LA-UR-98-4528.

Wendt, C. H.; Butt, D. P.; Lackner, K. S. & Ziock, H.-J. (1998b) *Thermodynamic considerations of using chlorides to accelerate the carbonate formation from magnesium silicates*, Los Alamos National Laboratory, Los Alamos, New Mexico, LA-UR-98-3612.

Wijngaart van den, R.; Ybema, J. R. (2002) *Referentieraming broeikasgassen. Emissieraming voor de periode 2001-2010*, RIVM, RIVM 773001020/2002 (in Dutch).

Wu, J. C. S.; Sheen, J.-D.; Chen, S.-Y. & Fan, Y.-C. (2001) *Feasibility of CO_2 fixation via artificial rock weathering,* Industrial and engineering chemistry research 40/18, pp. 3902-3905.

Yegulalp, T. M.; Lackner, K. S. & Ziock, H. J. (2001) *A review of emerging technologies for sustainable use of coal for power generation,* International journal of surface mining reclamation and environment 15/1, pp. 52-68.

Zevenhoven, R.; Kohlmann, J. (2002) *CO_2 sequestration by magnesium silicate mineral carbonation in Finland*, R'02 Recovery, Recycling, Re-integration, Geneva, Switzerland.

11. ANNEXES

ANNEX A ANALOGOUS CAPTURE PROCESSES
A.1 CO_2 capture with carbonation and calcination
A.2 SO_2 capture

ANNEX B ANALOGOUS SEQUESTRATION ROUTES
B.1 Mineral formation during oceanic CO_2 sequestration
B.2 Mineral formation in using brines

ANNEX A ANALOGOUS CAPTURE PROCESSES

A.1 CO_2 capture with carbonation and calcination

The carbonation of calcium and magnesium can also be used to capture CO_2 from flue gases. First, alkaline earth oxides are carbonated to extract to CO_2 from flue gases. In the next step the carbonates are calcined to produce a pure CO_2 stream and the alkaline earth oxides are recycled (Abanades *et al.*, 2002). Because the minerals are recycled, pure oxides can be used instead of silicates. This increases the reaction rate and the specific amount of carbon dioxide that can be stored. An important aspect of recycling the oxides is the decreasing capacity of the oxides. Studies have been carried out with calcium oxides (Abanades, 2002), cobalt complexes (Freeman *et al.*, 2001), lithium compounds (Kato *et al.*, 2002) and various others, e.g. magnesium and copper. Owing to the exothermic nature of the carbonation reaction the temperature rises. Heat removal from the reactor is most important in preventing temperature rising and subsequent calcination occurring in the same process step.

Green *et al.* proposed a separation process using a Na_2CO_3/$NaHCO_3$-cycle (Green *et al.*, 2002). First the CO_2(g) from the flue gas is captured by:

$$Na_2CO_3\ (s) + CO_2\ (g) + H_2O\ (g)\ T\ 2NaHCO_3\ (s) \qquad \text{(eq. 54)}$$

The natrium bicarbonate decomposes upon heating according to the reaction:

$$2NaHCO_3\ (s)\ T\ Na_2CO_3\ (s) + CO_2\ (g) + H_2O\ (g) \qquad \text{(eq. 55)}$$

After condensing and separating the formed steam a pure CO_2-stream for subsequent use or sequestration is created. Using sodium instead of calcium significantly decreases the loss of activity during carbonation/calcination cycles.

The major advantage of using solid sorbents for CO_2 capture is their ability to simultaneously reduce other acid pollutants such as SO_2 and HCl. In Section A.2 sulfation processes are described. An example of HCl capture is given by (Green *et al.*, 2002):

$$Na_2CO_3\ (s) + 2HCl\ (g)\ T\ 2NaCl\ (s) + CO_2\ (g) + H_2O\ (g) \qquad \text{(eq. 56)}$$

More sophisticated process concepts have been studied by Kim *et al.* (Kim *et al.*, 2001) using CO_2 capture by CaO carbonation simultaneously with coal gasification in order to produce hydrogen. The overall reaction can be written as:

$$C\ (s) + CaO\ (s) + 2H_2O\ (g)\ T\ CaCO_3\ (s) + 2H_2\ (g) \qquad \text{(eq. 57)}$$

Thus the endothermic coal gasification process ($\Delta H_{r,298}$ = 90.5kJ/mol) is transferred into an exothermic process ($\Delta H_{r,298}$ = -88kJ/mol). The high temperatures needed for the gasification process can thus be lowered. However, because the formed $CaCO_3$ has to be calcined and recycled, the overall process is still energy consuming.

A.2 SO_2 capture

A comparative process is the sulfation of e.g. limestone (Kaljuvee *et al.*, 2001; Qui *et al.*, 2000).

$$2CaCO_3\ (s) + 2SO_2\ (g) + O_2\ (g)\ T\ 2CaSO_4\ (s) + 2CO_2\ (g) \qquad \text{(eq. 58)}$$

This process is used commercially for the prevention of SO_x emissions. The reaction is carried in a direct gas-solid process route (Shimizu *et al.*, 2002). This is feasible because sulfation in general is faster than carbonation (Kaljuvee *et al.*, 2001) and because SO_x concentrations are much lower than CO_2. Two routes can be distinguished (Liu *et al.*, 2000a). The first is indirect sulfation in which limestone is first calcined and the formed CaO reacts with SO_2 in the presence of oxygen to gypsum. The second is direct sulfation is which limestone reacts directly with SO_2 in the presence of oxygen to form $CaSO_4$. A major advantage of this route is that due to simultaneously occurring CO_2 diffusion away from the particle the product layer formed during sulfation becomes porous. This way the reaction speed decreases less than during sulfation of calcium oxide. Being the same kind of base-acid reaction studying the sulfation reaction in more detail can be useful for carbon dioxide sequestration.

ANNEX B Analogous sequestration routes

B.1 Mineral formation during oceanic CO_2 sequestration

As mentioned in Chapter 1, another CO_2 sequestration route is storage in oceans. The main drawback of this route is the effect on the environment by lowering the pH of the ocean. This problem can be overcome by introducing alkalinity into the system in a similar way as in mineral CO_2 sequestration. Two approaches are possible. The first is to introduce alkalinity in the surface ocean and thus increase the absorption of atmospheric carbon dioxide by the ocean. The second is to carbonate calcium or magnesium compounds in an industrial process and inject the formed products into the ocean. This product can either be a bicarbonate solution or solid carbonates. An overview of the possibilities and a discussion of the ocean-atmospheric equilibrium are given by Lackner (Lackner, 2002). Two industrial processes are given as examples.

Carbonation of limestone

Golomb *et al.* proposed a sequestration route in which pulverised limestone ($CaCO_3$) is mixed at high pressures with liquid or supercritical CO_2 and seawater in a pressure vessel (Golomb *et al.*, 2000; Golomb, 2002). Thus equilibrium is established:

$$CaCO_3\ (s) + CO_2\ (g) + H_2O\ (l)\ \varsigma\ 2HCO_3^-\ (aq) + Ca^{2+}\ (aq) \qquad \text{(eq. 59)}$$

The resulting bicarbonate containing emulsion has a pH-value of about 5 at 100atm CO_2 pressure instead of 3 when liquid CO_2 is mixed with water without $CaCO_3$ present. Thus the pH of the ocean is affected less.

Carbonation of dolomite in seawater

An analogous process is the carbonation of dolomite in seawater (Haywood *et al.*, 2001). First, dolomite ($CaMg(CO_3)_2$) is mixed with seawater, then $MgCO_3$ is dissolved, the slurry is carbonated and a large amount of NaCl is added to precipitate $NaHCO_3$. The precipitated $NaHCO_3$ and the undissolved $CaCO_3$ from the dolomite are separated and the remaining solution is recycled. Overall, the NaCl is converted to bicarbonate according to:

$$MgCO_3\ (aq) + 2NaCl\ (aq) + H_2O\ (l) + CO_2\ (g)\ T\ MgCl_2\ (aq) + 2NaHCO_3\ (s) \qquad \text{(eq. 60)}$$

In both process routes the carbon dioxide ends as oceanic HCO_3^- in the carbon cycle. Therefore, although stable for a long time, part of the carbon dioxide comes in the atmosphere at the end. For permanent sequestration purposes it would be better to keep the carbon dioxide in the dolomite or calcite.

B.2 Mineral formation in using brines

As mentioned before carbonation of brines is an alternative approach to sequestrate CO_2. Although worth mentioning because of similarities with mineral CO_2 sequestration, this approach is outside the scope of this literature review because of two reasons. First, the practical potential of these routes is much smaller than the potential of the ones using ultramafic rocks due to the limited availability of useable brines (Haywood *et al.*, 2001). Furthermore, these routes when applied on a large scale produce enormous amounts of hydrochloric acid. The volumes would be larger than the HCl consumption and a major waste stream would remain (Haywood *et al.*, 2001). Two basically identical routes using magnesium and calcium respectively are described.

Route via magnesium hydroxide from brine

Brine solutions can be obtained from magnesium chloride-rich aquifers (Haywood *et al.*, 2001). The brine solution is diluted with water until magnesium hydroxide precipitates:

$$MgCl_2\ (aq) + H_2O\ (l)\ T\ Mg(OH)Cl\ (s) + HCl\ (g) \qquad \text{(eq. 61)}$$

$$2Mg(OH)Cl\ (s) + H_2O\ (l)\ T\ Mg(OH)_2\ (s) + MgCl_2\ (aq) \qquad \text{(eq. 62)}$$

The magnesium hydroxide is separated and directly carbonated:

$$Mg(OH)_2\ (s) + CO_2\ (g)\ T\ MgCO_3\ (s) + H_2O\ (g) \qquad \text{(eq. 63)}$$

Route via calcium hydroxide from brine

As an alternative feedstock calcium rich brine can be used (Dunsmore, 1992). First, gaseous CO_2 is dissolved in water.

$$CO_2\ (g) + H_2O\ (l)\ T\ H_2CO_3\ (aq)\ T\ 2H^+\ (aq) + CO_3^{2-}\ (aq) \qquad \text{(eq. 64)}$$

The brine dissociates into the separate ions,

$$CaCl_2\ (aq)\ T\ Ca^{2+}\ (aq) + Cl^-\ (aq) \qquad \text{(eq. 65)}$$

after which precipitation of calcite

$$Ca^{2+}\ (aq) + CO_3^{2-}\ (aq)\ T\ CaCO_3\ (s) \qquad \text{(eq. 66)}$$

and production of HCl follow.

$$H^+\ (aq) + Cl^-\ (aq)\ T\ HCl\ (l) \qquad \text{(eq. 67)}$$