IEA GREENHOUSE GAS R&D PROGRAMME

CARBON DIOXIDE STORAGE BY MINERAL CARBONATION

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Background to the study

In 2000 the IEA GHG R&D programme issued a comprehensive report on technologies for capture of CO_2 using mineral carbonation. This report evaluated 6 candidate processes but concluded that only one process involving a hot melt of magnesium chloride showed any promise. Mineral carbonation is attractive as a CO_2 storage option because of its permanency but would involve mining, processing and re-depositing of massive quantities of material. In the mean time research has continued and it was felt that it was timely to conduct a more up to date study. As a first step a short review of recent developments and literature was commissioned to ascertain whether it was worthwhile going ahead with a full scale study.

Approach adopted

Mineral carbonation is a specialised field with only a limited number of groups working in the field. One of these groups at ECN in the Netherlands had very recently conducted and published a literature survey on the subject and was thus selected to prepare the initial review and make a recommendation as to whether a full scale study would be worthwhile. The work was awarded on the basis of a negotiated contract.

Results and discussion

ECN produced a comprehensive review of the literature and analysis of the main process routes which have been researched since the earlier IEAGHG study was issued. Most current research is focussed on a number of more promising aqueous processes (Fig 1) and the processes identified in the earlier report are no longer under consideration. The quantities of raw material and product remain similar but energy requirements, although still considerable, can be reduced. Some work continues on a dry gas phase process.

The principal reaction of mineral CO_2 sequestration is:

$$\text{Ca/Mg-silicate (s)} + CO_2\ (g) \rightarrow \text{(Ca/Mg)}CO_3\ (s) + SiO_2\ (s)$$

The principal naturally occurring minerals which can be converted are:

Olivine	Mg_2SiO_4
Serpentine	$Mg_3Si_2O_5(OH)_4$

In addition some work has been done on Wollastonite, $CaSiO_3$, but this is much less abundant and larger quantities are required because of the higher molecular weight of calcium.

Some possibilities for carbonation of industrial waste streams have emerged and these appear to be more attractive from an economic and practical point of view. However the amount of CO_2 which they could store is limited by availability of the waste.

Although research is active, considerable breakthroughs are required to make any of the processes viable. The recommendation of ECN was to wait at least 3 years before considering again whether an in depth study is worthwhile.

Expert reviewers' comments

All reviewers found the report well written and comprehensive. A few additional references were pointed out and minor clarifications requested.

Major conclusions

There has been a shift to investigate other mineral carbonation processes since the IEAGHG 2000 report as researchers look for an economically viable route. Research is still active but in a relatively small number of institutions. Significant breakthroughs are needed but obstacles to be overcome are considerable. However the raw materials required for mineral carbonation are globally abundant and this potential still makes further research attractive.

Recommendations

A watching brief should be kept for significant advances in mineral carbonation. A similar short review in 3 -4 years time should be considered.

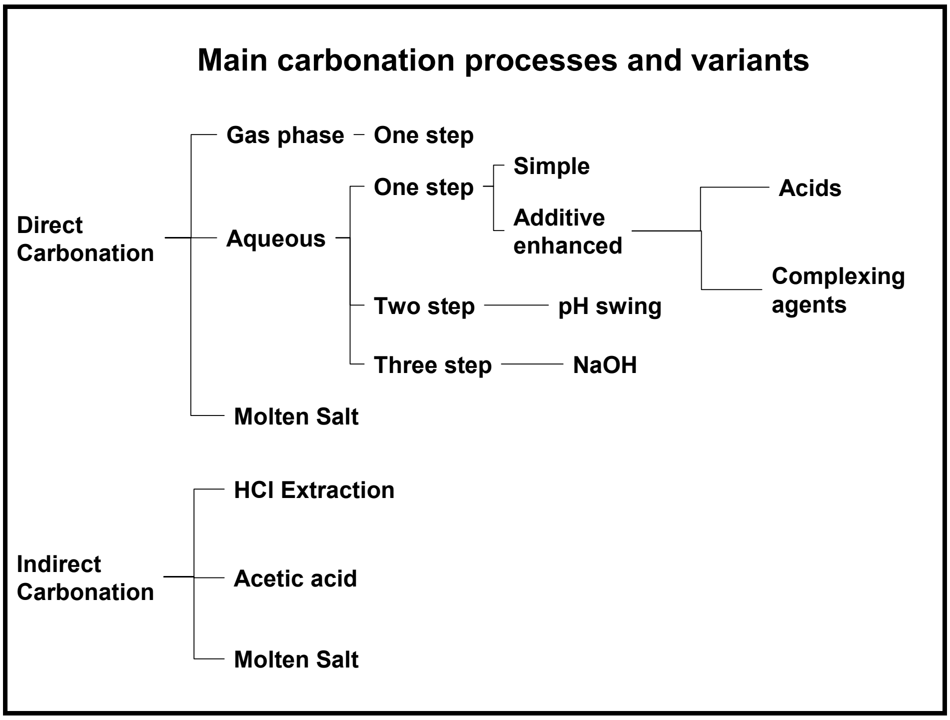

Figure 1. Main carbonation processes and variants considered in the report

ECN-C--05-022

Carbon dioxide sequestration by mineral carbonation

Literature Review Update 2003-2004

W.J.J. Huijgen

R.N.J. Comans

Revisions			
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Preface

This work was funded by the International Energy Agency (IEA) under contract number IEA/CON/05/112. The present report is part of a PhD-project on 'Mineral CO_2 sequestration', which has started 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). This report is an update of a previous ECN literature review (Huijgen, W.J.J. and R.N.J. Comans (2003), *Carbon dioxide sequestration by mineral carbonation, literature review;* Energy research Centre of the Netherlands, Petten, The Netherlands, ECN-C--03-016).

Abstract

The increasing interest in mineral CO_2 sequestration caused the need for an update of the ECN literature review on this subject (February 2003). The present report reviews literature published in 2003 and 2004 on the carbonation of solid Ca/Mg-silicates for CO_2 sequestration. This review update confirms the selection in the previous report of the so-called aqueous mineral carbonation route as the most promising process route. Much progress has been made on this route in recent years resulting in a system study that showed that this approach may be both technically and energetically feasible. However, sequestration costs are (still) too high compared to other CO_2 storage options and in view of expected CO_2 market prices. Cost reductions might be achieved by adding suitable additives to enhance the reaction rate in an (two-step) aqueous process, by developing large-scale continuous reactors and (on a limited scale) by using low-cost feedstock such as industrial alkaline solid residues. A breakthrough in further cost reduction of mineral sequestration probably has to come from totally new concepts, such as a mineral sequestration process integrated within a power plant. Very limited research has been published on such approaches. Beneficial re-use of carbonated products could also reduce sequestration costs for the first mineral CO_2 sequestration (demonstration) plants. Mineral CO_2 sequestration (still) is a longer-term option compared to other sequestration options, and probably has limited potential in the short term. Further technology development and cost reduction are needed for mineral CO_2 sequestration to become part of a broad portfolio of employable CO_2 sequestration technologies.

In the present report, the need for a new study on mineral CO_2 sequestration by the International Energy Agency (IEA) is also assessed. In 2000, the IEA published an evaluation of the technological and economical feasibility of a number of CO_2 mineralisation process routes. The main conclusion of that evaluation was that none of the process routes studied proved to be energetically and economically feasible. With regard to the process-routes evaluated in the IEA study, the present report confirms this conclusion. However, the IEA report did not include the most promising carbonation process route available today (*i.e.*, the aqueous carbonation route). Therefore, an update of the IEA-assessment on 'CO_2 storage as carbonate minerals' is, in principle, advisable. However, since a (cost-)evaluation of the aqueous carbonation route has been published recently, it is questionable whether a new IEA assessment study would provide sufficient new insights at this moment. Furthermore, more information is required on the feasibility of some potentially attractive developments that are currently in a conceptual state. In view of these considerations, the IEA is advised to repeat this literature review, with a similar scope, in 2-3 years. The developments over this period may provide the necessary new insights to warrant a new assessment on mineral CO_2 sequestration by the IEA.

Contents

1. Introduction

In 2003, the Energy Research Centre of the Netherlands (ECN) published a literature study on 'Carbon dioxide sequestration by mineral carbonation'[41], reviewing literature published before January 2003. The present review is an update of the previous report and focuses on the literature on mineral CO_2 sequestration published in 2003 and 2004.

Carbon dioxide capture and storage technologies (CCS) are based on separation and storage of CO_2 from flue gasses resulting from combustion of fossil fuels for energy generation. A short introduction on various forms of CO_2 sequestration is given by, for example, IEA GHG[44]. Mineral CO_2 sequestration is a relatively new CCS-technology. The idea of applying carbonation reactions for CO_2 storage was proposed by Seifritz in 1990[103] and the first studies on this concept were performed at Los Alamos National Laboratory (LANL) between 1995 and 1997[62-66]. During the last ten years, mineral CO_2 sequestration has been studied with increasing interest around the world, reflected by the large increase in literature published on this subject.

The principal reaction of mineral CO_2 sequestration is:

$$\text{Ca/Mg-silicate (s)} + CO_2\text{ (g)} \rightarrow \text{(Ca/Mg)}CO_3\text{ (s)} + SiO_2\text{ (s)} \qquad \text{(eq. 1)}$$

Gaseous carbon dioxide is converted into a solid carbonate in an industrial imitation of natural weathering processes involving alkaline silicate minerals. The present report discusses the state-of-the-art of CO_2 mineralisation research assuming the reader is familiar with this sequestration option. An extensive introduction in mineral CO_2 sequestration is given in the previous ECN (2003) report[41]. In this review, various process routes were compared and it was concluded that the most promising approach was the aqueous carbonation route using olivine, wollastonite or specific industrial residues as feedstock. Although the sequestration capacity of these materials is limited compared to another possible feedstock material, serpentine, their use would avoid the energy-intensive pre-treatment of serpentine and potentially enables the development of an energetically and cost-effectively feasible industrial process. In addition to the main conclusion, it was concluded that indirect routes using mild acids (*e.g.*, acetic acid) could be promising and needed further examination.

The present report reviews publicly available literature in the English language, including journal papers, conference contributions, reports and patents. The review is limited to processes that use a solid feedstock (*e.g.*, Ca/Mg-silicates) and to mineral CO_2 sequestration processes in which CO_2 is stored after carbonation in the form of solid alkaline earth carbonates. The stability of these minerals warrants a permanent character of the CO_2 sequestration. Only the sequestration step will be discussed; capture and transportation are outside the scope of this report. All costs in this report are given in the euro currency (with rate 1.3$ = 1€)[*].

In the present study, research developments will be discussed by process route. In the ECN (2003) review we have distinguished two types of process routes: (1) direct routes in which the mineral is carbonated in one step and (2) indirect routes in which the reactive component is first extracted from the mineral matrix and then carbonated in a separate step. The first type is discussed in Section 2.1 and the latter in 2.2. In addition, Chapter 2 deals with other processes that cannot be categorised strictly as a direct or indirect route (Section 2.3), pre-treatment options (2.4) and process layout (2.5). Progress in research not associated with a specific process route is discussed in Chapter 3 such as feedstock analysis (3.1) and environmental issues and re-use possibilities of products (3.3). Section 3.2 deals with mineral CO_2

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[*] Note that the dollar-euro rate used in this report differs from the one used in the ECN (2003) review.

sequestration by carbonation of industrial solid residues. Finally, the state of art in mineral CO_2 sequestration is summarised in Chapter 4.

Chapter 5 forms an additional section in which the need for an (updated) technical and economical assessment on mineral CO_2 sequestration by the International Energy Agency (IEA) is evaluated. In 2000, the IEA Greenhouse Gas R&D Programme published a report[*] in which the feasibility of six different mineral CO_2 sequestration process routes was assessed[43]. The main conclusion of that report was that only one of the processes had possible potential at that time, *i.e.* a process based on carbonation in a hot melt of magnesium chloride. However, none of the mineralisation processes appeared to be competitive with other capture and storage options. Since 2000, a large body of research has focused on mineral CO_2 sequestration[*]. Chapter 5 (1) gives a comprehensive overview of developments in mineral CO_2 sequestration research since the IEA (2000) publication, (2) specifically includes promising process routes for mineralisation of CO_2 that were not considered in the IEA report and (3) assesses the possible need for an updated IEA report in which promising process routes would be evaluated in depth.

An extensive bibliography of literature on mineral CO_2 sequestration is given in both Chapter 6 and Annex A of this report. Annex B briefly describes processes aiming at CO_2 storage in bicarbonate form and CO_2 sequestration processes based on the carbonation of brines because of their strong analogy with mineral CO_2 sequestration.

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[*] Prepared by Newall *et al.*, CSMA Consultants Limited.

[*] Only about 12% of the mineral CO_2 sequestration literature known to the authors was published before 2000.

2. Process routes

2.1 Direct carbonation

Direct gas-solid carbonation

The most straightforward approach for a carbonation process is direct gas-solid carbonation in which gaseous carbon dioxide reacts with, *e.g.*, solid Ca/Mg-silicate:

$$\text{Ca/Mg-silicate (s)} + CO_2\text{ (g)} \rightarrow (\text{Ca/Mg})CO_3\text{ (s)} + SiO_2\text{ (s)} \qquad \text{(eq. 2)}$$

Major advantages of this process route over three-phase carbonation processes are its simple process design and a better ability to apply the reaction heat generated by the carbonation reaction. Reaction kinetics, however, are very slow for Ca/Mg-silicates[*e.g.*,63,66]. Before 2000, direct gas-solid carbonation with Ca/Mg-silicates was investigated at, among others, LANL[63,66].Thereafter, research at most institutes has moved to other approaches. Today, only in Finland significant research effort is (still) put into this option[51-53,55,57-59,112,124-127]. Recently, an exergy analysis of direct dry carbonation of Mg-silicates has showed that this process can result in a net overall exothermic heat effect[124]. However, the authors' conclusion that the rate of direct mineral carbonation is the most urgent problem to be resolved can only be underlined. The experimentally obtained carbonation conversions of direct dry Ca/Mg-silicate carbonation are still insignificant, even at elevated pressure[*e.g.*,126]. Activation of the feedstock by heat treatment can improve the carbonation rate, but is very energy-consuming[125,127]. As was also concluded in the previous ECN review[41], the direct carbonation route using Ca/Mg-silicates probably does not have the perspective to become an industrially viable process.

Conversion of Ca/Mg-silicates into $(\text{Ca/Mg})(OH)_2$ and subsequent direct dry carbonation (*i.e.*, indirect carbonation) could be more attractive for reasons of carbonation kinetics. Direct dry carbonation of $Mg(OH)_2$ has been modelled and studied in detail at LANL[12,13] and Arizona State University[2,77,104] and was shown to occur rapidly[*e.g.*,63]. Focus within this research was on the dehydroxylation / rehydroxylation reactions of magnesium hydroxide, because control of these reactions can speed up the carbonation process further. Gas-solid carbonation of $Mg(OH)_2$ can be considered feasible, but since hydroxides do not occur in significant amounts in nature, these have to be produced from Mg-silicates. The conversion of Ca/Mg-silicates into hydroxides and subsequent direct dry carbonation is discussed in Chapter 2.2.

Aqueous scheme

The presence of water significantly enhances the reaction rate of carbonation processes, as can be learned from natural weathering processes. Therefore, a research group at the Albany Research Centre (ARC) proposed a process route in which a slurry of a Ca/Mg-mineral in water is carbonated directly at elevated CO_2 pressure and temperature[91]. A large amount of work has been done on this process route by a number of research institutes around the world: for example, ARC[19,28-30,46,81-92,97-99,109], LANL[15,102], ECN[42], Arizona State University[74,102], NETL[22-24] and Ohio State University[95]. This approach was selected as the most promising process route in the ECN (2003) study[41] and will therefore be discussed in detail below.

The aqueous mineral CO_2 sequestration process consists of three steps. All three reactions take place simultaneously in one reactor. First, carbon dioxide dissolves in the water phase resulting in a mildly acidic environment with HCO_3^- as the dominant carbonate species:

$$CO_2\text{ (g)} + H_2O\text{ (l)} \rightarrow H_2CO_3\text{ (aq)} \rightarrow H^+\text{ (aq)} + HCO_3^-\text{ (aq)} \qquad \text{(eq. 3)}$$

Secondly, Ca/Mg leaches from the mineral matrix, facilitated by the protons present:

$$\text{Ca/Mg-silicate (s)} + 2\ H^+ \text{(aq)} \rightarrow (\text{Ca/Mg})^{2+} \text{(aq)} + SiO_2 \text{(s)} + H_2O \text{(l)} \qquad \text{(eq. 4)}$$

Finally, magnesium or calcium carbonate precipitates:

$$(\text{Ca/Mg})^{2+} \text{(aq)} + HCO_3^- \text{(aq)} \rightarrow (\text{Ca/Mg})CO_3 \text{(s)} + H^+ \text{(aq)} \qquad \text{(eq. 5)}$$

A first step to maximise the reaction rate is a careful selection of process conditions such as particle size, temperature and CO_2 pressure[*]. Optimal conversions published are 91% in 6 h (olivine, Mg_2SiO_4)[86], 34% in 6 h (serpentine, $Mg_3Si_2O_5(OH)_4$)[86] and 82% in 1 h (wollastonite, $CaSiO_3$)[90]. By far most research has been done on Mg-silicates. Limited research has been published on the carbonation of wollastonite via the aqueous route[90]. Wollastonite reacts faster than Mg-silicates, thus a lower CO_2 pressure (typical 10-40 bar instead of 150-200 bar) and no additives (see below) are required to obtain a high conversion[*]. However, less CO_2 can be sequestrated per kilo feedstock due to the higher molar mass of Ca. In addition, the worldwide availability of wollastonite is limited compared to Mg-silicates, although the exact amount is unknown[90].

The use of high pressure CO_2 and the fine grinding of the feedstock in the direct aqueous scheme are expensive and energy consuming. Therefore, research has been performed on a further increase of the reaction rate. An important aspect therein is the determination of the reaction mechanisms of direct aqueous carbonation and the corresponding rate-limiting reaction step. Various studies using different feedstock and different research approaches have lead to corresponding conclusions on these subjects, *e.g.* olivine[16,17] (modelling and analysis of the formed SiO_2 layer), serpentine[102] (feedstock and product analysis), olivine and serpentine[89] (product analysis) and steel slag (see Chapter 3.2)[42] (influence process variables and product analysis). Aqueous carbonation of Ca/Mg-silicates was reported to occur in two steps rather than single step solid-state conversion, *i.e.* (1) dissolution of Ca/Mg while forming an amorphous SiO_2-rim and (2) precipitation of Ca/Mg-carbonate. The rate-determining reaction step found at typical process conditions is the leaching of Ca/Mg from Ca/Mg-silicates.

However, at specific process conditions (*e.g.* higher temperature), the carbonation of serpentine becomes limited by other factors than the dissolution step, *e.g.* inhibition of growth or suppression of nucleation of magnesite[15]. This observation is confirmed by the temperature influence reported for olivine[90]. One important difference in reaction mechanisms between the studies published that has not been resolved yet is the exact location of carbonate precipitation. O'Connor *et al.* showed that magnesite precipitated as separate small particles (<10 μm) during Mg-silicate carbonation[28,84]. Thus, recycling of unconverted feedstock in a process design would be feasible[90]. However, research by the authors of this report on aqueous steel slag carbonation indicated that $CaCO_3$ precipitated as a coating on the steel slag particles[42] thus hindering further carbonation and making recycling of unconverted feedstock impossible.

A more fundamental approach to study aqueous mineral carbonation was taken at Arizona State University[1,16,17,121]. A micro-reaction system was developed with which in-situ observations of aqueous mineral CO_2 sequestration reactions can be made using synchronotron X-ray diffraction and Raman spectroscopy[121]. Preliminary results showed that magnesite precipitated directly (*i.e.*, without observable intermediates) when the temperature of heat-activated serpentine slurry exposed to 150 bar CO_2 was gradually increased to 150 °C. The structure, composition and dissolution mechanisms of the SiO_2-rim hindering further carbonation were

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[*] Standard optimal process conditions applied at ARC are 80% of feedstock ground to <37 μm, CO_2 pressure of 150 atm and 185 °C[90].

[*] Lackner states in his review that "magnesium silicates are usually more reactive than calcium silicates"[60,p219]. The results obtained with the direct aqueous carbonation scheme suggest that this is incorrect and that Ca is the more reactive of the two, as was concluded before[41].

studied[16]. An interesting result is the demonstration of intergrowth of carbonate minerals within in an olivine matrix[17].

The dissolution of Ca/Mg from the solid silicate particles has been studied because of its importance for the aqueous scheme. The dissolution of serpentine, for example, has been found to occur in two steps; first rapid dissolution, followed by a relatively slow phase[15]. The last phase is most relevant to enhance mineral CO_2 sequestration. Dissolution is affected by the temperature (Ea = 18-35 kJ/mol) and the presence of CO_2 through a pH effect. Many papers from the research area of geology on dissolution of Ca/Mg-silicates exist and have been studied for mineral CO_2 sequestration purposes (Annex C). Unfortunately, all these studies were performed at (near) atmospheric conditions. Although they are certainly useful to understand dissolution mechanisms, studies on dissolution kinetics at elevated temperature and CO_2 pressure are required to enhance reaction rates.

The mechanisms of aqueous mineral CO_2 sequestration are qualitatively well understood. These mechanisms indicate that an increase of the dissolution rate could be accomplished by, for example, an increase of the specific surface area, removal of the SiO_2-layer and lowering the $(Ca,Mg)^{2+}$-activity in solution. Published options are pre-treatment of the silicate ore (see Chapter 2.4), the application of additives (salts, complexing agents, acids or bases) and non-chemical removal of the developed SiO_2-layer.

Salt additives that have been used in most aqueous carbonation studies are NaCl and $NaHCO_3$. The sodium bicarbonate increases the HCO_3^- concentration and buffers the solution at pH 7.7 to 8.0[83]. At these pH-values the sequence of reactions changes to (*e.g.* for olivine):

$$Mg_2SiO_4\,(s) + 2\,HCO_3^-\,(aq) \rightarrow 2\,MgCO_3\,(s) + SiO_2\,(s) + 2\,OH^-\,(aq) \qquad \text{(eq. 6)}$$

Reaction of the hydroxyl ion with gaseous carbon dioxide regenerates the bicarbonate ion:

$$OH^-\,(aq) + CO_2\,(g) \rightarrow HCO_3^-\,(aq) \qquad \text{(eq. 7)}$$

Another salt additive proposed is $(Na/K)NO_3$[79]. The function of all salt additives is first to increase the ionic strength of the solution and secondly to possibly form complexes with dissolved Ca or Mg. Thus, the Ca/Mg-activity in solution is lowered and the release of Ca^{2+}/Mg^{2+}-ions from the silicate is enhanced[22]. Application of these additives resulted in an increase of the olivine and serpentine carbonation grade to 81% and 92% in 1 hour, respectively[90] (including heat-treatment of feedstock for serpentine) compared to *e.g.* 91% in 6 h for olivine without additives.

Acids and complexing agents can also be used to increase the reaction rate. Possible additives include HCl[96], acetic acid[96] and citric acid[60]. A combination of orthophosphoric acid, oxalic acid and EDTA has been reported to increase the dissolution of serpentine most effectively[96]. In that case, the dissolution step no longer controls the overall reaction rate, but the dissolution of CO_2 becomes rate-limiting[95]. It is important to realise that acids and complexing agents, while enhancing the dissolution step, can complicate the carbonation/precipitation-step by lowering the pH too much for carbonate precipitation to occur or by the formation of too strong complexes. If one does not want to execute both reactions in two separate steps (see Chapter 2.2), a careful optimisation is needed. The application of a base to enhance the Ca/Mg-dissolution (*e.g.* in the direct aqueous process route) seems attractive since it elevates the pH, which is advantageous for the carbonation/precipitation reaction. However, CO_2 being an acid will react with the added base making solvent recycling impossible and thus causing high extra costs (see also Section 2.2).

A next step in the development of aqueous mineral carbonation is research on the process under industrial conditions. A study on the effect of SO_2 originating from the flue gas on the batch carbonation of silicates shows that no solid sulphates are formed, but that SO_2 can effectively be removed from the gaseous phase into the process water[109]. Performing mineral CO_2 sequestration on any significant scale causes the need for other reactors than an autoclave. Among the reactors proposed are a high temperature and pressure fluidised bed[94] and a continuous pipeline reactor[98]. Studies on the latter have started with a prototype continuous flow-loop reactor to determine the (mechanical) behaviour of such a reactor and formulate design specifications for a pilot-scale pipeline reactor. Remarkably, a higher conversion for coarse particles has been obtained in the continuous reactor than in an autoclave system[98]. Probably, the intensified mixing causes high-energy particle-particle interactions, which remove the SiO_2 (and possibly the carbonate)-layer and enhance the reaction rate[30]. Further research is performed to show if this effect can be used to lower the sequestration costs for a large-scale sequestration plant.

Aqueous carbonation is the only process route of which a detailed energy and economic evaluation has been made[81,82,90*]. This evaluation is based on a conventional continuous-flow autoclave reactor. A 27% energy penalty was reported for a power plant[*]. 75% of the energy consumption is due to grinding of the feedstock. Seven regions in the USA were studied where both large ultramafic ores and large amounts of CO_2 are present. The sequestration costs were calculated for these regions with a possible feedstock activation step. The best-case costs were 42 €/ton CO_2 sequestrated for olivine, 49 €/ton for wollastonite and 78 €/ton for serpentine of which nearly 50% of the total capital costs were caused by the reactor. Sequestration costs rise to 67 €/ton CO_2 avoided for olivine if the extra energy consumption due to CO_2 mineralisation is taken into account. These costs have to be reduced significantly in order to become economically competitive with other sequestration options.

Aqueous mineral carbonation has been shown to be, in principle, technically and energetically feasible thanks to the obtained acceleration of the reactions resulting in applicable reaction rates. However, the costs of the current technology are too high and major cost reductions are needed. The high costs of ex-situ mineralisation has lead to the extension of mineral sequestration research at the Albany Research Centre (ARC) to in-situ mineral CO_2 sequestration[101]. Cost reductions of ex-situ aqueous mineral carbonation might be achieved by *e.g.* further development of suitable large-scale reactors, development of more sophisticated additives to promote dissolution and developing integrated carbon capture and sequestration processes (see Chapter 2.5).

Direct molten salt process

Carbonation of serpentine in a $MgCl_2{\cdot}3.5H_2O$ melt was proposed by Wendt *et al.*[116-119]:

$$Mg_3Si_2O_5(OH)_4\ (s) + 3\ CO_2\ (g) \rightarrow 3\ MgCO_3\ (s) + 2\ SiO_2\ (s) + 2\ H_2O\ (l) \qquad \text{(eq. 8)}$$

No developments have been published for this process route since 2003 and the conclusions of the previous ECN review still hold; the high costs associated with the use of corrosive chemicals, the make-up HCl or $MgCl_2$ required and the energy consumption make this process route economically unattractive[41].

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[*] Unfortunately, the cost evaluation study itself as published by Lyons *et al.* from NETL is not available to the authors (Annex A, ref. 20). However, the outcome of this study is discussed in reference 90.

[*] Overall, aqueous mineral CO_2 carbonation consumes energy. The energy consumption of grinding, heating etc. is larger than the heat generated by the exothermic reaction.

2.2 Indirect carbonation

Carbonation proceeds much faster for Ca/Mg-(hydr)oxides than for silicates. Many process schemes have been proposed and studied based on extraction of the reactive compound (*i.e.*, Ca or Mg), conversion to a (hydr)oxide and subsequent carbonation.

HCl extraction route

The most obvious way to extract Ca or Mg from a silicate matrix is the use of HCl, which was proposed by Lackner *et al.* at Los Alamos National Laboratory[12,14,66] in a early stage of mineral CO_2 sequestration research. As an example, the process steps using serpentine as feedstock are given. First, the magnesium is extracted from the mineral using HCl.

$$Mg_3Si_2O_5(OH)_4\ (s) + 6\ HCl\ (l) + H_2O\ (l) \rightarrow 3\ MgCl_2{\cdot}6H_2O\ (aq) + 2\ SiO_2\ (s) \qquad \text{(eq. 9)}$$

The solution is heated to recover the HCl. $MgCl_2{\cdot}6H_2O$ 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:

$$MgCl_2{\cdot}6H_2O\ (aq/l) \rightarrow MgCl(OH)\ (l) + HCl\ (l) + 5\ H_2O\ (l) \qquad \text{(eq. 10)}$$

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

$$2\ MgCl(OH)\ (l) \rightarrow Mg(OH)_2\ (s) + MgCl_2\ (l/s) \qquad \text{(eq. 11)}$$

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

$$Mg(OH)_2\ (s) + CO_2\ (g) \rightarrow MgCO_3\ (s) + H_2O\ (l/g) \qquad \text{(eq. 12)}$$

More details are given in the previous ECN review[41]. Major drawbacks of this approach are the costs associated with the use of HCl (*i.e.*, make-up and the need for corrosion resistant materials) and the energy consumption caused by the H_2O evaporation step. It was demonstrated that the energy consumption of the dehydration and crystallisation steps in the process exceed the energy generated by the power station producing the carbon dioxide by a factor 4[43]. Furthermore, the sequestration costs calculated are >150 €/ton CO_2[43]. No new research has been published on this area since 2002 and there are no reasons to change the conclusions drawn in the ECN (2003) report.

Indirect molten salt process

A potential way to reduce the energy consumption caused by the H_2O evaporation step in the HCl extraction route, is the application of other extraction agents, *e.g.* $MgCl_2$[116-119]. Using serpentine again as example, serpentine is first dissolved in the molten salt:

$$\begin{aligned} &Mg_3Si_2O_5(OH)_4\ (s) + 3\ MgCl_2{\cdot}3.5H_2O\ (l) \rightarrow \qquad \text{(eq. 13)} \\ &\qquad 6\ Mg(OH)Cl\ (l) + 2\ SiO_2\ (aq) + 2.5\ H_2O\ (l) \end{aligned}$$

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

$$2\ Mg(OH)Cl\ (l) + n\ H_2O\ (l) \rightarrow MgCl_2{\cdot}nH_2O\ (l) + Mg(OH)_2\ (s) \qquad \text{(eq. 14)}$$

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

$$MgCl_2{\cdot}nH_2O\ (l) \rightarrow MgCl_2{\cdot}3.5H_2O\ (l) + (n-3.5)\ H_2O\ (l) \qquad \text{(eq. 15)}$$

The magnesium hydroxide is separated and carbonated:

$$Mg(OH)_2\ (s) + CO_2\ (g) \rightarrow MgCO_3\ (s) + H_2O\ (g) \quad \text{(eq. 16)}$$

The process steps can be integrated resulting in a process in which Mg-silicate is carbonated directly in a molten salt (see Chapter 2.1, direct molten salt process). No progress has been published on the indirect molten salt process since 2002 and, therefore, the conclusion of the ECN (2003) report is still valid, *i.e.* the net CO_2 savings are probably negligible given the presence of the energy consuming partial dehydration and evaporation stage[41].

Acetic acid route

A process route that was identified as possibly attractive in the ECN (2003) report is the carbonation of *e.g.* wollastonite in the presence of acetic acid[41,49]. The route consists of two steps. First, wollastonite is treated with acetic acid:

$$CaSiO_3\ (s) + 2\ CH_3COOH\ (l) \rightarrow Ca^{2+}\ (aq) + 2\ CH_3COO^-\ (aq) + H_2O\ (l) + SiO_2\ (s) \quad \text{(eq. 17)}$$

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

$$Ca^{2+}\ (aq) + 2\ CH_3COO^-\ (aq) + CO_2\ (g) + H_2O\ (l) \rightarrow CaCO_3\ (s)\downarrow + 2\ CH_3COOH\ (l) \quad \text{(eq. 18)}$$

An energy consumption of 20 MW for a 100 MW power plant was reported. Sequestration costs of 21 €/ton CO_2 avoided were estimated on the basis of only a rough estimation of the energy costs[41,49]. Unfortunately, since this estimate does not include other variable and investment costs, these values cannot be compared directly to the costs of e.g. the aqueous carbonation process (Section 2.1). The application of a non-corrosive acid to enhance the carbonation rate in combination with these figures makes this a potentially attractive process route. However, it is unclear if this approach can resolve the problems associated with indirect process routes (*i.e.*, cost-effective and energetically feasible recycling of the acetic acid). Since no progress on this process route has been published since the previous ECN report, no better-founded judgement on this approach can be given.

Two-step aqueous route

As stated in the discussion on the direct aqueous scheme, the addition of acids and complexing agents in a single step aqueous carbonation process causes the need to balance the process conditions between an optimum for the dissolution (eq. 3 and 4) and for the precipitation step (eq. 5). Therefore, it might be advantageous to perform the aqueous route in two steps. Park *et al.* have studied this concept[93]. Their process is based on the aqueous carbonation route extended with a so-called pH swing process and in-situ activation. The pH swing process consists of a first step at low pH to dissolve the Mg from the serpentine that was used and a second step at higher pH to form carbonates. In-situ physical activation is applied to remove the passivating SiO_2-rim. Various forms of in-situ activation were tested such as internal grinding by *e.g.* balls and ultrasonic and acoustic treatment[93]. Internal grinding in combination with an acidic environment proved to be most successful. The process conditions required to obtain a significant conversion (70 °C and 1 atm) are much milder than those typical for direct aqueous carbonation (185 °C and 150 atm). As for all indirect process routes, heat integration between the two reaction steps is essential for the further development of this process. Furthermore, since different chemicals are used in the process, a detailed study of costs and environmental impact is recommended. At this stage, it is too premature to draw a final conclusion on the perspective of this process route.

Application of NaOH

Blencoe *et al.* (Oak Ridge National Laboratory) have developed a new approach for mineral CO_2 sequestration in an attempt to overcome disadvantages associated with the aqueous carbonation route (*i.e.*, elevated temperatures and pressures, use of additives and possible heat-treatment)[3,4]. Their process is based on plagioclase carbonation, which in their opinion is the most suitable feedstock being the only abundant Ca/Mg-source that is relatively evenly distributed among the globe. The approach can, in principle, also be applied to other Ca/Mg-silicates. NaOH is used to enhance the extraction of calcium from its three-dimensional structure in which it is kept by silicon and aluminium atoms. A three-stage process was developed:

$$3\ CaAl_2Si_2O_8\ (\text{anorthite, s}) + 8\ NaOH\ (aq) \rightarrow 3\ Ca(OH)_2\downarrow + Na_8(AlSiO_4)_6(OH)_2\downarrow \quad \text{(eq. 19)}$$

$$2\ NaOH\ (aq) + CO_2\ (g) \rightarrow Na_2CO_3\ (aq) + H_2O\ (l) \quad \text{(eq. 20)}$$

$$2\ Na_2CO_3\ (aq) + Ca(OH)_2\ (s) + Na_8(AlSiO_4)_6(OH)_2 + 2\ H_2O\ (l) \rightarrow 4\ NaOH\ (aq) + CaCO_3\downarrow + Na_8(AlSiO_4)_6CO_3\cdot 2H_2O\downarrow \quad \text{(eq. 21)}$$

If all precipitated portlandite is carbonated and the NaOH from reaction 21 is recycled for reaction 19, the overall reaction becomes ($T = 200$ °C, $p < 15$ atm, $t = 1$ h - 3 days):

$$3\ CaAl_2Si_2O_8\ (s) + 4\ CO_2\ (g) + 8\ NaOH\ (aq) \rightarrow 3\ CaCO_3\downarrow + Na_8(AlSiO_4)_6CO_3\cdot 2H_2O\downarrow + 2\ H_2O\ (l) \quad \text{(eq. 22)}$$

Three major drawbacks of this route can be distinguished: (1) reaction times reported are still (too) long for industrial application, (2) the feedstock was milled to <10 μm for the experiments presented which causes a significantly higher energy consumption because of grinding compared to the <38 μm typically applied in aqueous carbonation and (3) large quantities of NaOH will be required. Since there are no indications how these drawbacks could be overcome, the process as proposed seems unattractive.

Acids

Maroto-Valer *et al.* proposed another process based on the application of acids to enhance the dissolution of Ca/Mg from its matrix[73]. This process consists of two steps, *e.g.* serpentine with sulphuric acid:

$$Mg_3Si_2O_5(OH)_4\ (s) + 3\ H_2SO_4\ (aq) \rightarrow 3\ MgSO_4\ (aq) + 5\ H_2O\ (l) + 2\ SiO_2\ (aq) \quad \text{(eq. 23)}$$

$$3\ MgSO_4\ (aq) + 3\ H_2O\ (l) + 2\ SiO_2\ (aq) + 3\ CO_2\ (g) \rightarrow 3\ MgCO_3\ (s) + 2\ SiO_2\ (s) + 3\ H_2SO_4\ (aq) \quad \text{(eq. 24)}$$

This route is basically the same as the HCl-extraction route. It can be extended with an extra step in order to form $Mg(OH)_2$ to be carbonated[76].

Alternative 1, after reaction 23:

$$3\ MgSO_4\ (aq) + 2\ NaOH \rightarrow Mg(OH)_2 + Na_2SO_4 \quad \text{(eq. 25)}$$

$$Mg(OH)_2 + CO_2\ (g) \rightarrow MgCO_3\ (s) \quad \text{(eq. 26)}$$

Another possibility proposed is the addition of both $Ca(NO_3)_2$ and $Ca(OH)_2$ in the following scheme:

Alternative 2, after reaction 23:

$$MgSO_4 + Ca(NO_3)_2 + 2\ H_2O \rightarrow CaSO_4\bullet 2H_2O + Mg(NO_3)_2 \quad \text{(eq. 27)}$$

$$Mg(NO_3)_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + Ca(NO_3)_2 \quad \text{(eq. 28)}$$

$$Mg(OH)_2 + CaSO_4\bullet 2H_2O + 2\ CO_2\ (g) \rightarrow MgCO_3\ (s) + CaCO_3\ (s) + H_2SO_4 + H_2O\ (l) \quad \text{(eq. 29)}$$

overall:

$$Mg_3Si_2O_5(OH)_4\ (s) + Ca(OH)_2\ (s) + 4CO_2\ (g) \rightarrow 3\ MgCO_3\ (s) + CaCO_3\ (s) + 2SiO_2\ (s) \quad \text{(eq. 30)}$$

$Ca(OH)_2$ is consumed in the process and its source on any large scale remains unclear from the literature published. Also in alternative 1, NaOH is converted to $NaSO_4$ and thereby consumed. Any application of chemicals without recycling should be avoided for both cost and environmental reasons given the large scale of any industrial mineral CO_2 sequestration plant[*]. Therefore, both alternative routes proposed seem to be unfeasible.

It is unclear if the use of sulphuric acid instead of HCl could lead to a reduction of the drawbacks of the HCl extraction route. The idea has only been proposed in a patent and no technological and cost evaluation of such a process has been made. Since we do not expect large differences between the H_2SO_4 and HCl-processes, we assume that the conclusions of the HCl extraction route also apply for the H_2SO_4 process.

2.3 Other processes

Iron carbonates

Another possible CO_2 storage option via mineral carbonation is the formation of iron carbonates[100]. Fayalite (Fe_2SiO_4) was significantly carbonated using the direct aqueous scheme (66% in 6 h)[90]. The conclusions drawn above on the direct aqueous scheme also applies to a large extent for iron carbonates. A drawback of mineral CO_2 sequestration based on the formation of iron carbonates may be the consumption of potentially valuable iron ore (*i.e.*, in the case of iron oxides). However, these iron oxides (magnetite) seem to be less reactive than fayalite (only 8% conversion in 6 h)[90]. An alternative iron carbonate process proposed is based on oxidation and subsequent carbonation of metallic iron originating from iron scrap[100]. No experimental research has been done on this subject, which makes the feasibility of such a process speculative. Furthermore, the stability of iron carbonates for long-term CO_2 sequestration has to be assessed.

Application of enzymes

A new research field that has emerged since 2001 is the application of the enzyme carbonic anhydrase for mineral CO_2 sequestration[78]. This enzyme catalyses the hydration of CO_2 and could thereby, in principle, enhance the carbonation rate of mineral CO_2 sequestration. A large amount of research has been done at New Mexico Tech (USA) on this subject[5-10,78,105,106]. Strictly speaking, this approach lies outside the scope of this report since typically brines are used as the cation source in the research published. However, the enzyme could, in principle, also be applied for the aqueous carbonation of Ca/Mg-silicates as was indicated in the ECN (2003) study[41].

Recently published research on aqueous Ca/Mg-silicate carbonation shows that processes involving CO_2 or (bi)carbonate are probably only rate limiting at either low CO_2 pressure or high temperature[42,90]. The enzyme is not expected to function well at the high temperatures applied in aqueous mineralisation (typically >175 °C). At low CO_2 pressure, application of carbonic anhydrase might accelerate the process. Although it is unlikely that the application of this enzyme will increase the conversion rate beyond values obtained at higher CO_2 pressure, given that the silicate dissolution becomes rate limiting, this approach may contribute to making the conversion more energetically favourable. In addition, it might also be an interesting concept when carbonating liquids that already contain dissolved cations, such as brines (Section 0).

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[*] Therefore, any chemical to be added in order to enhance the carbonation process should be carefully selected. For example, additives of which the anion may precipitate with Ca/Mg are not suitable. Irreversible reactions following from the addition of multiple chemicals can also make the process non-feasible (as is the case in alternatives 1 and 2).

2.4 Pre-treatment options

Research on pre-treatment options other than conventional grinding that can activate the mineral for carbonation was performed because it had turned out that the slow reaction kinetics for some potentially attractive Ca/Mg-silicates, particularly serpentine, could not be enhanced sufficiently by careful selection of a process route and process conditions only. Pre-treatment can be conducted by thermal[e.g.,75,90], chemical[e.g.,128] or mechanical means[e.g.,90]. All options aim at destruction or disordering of the mineral lattice and thus an increase of the specific surface area[90]. The state of the research on pre-treatment options will be discussed briefly below.

Heat activation

Heat activation was the first pre-treatment option to be studied to activate serpentine for carbonation. By heating the serpentine to typically 600-650 °C the hydroxyl groups are removed and a significant improvement of the carbonation rate was established[e.g.84]. However, heat-treatment is energy intensive (~300 kWh/ton feedstock) resulting in a process that sequestrates negative amounts of CO_2[82]. At Arizona State University the mechanisms of dehydroxylation and rehydroxylation reactions and the role of heat activation of enhancing aqueous serpentine carbon sequestration have been studied in detail[18,75-77]. At the moment, there seems to be general consensus that heat activation is impractical from an energetic point-of-view and this route should therefore be abandoned[90].

Surface activation techniques

At the Pennsylvania State University a number of so-called surface activation techniques including both physical activation by steam treatment and chemical activation by acids (*e.g.* sulphuric or nitric acid) has been investigated[69-73]. Thus, the specific surface area of serpentine could be increased from 8 to 330 m^2/g resulting in an increase of the reactivity[71]. Drawbacks of chemical activation are the increased sequestration costs and a reduction of the Mg-content of the feedstock due to leaching[70]. The benefits of the activation (*i.e.*, faster carbonation reaction) should be balanced against the extra costs in a process evaluation study.

Other pre-treatment options

Many pre-treatment options have been tested that did not result in a higher reactivity, such as ultrasonic treatment and wet grinding in a caustic solution[83]. Other pre-treatment options such as high-energy attrition grinding of serpentine resulted in a higher conversion but consume too much energy[28,90].

The pre-treatment step (grinding) and the carbonation reaction can be integrated in a mechanochemical process[80]. Thus, the reaction potentially proceeds fast because fresh surface area is created during the reaction. Process costs are potentially lower due to a simplification of the process design. Research performed on this approach, however, has not succeeded in significant carbonation of various silicate minerals so far[80].

Conclusion

The only available pre-treatment option that has proven to be energetically and potentially economically feasible is conventional grinding[90]. The feasibility of chemical activation methods is unclear and needs further investigation. In-situ activation methods, such as discussed in Chapter 2.2 in the section on the two-step aqueous process route, could possibly be attractive but are largely unknown territory.

2.5 Process lay-out

Most research on ex-situ CO_2 mineralisation has been done on a process that stands on its own assuming that the carbon dioxide and solid feedstock generation occur at different places and that the transport of the solid feedstock is impractical[*]. However, since a large part of the sequestration costs is due to the extra energy consumption caused (*i.e.*, both in terms of direct energy costs and conversion of gross into net CO_2 sequestration costs) it could be worthwhile to develop integrated concepts of a mineral CO_2 sequestration plant with *e.g.* a power plant. Thus, energy and cost savings could possibly be obtained due to energy integration[54]. Studies have been performed on hydrogen production based on integrated coal gasification and mineral CO_2 sequestration[111,123]. Unfortunately, conditions required for both processes probably differ too much to integrate these into a single unit[110]. The application of industrial solid residues as feedstock for mineral CO_2 sequestration (see Chapter 3.2) offers another integration possibility since carbon dioxide and the solid feedstock are produced at the same location and transport is avoided.

Another integration possibility proposed is the combination of CO_2 capture/separation with carbonation[120]. Thus, the significant costs and energy consumption associated with state-of-the-art CO_2 separation techniques might be lowered, *e.g.* by utilizing the reaction heat of the carbonation process. Possibly, such a system can be extended with the use of enzymes such as discussed in Chapter 2.2. Carbon dioxide is dissolved in a water phase (accelerated by carbonic anhydrase) and the carbonate ion reacts with $(Ca,Mg)^{2+}$ (from different sources) to form carbonates[11,21]. However, the possible accompanying need for large-scale transport of solid feedstock is unattractive for both energetic and economic reasons.

All studies on integrated concepts are in a first design phase and no detailed technical and economical assessment of such an approach has been made yet. More research on these concepts seems highly warranted given their potential benefits. Probably the only way in which mineral CO_2 sequestration would ever be able to compete on costs with geological sequestration is by integration of capture and mineral CO_2 sequestration. For geological carbon storage, CO_2 separation from a flue gas, which is costly and energy consuming, is always required. If mineral CO_2 sequestration could be operated at low CO_2 pressures, a separate CO_2 capture step might no longer be required and mineral CO_2 sequestration might use CO_2 directly from the flue gas, thus saving on costs and energy.

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[*] If possible, transportation of solid feedstock should be avoided because of costs[*e.g.*,60] and environmental impact.

3. Other aspects of mineral CO_2 sequestration

3.1 Feedstock analysis

During the end of the nineties Los Alamos National Laboratory has investigated the suitability, amounts and occurrence of ultramafic rocks (*i.e.*, Ca/Mg-silicates), mainly in the USA, for mineral CO_2 sequestration[31-36]. In recent years, an extensive source and sink mapping has been made for the USA[90] and a first start has been published for British Colombia, Canada[114]. For the rest of the world only limited information is available. A major gap in mineral CO_2 sequestration research is a worldwide evaluation of the amount and occurrence of silicate ores that can (cost-)effectively be excavated for mineral CO_2 sequestration. Only then, a more realistic estimation of the practically feasible sequestration capacity of mineral CO_2 sequestration can be made.

3.2 Industrial solid residues

Solid industrial residues are generally alkaline, inorganic and rich in Ca/Mg and can therefore be applied as an additional feedstock for mineral CO_2 sequestration, as was already discussed in the previous ECN review[25,41]. Residues tend to have a number of advantages compared to ores, e.g., their availability in industrial areas, low costs and possibly higher reactivity due to their chemical instability[42]. Although their total CO_2 sequestration capacity is limited, the use of residues as feedstock could contribute to make the first mineral CO_2 sequestration (demonstration) plants economically feasible. For reasons of economy of scale, it could be advantageous to use a blend of industrial residues with primary ores as feedstock for mineral CO_2 sequestration. Solid residues alone are particularly suitable for niche applications, such as at steel plants and municipal solid waste incinerators, where both the residue and the carbon dioxide are present.

Many studies have been published on the carbonation of residues either for the purpose of studying the effect of accelerated carbonation on their environmental properties (*i.e.*, contaminant leaching, see Chapter 3.3), the effect of long-term atmospheric carbonation on contaminant leaching during re-use applications, or the effect of carbonation on mechanical properties. All these studies are typically characterised by low carbonation grades and deal with the storage of CO_2 as an additional side effect. In this report, only studies that directly aim at CO_2 storage by carbonation are reviewed. Mineral CO_2 sequestration based on solid residue carbonation has been studied for *e.g.* municipal waste incinerator bottom ash[20], FBC ash and FGD spray dryer ash[25], waste concrete and cement[27,45,107,108], steel slag[42,107,108] and fly ashes[48]. A low-tech approach for carbonation of residues is sprinkling CO_2 containing water on heaps of residues[*e.g.* 107,108]. Such a process could be relatively cheap, but the amounts of CO_2 that can be sequestrated in such a set-up are small. Therefore, these approaches of direct aqueous carbonation are not suitable for mineral CO_2 sequestration purposes and do not need further consideration.

The conclusions drawn in Chapter 2 on the various process routes are, in principle, also valid for alkaline solid residues. Indirect carbonation routes, however, are less attractive for residues because of the diversity of elements present. The recycling of *e.g.* the applied acid is complicated by side-reactions of these elements and higher solvent costs result. A study on steel slag carbonation has shown that steel slag can be significantly carbonated using the direct aqueous route and that the carbonation mechanisms are roughly the same as for Ca-silicate ores[42].

3.3 Environmental issues and re-use possibilities for products

In addition to mitigation of the greenhouse effect, mineral CO_2 sequestration has other environmental effects. Examples of these are: (1) the environmental impact of large-scale mining of ores, (2) the extra emission of non-CO_2 pollutants by the increased energy consumption and (3) the fate of the carbonated products.

The fate of the products is an issue that has not been given much attention in literature so far. The amount of products of CO_2 mineralisation on any significant scale is large and, therefore, studies on re-use possibilities and the environmental impact of carbonated products are required. In addition, a beneficial application of the obtained products, *e.g.* in construction materials, could reduce the sequestration costs. Re-use possibilities are limited due to the small particle size of the products. However, for *e.g.* cement additives fine grinding is already required. If the carbonated products of a mineral CO_2 sequestration process are used as a cement additive, a part of the costs and energy consumption associated with the sequestration process can be allotted to the cement production and, thus, the specific sequestration costs and energy consumption can be lowered[108].

A positive environmental side effect of mineral CO_2 sequestration based on the carbonation of solid residues is the potential improvement of residue properties that could facilitate their utilisation in construction. First, carbonation can improve the constructive properties of materials. The application of slags in concrete, asphalt aggregate and filling materials is often hindered by the high water absorption and expansion properties due the hydration of (Ca,Mg)-oxides. Carbonation can prevent these problems by conversion of the oxides into carbonates[108]. Furthermore, carbonation has also been shown to be able to improve the leaching behaviour of certain solid residues due to, among other factors, pH-neutralisation, mineral formation and sorption effects (Annex C).

Very limited research on the environmental issues associated with mineral CO_2 sequestration has been published. However, at the current state of development of mineral CO_2 sequestration, a thorough investigation of these issues seems a bit premature, because no cost-effective process has been developed yet. One exception is the re-use of the carbonated products. Research on this subject is required because an environmentally acceptable and cost-effective application of the products can potentially increase public acceptance and lower sequestration costs. It is important to note that large-scale mineral CO_2 sequestration could produce such large quantities of products that any possible application market would be over-saturated. However, it might well turn out that mineral CO_2 sequestration can only be cost-effective if the product can be usefully applied, which may put limits on the scale of application.

4. Discussion and conclusions

A very limited number of other review studies has been published in which the state-of-the-art of mineral CO_2 sequestration research has been reviewed and process routes have been compared. A review on 'carbonate chemistry for sequestering fossil carbon'[60] was published by Lackner and gives an extensive overview of sequestration routes based on carbonation chemistry, which could be used to store carbon dioxide (*i.e.*, both in oceanic, underground and solid carbonate storage). However, only a few possible process routes aiming at storing CO_2 as a stable carbonate have been discussed and, unfortunately, no comparison of these routes has been made. In another publication by the same author, the carbonation of serpentine via the direct aqueous carbonation route has been identified as being the most promising option at that moment[61]. However, this process includes an energy-intensive heat-treatment step, which has turned out to make the process energetically and economically unfeasible (see Chapters 2.1 and 2.4 for more details). Another overview of mineral CO_2 sequestration technologies is given by Wei in his masters thesis[115]. The main candidate process routes for CO_2 mineralisation under development at that moment (2003) have been described and technologically assessed. He concluded that the most promising approach seemed the direct carbonation in aqueous solution.

The ECN (2003) review study also concluded that the direct aqueous carbonation route had the best perspective of the mineral CO_2 sequestration process routes studied. In this report we have reviewed the progress made in mineral CO_2 sequestration research as published in 2003 and 2004. The developments discussed in the previous chapters give no reason to change the assessment of the different routes in the ECN (2003) report. Direct aqueous mineral CO_2 sequestration was shown to be, in principle, energetically and technically feasible, but costs are (still) too high to be competitive with other carbon sequestration processes. Cost savings could be achieved by *e.g.* developing suitable large-scale continuous reactors and by applying (new) additives to enhance the dissolution step. Any additives applied should however be (almost) completely regenerable and recyclable. A major breakthrough in reducing mineral CO_2 sequestration costs may be obtained when the substantial CO_2 capture costs can be reduced by integration of CO_2 capture and sequestration. In addition to process development, research on the use of alkaline solid residues as carbonation feedstock and re-use possibilities of carbonated products is recommended, since the beneficial utilisation of carbonation products can contribute to the reduction of sequestration costs.

Mineral CO_2 sequestration (still) is a longer-term option compared to other carbon sequestration possibilities. Its sequestration potential in the short term is limited because of the state of development of the technology. Furthermore, its current sequestration costs are too high compared to other sequestration options and given the expected short-term CO_2 market prices. Only specific applications with an additional benefit such as a useful application of the carbonated product might become feasible. In the long term, mineral CO_2 sequestration could become an employable technology that is part of a broad portfolio of CO_2-reducing technologies, each of which should be applied at its most appropriate situation. Mineral CO_2 sequestration is a relatively new research area and large progress has been made in enhancing the carbonation rate. This observation together with the permanent character of the CO_2 sequestration and the large sequestration potential warrant further research on mineral CO_2 sequestration.

5. Recommendations to the IEA

The IEA Greenhouse Gas R&D Programme published a report in 2000, which assessed the feasibility of six different mineral CO_2 sequestration process routes[43]. These six process routes are:

- Route 1 (reaction with magnesium hydroxide produced from dissolution of a suitable Mg-silicate), which has been discussed in Section 2.2 as the 'HCl extraction route'.
- Route 2 (reaction with magnesium hydroxide produced from dehydration of magnesium-rich brine), which is an example of the processes discussed in Section 0.
- Route 3a (reaction with magnesium hydroxide produced from dissolution of magnesium silicate rock in magnesium chloride melt). See Section 2.2 'Indirect molten salt process'.
- Route 3b (direct carbonation from dissolution of magnesium silicate rock by $MgCl_2$ melt), which has been discussed in Section 2.1 as 'Direct molten salt process'.
- Route 4 (reaction with calcium hydroxide produced from dissolution of a suitable calcium-rich rock). See Section 2.2, 'HCl extraction route'.
- Route 5 (reaction of pressurised CO_2 with seawater-dissolved dolomite), which aims at storing CO_2 in $NaHCO_3$ and is therefore part of Section 0.

The IEA (2000) report identified the 'direct molten salt process' (route 3b) as the only process that had possible potential. However, none of the process routes investigated appeared to lead to a technically, energetically and economically feasible process that could become competitive with other carbon capture and storage technologies.

No recent developments in these process routes have been identified in both the ECN (2003) report and the present update that give reason to change these conclusions and these routes are (still) considered unfeasible. However, almost all research performed in the period 2000-2004 was on routes not considered in the IEA (2000) report. The most important process route that has not been taken into account in the IEA (2000) is the aqueous carbonation route (Section 2.1). A process evaluation study of this process has shown major improvements in energy efficiency and sequestration costs compared to the figures presented in the IEA (2000) report[81,82,*]. As stated above, this process route was selected as the most promising route in the ECN (2003) review and this is confirmed by the present review update.

Given the limited scope of the IEA (2000) report in view of today's knowledge, and the large progress made in mineral CO_2 sequestration research in recent years, an update of the IEA assessment on 'CO_2 storage as carbonate minerals' is, in principle, advisable. However, since a (cost-)evaluation of the most promising process route has been published recently (see Section 2.1), it is questionable whether a new IEA assessment study would provide sufficient new insights at this moment. Furthermore, more information is required on the feasibility of some potentially attractive carbonation routes that are currently in a conceptual stage and on, for example, continuous large-scale carbonation reactors for the aqueous carbonation route. In view of these considerations, the IEA is advised to repeat this literature review, with a similar scope, in 2-3 years. The developments over this period may provide the necessary new insights to warrant a new assessment on mineral CO_2 sequestration by the IEA.

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[*] The calculated mineral CO_2 sequestration costs in the IEA (2000) report are 179 €/ton CO_2 (HCl extraction route) not considering route 3b since the reaction kinetics are unknown. In addition, the net CO_2 sequestration was shown to be negative. In recent years, sequestration costs have been reduced to 67 €/ton CO_2 avoided in the most favourable case (aqueous route) and a net CO_2 sequestration efficiency of 73% has been reported.

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Appendix A Supplementary bibliography mineral CO_2 sequestration

This additional bibliography contains three kinds of papers: (1) papers that are not available to the authors, (2) papers of which only an abstract is available to the authors and (3) conference contributions of which only slides are available but no paper. The full known mineral CO_2 sequestration bibliography (published before January 2005) consists of this annex and the mineral CO_2 sequestration references studied (Chapter 6).

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Appendix B Analogous sequestration routes

Bicarbonate routes

As an alternative to the carbon dioxide sequestration in carbonates, CO_2 can be stored in bicarbonates[41,60]. This route involves the formation of bicarbonates by the further carbonation of carbonate minerals. Main advantages of bicarbonate routes are (1) a wide abundance of carbonate minerals that can be obtained relatively easily compared to silicate ores, (2) the relatively fast formation reaction (*i.e.*, reaction of CO_2 with carbonates is much faster than with (Ca,Mg)-silicates) and (3) a twice as high sequestration potential per mole Ca/Mg when silicates are used as starting material. However, bicarbonates are too soluble to form a solid product in which carbon dioxide can be sequestrated permanently. Therefore, bicarbonate processes typically produce a bicarbonate-containing slurry that has to be disposed of in *e.g.* the ocean or underground.

An example of a bicarbonate route is the reaction of $CaCO_3$ with CO_2 to form a bicarbonate containing slurry that is meant to be disposed of in the ocean[*e.g.*,B.1.1-B.1.2.]. This process might form a relatively cheap and low-tech sequestration alternative assuming disposal does not have negative effects on the oceanic environment. However, the fate of the carbon on the long-term after being returned into the carbon cycle in the form of oceanic bicarbonates has to be assessed.

Brines

Brines typically contain large amounts of cations such as Ca and could therefore be used as feedstock for ex-situ mineral CO_2 sequestration[60,B.2.3]. However, ex-situ CO_2 mineralisation by brine carbonation is impractical due to the huge volumes of hydrochloric acid that would be produced and the limited CO_2 sequestration capacity of useable brines[41].

An alternative could be in-situ carbonation of brines. This so-called mineral trapping mechanism during CO_2 storage in brines has been studied by several researchers[*e.g.*,B.2.1,B.2.4-B.2.6]. The knowledge obtained from research on ex-situ mineral CO_2 sequestration can be applied potentially usefully in the research on mineral trapping due to strong analogies (and vice versa). The same holds for mineral trapping studies during geological storage of CO_2 in *e.g.* saline aquifers[*e.g.*,B2.2] and empty gas fields.

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