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Mineral carbonation and industrial uses of carbon dioxide

Coordinating Lead Author
Marco Mazzotti (Italy and Switzerland)

Lead Authors
Juan Carlos Abanades (Spain), Rodney Allam (United Kingdom), Klaus S. Lackner (United States), Francis Meunier (France), Edward Rubin (United States), Juan Carlos Sanchez (Venezuela), Katsunori Yogo (Japan), Ron Zevenhoven (Netherlands and Finland)

Review Editors
Baldur Eliasson (Switzerland), R.T.M. Sutamihardja (Indonesia)

Contents

EXECUTIVE SUMMARY

This Chapter describes two rather different options for carbon dioxide (CO_2) storage: (i) the fixation of CO_2 in the form of inorganic carbonates, also known as 'mineral carbonation' or 'mineral sequestration', and (ii) the industrial utilization of CO_2 as a technical fluid or as feedstock for carbon containing chemicals.

In the case of mineral carbonation (see Section 7.2), captured CO_2 is reacted with metal-oxide bearing materials, thus forming the corresponding carbonates and a solid byproduct, silica for example. Natural silicate minerals can be used in artificial processes that mimic natural weathering phenomena, but also alkaline industrial wastes can be considered. The products of mineral carbonation are naturally occurring stable solids that would provide storage capacity on a geological time scale. Moreover, magnesium and calcium silicate deposits are sufficient to fix the CO_2 that could be produced from the combustion of all fossil fuels resources. To fix a tonne of CO_2 requires about 1.6 to 3.7 tonnes of rock. From a thermodynamic viewpoint, inorganic carbonates represent a lower energy state than CO_2; hence the carbonation reaction is exothermic and can theoretically yield energy. However, the kinetics of natural mineral carbonation is slow; hence all currently implemented processes require energy intensive preparation of the solid reactants to achieve affordable conversion rates and/or additives that must be regenerated and recycled using external energy sources. The resulting carbonated solids must be stored at an environmentally suitable location. The technology is still in the development stage and is not yet ready for implementation. The best case studied so far is the wet carbonation of the natural silicate olivine, which costs between 50 and 100 US\$/tCO_2 stored and translates into a 30-50% energy penalty on the original power plant. When accounting for the 10-40% energy penalty in the capture plant as well, a full CCS system with mineral carbonation would need 60-180% more energy than a power plant with equivalent output without CCS.

The industrial use of CO_2 (see Section 7.3) as a gas or a liquid or as feedstock for the production of chemicals could contribute to keeping captured CO_2 out of the atmosphere by storing it in anthropogenic carbon products. Industrial uses provide a carbon sink, as long as the pool size keeps growing and the lifetime of the compounds produced is long. Neither prerequisite is fulfilled in practice, since the scale of CO_2 utilization is small compared to anthropogenic CO_2 emissions, and the lifetime of the chemicals produced is too short with respect to the scale of interest in CO_2 storage. Therefore, the contribution of industrial uses of captured CO_2 to the mitigation of climate change is expected to be small.

7.1 Introduction

This chapter deals with: (i) the fixation of CO_2 in the form of inorganic carbonates, also known as 'mineral carbonation' or 'mineral sequestration' that is discussed in Section 7.2, and (ii) the industrial uses of CO_2 as a technical fluid or as feedstock for carbon containing chemicals, which is the subject of Section 7.3.

7.2 Mineral carbonation

7.2.1 Definitions, system boundaries and motivation

Mineral carbonation is based on the reaction of CO_2 with metal oxide bearing materials to form insoluble carbonates, with calcium and magnesium being the most attractive metals. In nature such a reaction is called silicate weathering and takes place on a geological time scale. It involves naturally occurring silicates as the source of alkaline and alkaline-earth metals and consumes atmospheric CO_2. This chapter deals, however, with so-called mineral carbonation, where high concentration CO_2 from a capture step (see Chapter 3) is brought into contact with metal oxide bearing materials with the purpose of fixing the CO_2 as carbonates (Seifritz, 1990; Dunsmore, 1992; Lackner *et al.*, 1995). Suitable materials may be abundant silicate rocks, serpentine and olivine minerals for example, or on a smaller-scale alkaline industrial residues, such as slag from steel production or fly ash. In the case of silicate rocks, carbonation can be carried out either *ex-situ* in a chemical processing plant after mining and pretreating the silicates, or *in-situ*, by injecting CO_2 in silicate-rich geological formations or in alkaline aquifers. Industrial residues on the other hand can be carbonated in the same plant where they are produced. It is worth noting that products of *in-situ* mineral carbonation and geological storage may be similar for the fraction of the CO_2 injected for geological storage that reacts with the alkaline or alkaline-earth metals in the cap rock leading to 'mineral trapping' (see Chapter 5.2.2).

In terms of material and energy balances, mineral carbonation can be schematized as illustrated in Figure 7.1, which applies to a power plant with CO_2 capture and subsequent storage through mineral carbonation. With respect to the same scheme for a power plant with capture and either geological or ocean storage (see Figure 1.4) two differences can be observed. First, there is an additional material flux corresponding to the metal oxide bearing materials; this is present as input and also as output, in the form of carbonates, silica, non-reacted minerals and for some input minerals product water. Secondly, for the same usable energy output, the relative amounts of fossil fuels as input and of energy rejected as lower grade heat are different. *In-situ* carbonation is an operation similar to geological storage, while *ex-situ* carbonation involves processing steps requiring additional energy input that are difficult to compensate for with the energy released by the carbonation reaction. Given the similarities of *in-situ* carbonation with geological storage, this chapter will focus on *ex-situ* mineral carbonation. With present technology there is always a net demand for high grade energy to drive the mineral carbonation process that is needed for: (i) the preparation of the solid reactants, including mining, transport, grinding and activation when necessary; (ii) the processing, including the equivalent energy associated with the use, recycling and possible losses of additives and catalysts; (iii) the disposal of carbonates and byproducts. The relative importance of the three items differs depending on the source of the metal oxides, for example whether they are natural silicates or industrial wastes.

Despite this potential energy penalty, interest in mineral carbonation stems from two features that make it unique among the different storage approaches, namely the abundance of metal oxide bearing materials, particularly of natural silicates, and the permanence of storage of CO_2 in a stable solid form. However,

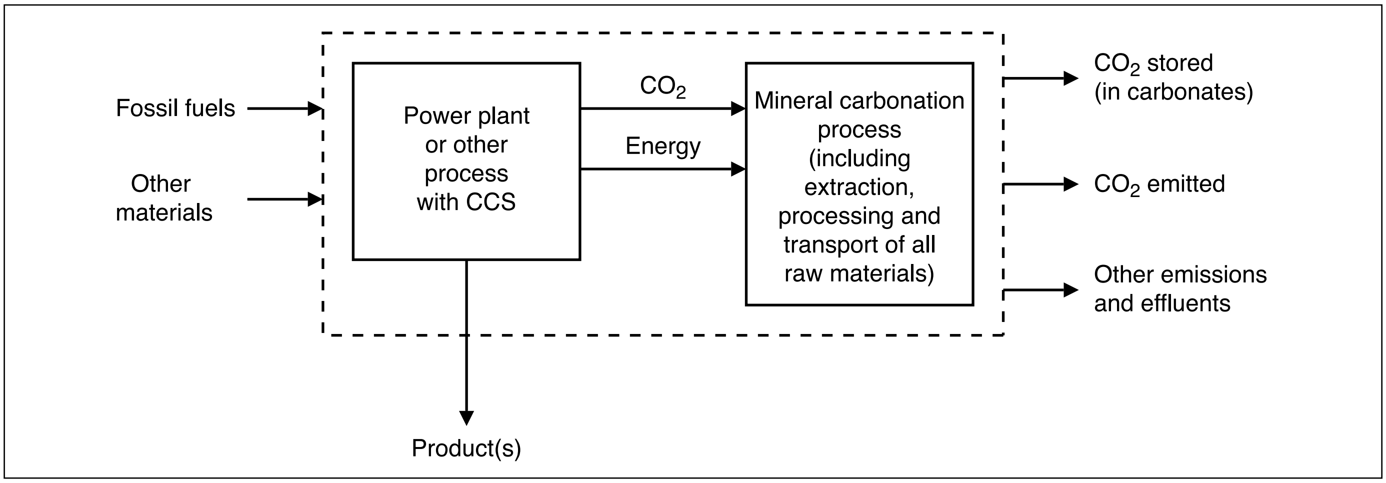

Figure 7.1 Material and energy balances through the system boundaries for a power plant with CO_2 capture and storage through mineral carbonation. The fossil fuel input provides energy both to the power plant that produces CO_2 and to the mineralization process (either directly or indirectly via the power plant). The 'other materials' input serves all processes within the system boundaries and includes the metal oxide bearing materials for mineralization. The 'other emissions' output is made up of the byproducts of the mineralization reaction - silica and possibly water - as well as of non-reacted input materials.

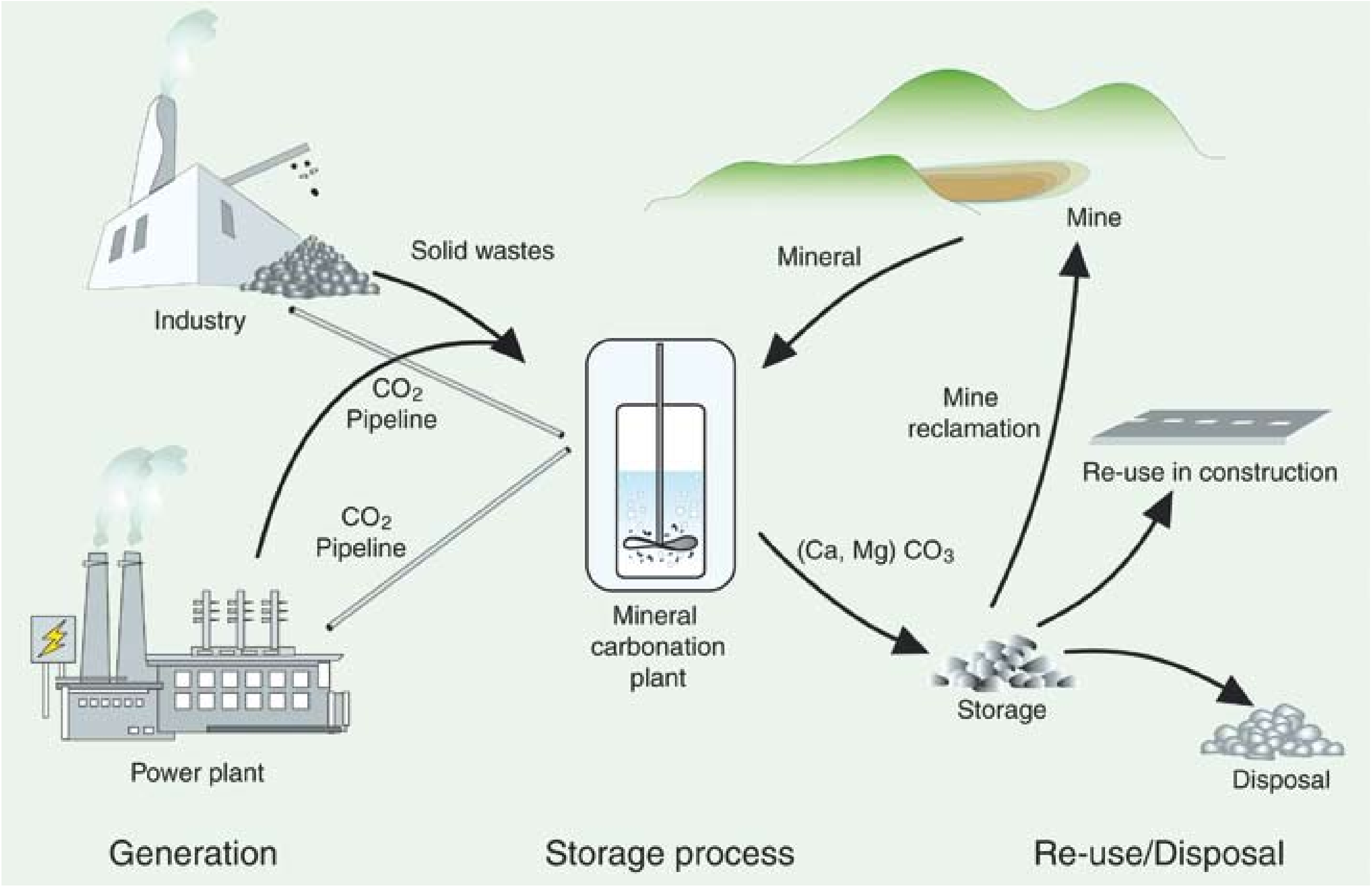

Figure 7.2 Material fluxes and process steps associated with the ex-situ mineral carbonation of silicate rocks or industrial residues (Courtesy Energy Research Centre of the Netherlands (ECN)).

mineral carbonation is today still an immature technology. Studies reported in the literature have not yet reached a level where a thorough assessment of the technology, potential, costs and impacts is possible.

7.2.2 Chemistry of mineral carbonation

When CO_2 reacts with metal oxides (indicated here as MO, where M is a divalent metal, e.g., calcium, magnesium, or iron) the corresponding carbonate is formed and heat is released according to the following chemical reaction:

$$MO + CO_2 \rightarrow MCO_3 + \text{heat} \qquad (1)$$

The amount of heat depends on the specific metal and on the material containing the metal oxide. In general this is a large fraction (up to 46% in the case of calcium oxide) of the heat released by the upstream combustion process forming CO_2 (393.8 kJ $mol^{-1}CO_2$ for combustion of elemental carbon). In the case of a few natural silicates the following exothermic chemical reactions take place (in all cases heat values are given per unit mol of CO_2 and standard conditions 25°C and 0.1 MPa, Robie *et al*. 1978):

Olivine:

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 + 89 \text{ kJ mol}^{-1}CO_2 \qquad (2a)$$

Serpentine:

$$Mg_3Si_2O_5(OH)_4 + 3\ CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O + 64 \text{ kJ mol}^{-1}CO_2 \qquad (2b)$$

Wollastonite:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 + 90 \text{ kJ mol}^{-1}CO_2 \qquad (2c)$$

Since the reaction releases heat, the formation of carbonates is thermodynamically favoured at low temperature, whereas at high temperature (above 900°C for calcium carbonate and above 300°C for magnesium carbonate, at a CO_2 partial pressure of one bar) the reverse reaction, that is calcination, is favoured. The representative member of the olivine family considered in the first reaction above is forsterite, which is iron-free. In nature most olivines contain some iron that can form iron oxides or siderite ($FeCO_3$).

Even at the low partial pressure of atmospheric CO_2 and at ambient temperature, carbonation of metal oxide bearing minerals occurs spontaneously, though on geological time scales (Robie *et al*., 1978; Lasaga and Berner, 1998). Limitations arise from the formation of silica or carbonate layers on the mineral surface during carbonation that tend to hinder further reaction and to limit conversion (Butt *et al.*, 1996) and from the rate of CO_2 uptake from the gas phase in the case of aqueous reactions. The challenge for mineral carbonation is to find ways to accelerate carbonation and to exploit the heat of reaction within the environmental constraints, for example with minimal energy and material losses.

7.2.3 Sources of metal oxides

Most processes under consideration for mineral carbonation focus on metal oxide bearing material that contains alkaline-earth metals (such as calcium and magnesium) as opposed to alkali metals (such as sodium and potassium) whose corresponding carbonates are very soluble in water. Oxides and hydroxides of calcium and magnesium would be the ideal source materials, but because of their reactivity they are also extremely rare in nature. Therefore, suitable metal oxide bearing minerals may be silicate rocks or alkaline industrial residues, the former being abundant but generally difficult to access and the latter scarcer but easily available.

Among silicate rocks, mafic and ultramafic rocks are rocks that contain high amounts of magnesium, calcium and iron and have a low content of sodium and potassium. Some of their main mineral constituents are olivines, serpentine, enstatite ($MgSiO_3$), talc ($Mg_3Si_4O_{10}(OH)_2$) and wollastonite. Although molar abundances of magnesium and calcium silicates in the Earth's crust are similar, rocks containing magnesium silicate exhibit a higher MgO concentration (up to 50% by weight, corresponding to a theoretical CO_2 storage capacity of 0.55 kg CO_2/kg rock), than rocks containing calcium silicates, for example basalts, that have CaO content of about 10% by weight only (with a theoretical CO_2 storage capacity of 0.08 kg CO_2/kg rock) (Goff and Lackner, 1998). Deposits of wollastonite, the most calcium-rich silicate, are much rarer than those of magnesium-rich silicates.

Serpentine and olivine are mainly found in ophiolite belts – geological zones where colliding continental plates lead to an uplifting of the earth's crust (Coleman 1977). For example, considering ultramafic deposits containing serpentine and olivine in the Eastern United States and in Puerto Rico, it was found that they have R_{CO2} values between 1.97 and 2.51, depending on purity and type (the R_{CO2} is the ratio of the mass of mineral needed to the mass of CO_2 fixed when assuming complete conversion of the mineral upon carbonation, that is the reciprocal of the theoretical CO_2 storage capacity introduced above). Peridotites and serpentinites exceed the total Mg requirement to neutralize the CO_2 from all worldwide coal resources estimated at 10,000 Gt (Lackner *et al.*, 1995). Specific ore deposits identified in two studies in the USA and Puerto Rico add to approximately 300GtCO$_2$ (Goff and Lackner, 1998; Goff *et al.*, 2000). This should be compared to CO_2 emissions of about 5.5 GtCO$_2$ in the United States and about 24 GtCO$_2$/yr^{-1} worldwide. No comprehensive mapping of the worldwide storage potential in ophiolite belts has been reported. However, their total surface exposure is estimated to be of the order of 1000 km by 100 km (Goff *et al.*, 2000). It is well known however that magnesium silicate reserves are present in all continents, but since they tend to follow present or ancient continental boundaries, they are not present in all countries. The feasibility of their use for *ex-situ* or *in-situ* mineral carbonation is yet to be established (Brownlow, 1979; Newall *et al.*, 2000).

On a smaller-scale, industrial wastes and mining tailings provide sources of alkalinity that are readily available and reactive. Even though their total amounts are too small to substantially reduce CO_2 emissions, they could help introduce the technology. Waste streams of calcium silicate materials that have been considered for mineral carbonation include pulverized fuel ash from coal fired power plants (with a calcium oxide content up to 65% by weight), bottom ash (about 20% by weight CaO) and fly ash (about 35% by weight CaO) from municipal solid waste incinerators, de-inking ash from paper recycling (about 35% by weight CaO), stainless steel slag (about 65% by weight CaO and MgO) and waste cement (Johnson, 2000; Fernández Bertos *et al.*, 2004; Iizuka *et al.*, 2004).

7.2.4 Processing

7.2.4.1 Mining and mine reclamation

Mining serpentine would not differ substantially from conventional mining of other minerals with similar properties, for example copper ores. Serpentine and olivine are both mined already, although rarely on the scale envisioned here (Goff and Lackner, 1998; Goff *et al.*, 2000). Like in other mining operations, disposal of tailings and mine reclamation are important issues to consider. Tailing disposal depends on the material characteristics – particle size and cohesion, moisture content and chemical stability against natural leaching processes – and these depend in turn on the specific process. It is likely that carbonation plants will be located near the metal oxide bearing material, either the factory producing the residues to be treated or the silicate mine, to avoid transport of solid materials (see Figure 7.2).

Economies of scale applying to today's mining technology suggest a minimum mining operation of 50,000 to 100,000 tonnes day^{-1} (Hartman, 1992), which translates into a minimum mineable volume of about 0.3 km^3 for a mine with a 30 year life. This is a rather small size for ophiolite ore bodies, which are often kilometres wide and hundreds of meters thick (Goff and Lackner, 1998; Goff *et al.*, 2000; Newall *et al.*, 2000). Since coal, in contrast to ophiolite bodies, occurs in thin seams and is buried under substantial overburden, it has been argued that a typical above ground coal mine must move more material (Lackner *et al.*, 1995) and disturb a far larger area (Ziock and Lackner, 2000) for the same amount of carbon atoms treated than the equivalent ophiolite mine, assuming maximum conversion of the mineral to carbonate (one carbon atom yields one CO_2 molecule upon combustion, which has to be fixed in one molecule of carbonate).

Serpentine can take many different forms, from decorative stones to chrysotile asbestos (O'Hanley, 1996). The possibility of encountering asbestos requires adequate precautions. With current best practice it would reportedly not be an obstacle

(Newall et al., 2000). Moreover, since the asbestos form of serpentine is the most reactive, reaction products are expected to be asbestos free (O'Connor et al., 2000). Mineral carbonation could therefore remediate large natural asbestos hazards that occur in certain areas, in California for example (Nichols, 2000).

7.2.4.2 *Mineral pretreatment*

Mineral pretreatment, excluding the chemical processing steps, involves crushing, grinding and milling, as well as some mechanical separation, for example magnetic extraction of magnetite (Fe_3O_4).

7.2.4.3 *CO_2 pre-processing*

Mineral carbonation requires little CO_2 pre-processing. If CO_2 is pipelined to the disposal site, the constraints on pipeline operations are likely to exceed pre-processing needs for mineral carbonation. The current state of research suggests that CO_2 should be used at a pressure similar to the pipeline pressure, thus requiring minimal or no compression (Lackner, 2002; O'Connor *et al*., 2002). Purity demands in carbonation are minimal; acidic components of the flue gas could pass through the same process as they would also be neutralized by the base and could probably be disposed of in a similar manner. Most carbonation processes would preheat CO_2, typically to between 100°C and 150°C for aqueous processes, whereas in gas-solid reactions temperatures could reach 300°C to 500°C (Butt *et al*., 1996).

7.2.4.4 *Carbonation reaction engineering*

The simplest approach to mineral carbonation would be the reaction of gaseous CO_2 with particulate metal oxide bearing material at suitable temperature and pressure levels. Unfortunately, such direct gas-solid reactions are too slow to be practical in the case of the materials mentioned in Section 7.2.3 (Newall *et al*., 2000) and are only feasible at reasonable pressures for refined, rare materials like the oxides or hydroxides of calcium and magnesium (Butt and Lackner, 1997; Bearat *et al.,* 2002; Zevenhoven and Kavaliauskaite, 2004). As a result, mineral carbonation without refined materials cannot directly capture CO_2 from flue gases, but could possibly in the case of pressurized CO_2 rich gases from IGCC plants.

Since the direct fixation of carbon dioxide on solid unrefined material particles seems at present not feasible, the alternative requires the extraction of the metal from the solid. This can be accomplished by suspending the solid material in an aqueous solution and by letting it dissolve and release metal ions, for example calcium or magnesium ions. These ions come in contact with carbonic acid (H_2CO_3) that is formed in the same solution upon carbon dioxide dissolution. Conditions can be achieved where the carbonate and the byproducts – silica in the case of silicate carbonation for example – precipitate. This involves proper choice of the operating parameters of this single-step or multi-step process – particularly temperature, concentration of possible additives and CO_2 pressure (that controls the carbonic acid concentration in solution). At the end of the operation a suspension of fine particles of carbonate, byproducts and non-reacted solid materials remains. These have to be separated by filtration and drying from the solution from which residual metal ions and additives are to be quantitatively recovered.

This wet process scheme is currently in the research phase and has to overcome three major hurdles to become cost-effective and to be considered as a viable option for carbon storage: (i) acceleration of the overall rate of the process, which may be limited by the dissolution rate of the metal oxide bearing material; (ii) elimination of the interference between the concomitant metal oxide dissolution and carbonate precipitation; (iii) complete recovery of all the chemical species involved, if additives are used.

Mineral carbonation starting from natural silicates is a slow process that can be kinetically enhanced by raising the temperature, although thermodynamics are a limiting factor. In aqueous systems, this is typically kept below 200°C, since high temperature favours gaseous CO_2 over precipitated carbonates. It is believed that the metal oxide dissolution constitutes the rate-limiting step and most research efforts have been devoted to finding ways to speed up the metal extraction from the solid input materials. This could be achieved either by activating the mineral to make it more labile and reactive, or by enhancing the metal oxide extraction through the presence of additives or catalysts in solution. Activation can take different forms, namely heat-treatment at 650ºC for serpentine (Barnes *et al*., 1950; Drägulescu *et al*., 1972; O'Connor *et al*., 2000) and ultra-fine (attrition) grinding for olivine and wollastonite (O'Connor *et al*., 2002; Kim and Chung, 2002). The energy cost of activation has been estimated to be of 300 kWh t^{-1} of mineral and 70–150 kWh t^{-1} of mineral for thermal and mechanical activation, respectively (O'Connor *et al*., 2005). Carbonation has been successfully performed after such pretreatment, but it is so expensive and energy-intensive that its feasibility is questionable (see Box 7.1 and O'Connor *et al*., 2005). Dissolution catalysts that can be added to the aqueous solution include strong and weak acids (Pundsack, 1967; Lackner *et al.,* 1995; Fouda *et al.,* 1996; Park *et al.,* 2003; Maroto-Valer *et al*., 2005), bases (Blencoe *et al.,* 2003) and chelating agents to extract SiO_2 or MgO groups from the mineral (Park *et al.,* 2003). All three approaches have been studied and at least partially experimentally tested, but in all cases catalyst recovery represents the key hurdle. It is worth noting that the carbonation of metal oxides from industrial wastes can be faster than that of natural silicates (Johnson, 2000; Fernández Bertos *et al*., 2004; Huijgen *et al*., 2004; Iizuka *et al*., 2004; Stolaroff *et al*., 2005).

Hydrochloric acid (HCl) dissolution of serpentine or olivine was proposed first (Houston, 1945; Barnes *et al*., 1950; Wendt *et al*., 1998a). The process requires a number of steps to precipitate magnesium hydroxide ($Mg(OH)_2$), which can then directly react with gaseous CO_2, and to recover HCl. Exothermic and endothermic steps alternate and heat recovery is not always possible, thus making the overall process very energy-intensive and not viable (Wendt *et al*., 1998a; Newall *et al*., 2000; Lackner, 2002). Likewise, strong alkaline solutions (with NaOH) will dissolve the silica from the magnesium

Box 7.1 Wet mineral carbonation process.

A comprehensive energy and economic evaluation of the single-step wet carbonation process has been reported (O'Connor et al., 2005). Though limited to the specific carbonation process illustrated in Figure 7.3, this study is based on about 600 experimental tests and looks not only at the fundamental and technical aspects of the process, but also at the matching of carbon dioxide sources and potential sinks that in this case are natural silicate deposits. In particular, seven large ultramafic ores in the USA have been considered (two olivines, four serpentines (three lizardites and one antigorite) and one wollastonite). Three are located on the west coast, three on the east coast and one in Texas. The selection of the seven ores has also been based on considerations of regional coal consumption and potential CO_2 availability.

The three different minerals exhibit different reactivity, measured as the extent of the carbonation reaction after one hour under specified operating conditions. A trade-off has been observed between the extent of reaction and mineral pretreatment, thus higher reactivity is obtained for more intense pretreatment, which represents an energy cost. Mechanical activation is effective for the olivine and the wollastonite and involves the use of both conventional rod and ball milling techniques with an energy consumption of up to about 100 kWh t^{-1} mineral (standard pretreatment) and ultra-fine grinding for up to more than 200 kWh t^{-1} mineral (activated process). Conversion is no more than 60% in the former case and up to above 80% in the latter. In the case of the serpentine, after milling (standard pretreatment), thermal activation at 630°C is effective for the antigorite (up to 92% conversion) but only partially for the lizardite (maximum conversion not larger than 40%) and requires an energy consumption of about 350 kWh t^{-1} mineral. Optimal operating conditions for this wet process are mineral dependent and correspond to 185°C and 15 MPa for the olivine, 155°C and 11.5 MPa for the heat treated serpentine, and 100°C and 4 MPa for the wollastonite. In the first two cases, the carbonation reaction takes place in the presence of 0.64 mol L^{-1} sodium bicarbonate and 1 mol L^{-1} sodium chloride.

Table 7.1 Mineral carbonation storage costs for CO_2.

Ore (type of pre-treatment)	Conversion after 1 hour (%)	Cost (US$/t ore)	Energy input[a] (kWh/tCO_2 stored)	Cost (US$/t$CO_2$ stored)
Olivine (standard)	61	19	310	55
Olivine (activated)	81	27	640	59
Lizardite (standard)	9	15	180	430
Lizardite (activated)	40	44	180+2120=2300	210
Antigorite (standard)	62	15	180	250
Antigorite (activated)	92	48	180+830=1010	78
Wollastonite (standard)	43	15	190	91
Wollastonite (activated)	82	19	430	64

[a] The study assumes a coal fired power plant with 35% efficiency, corresponding to one tonne of CO_2 released per 1000 kWh electricity. The equivalent heat value for the same coal input is then 2,850 kWh. The two items in the sum break the total energy input into electrical + thermal; in all other cases it is pure electrical energy.

Process costs have been calculated for these seven ores in the case of both standard mineral pretreatment and activated process. Costs include only storage, thus neither CO_2 capture nor CO_2 transport and are based on the assumption that CO_2 is received pure at 15 MPa at the plant. Investment costs are calculated accounting for the different reactor costs depending on the different operating conditions corresponding to the different mineral ores. Storage costs are calculated per tonne of silicate ore and per tonne of CO_2 stored and are complemented by the energy consumption per tonne of CO_2 stored in the above Table. The table highlights a trade-off between energy input associated with the pretreatment procedure and cost per unit carbon dioxide stored. Assuming that the cheapest technology is used for each mineral, costs range from 55 US$/t$CO_2$ stored for olivine (standard pretreatment), to 64 US$/t$CO_2$ stored for wollastonite (activated), to 78 US$/t$CO_2$ stored for antigorite (activated), to 210 US$/t$CO_2$ stored for lizardite (activated). Since the last case requires too large an energy input, the cost of the most realistic technologies falls into a range from 50 to 100 US$/t$CO_2$ stored.

silicate, thus allowing for further digestion of the remaining ($Mg(OH)_2$); however, also in this case the recovery of the NaOH catalyst seems to be very difficult (Blencoe *et al.,* 2003). To overcome the substantial energy penalty of water evaporation in the hydrochloric acid process, it was proposed to dissolve the silicate minerals in a magnesium chloride melt in order either to precipitate $Mg(OH)_2$ as before or to allow for direct carbonation in the melt (Wendt *et al.*, 1998a; 1998b; 1998c; 1998d). No experimental demonstration of this process has been provided, possibly also because of the corrosive conditions of the reaction; energy and material balances indicate that either version of the process will hardly be viable (Newall *et al.*, 2000; Haywood *et al.*, 2001).

Weaker acids that might reduce the energy requirements for recovery include acetic acid (Kakizawa *et al.*, 2001), oxalic acid (Park *et al.*, 2003), orthophosphoric acid (Park *et al.*, 2003) and ammonium bisulphate (Pundsack 1967). Among the possible chelating agents that keep either silicates or magnesium ions in solution by forming water-soluble complexes, is EDTA – ethylene-diamine-tetra-acetic acid (Carey *et al.*, 2003; Park *et al.*, 2003; Park and Fan, 2004). Citric acid is also effective because it combines its acidic properties with strong chelating properties (Carey *et al.*, 2003). All these additives have been proven to enhance the dissolution of silicate minerals, but only in the acetic acid case has a complete process scheme, including acid recovery, been described and evaluated (Kakizawa *et al.*, 2001). This is based on two steps, whereby the metal ions are extracted first using acetic acid and then the carbonate is

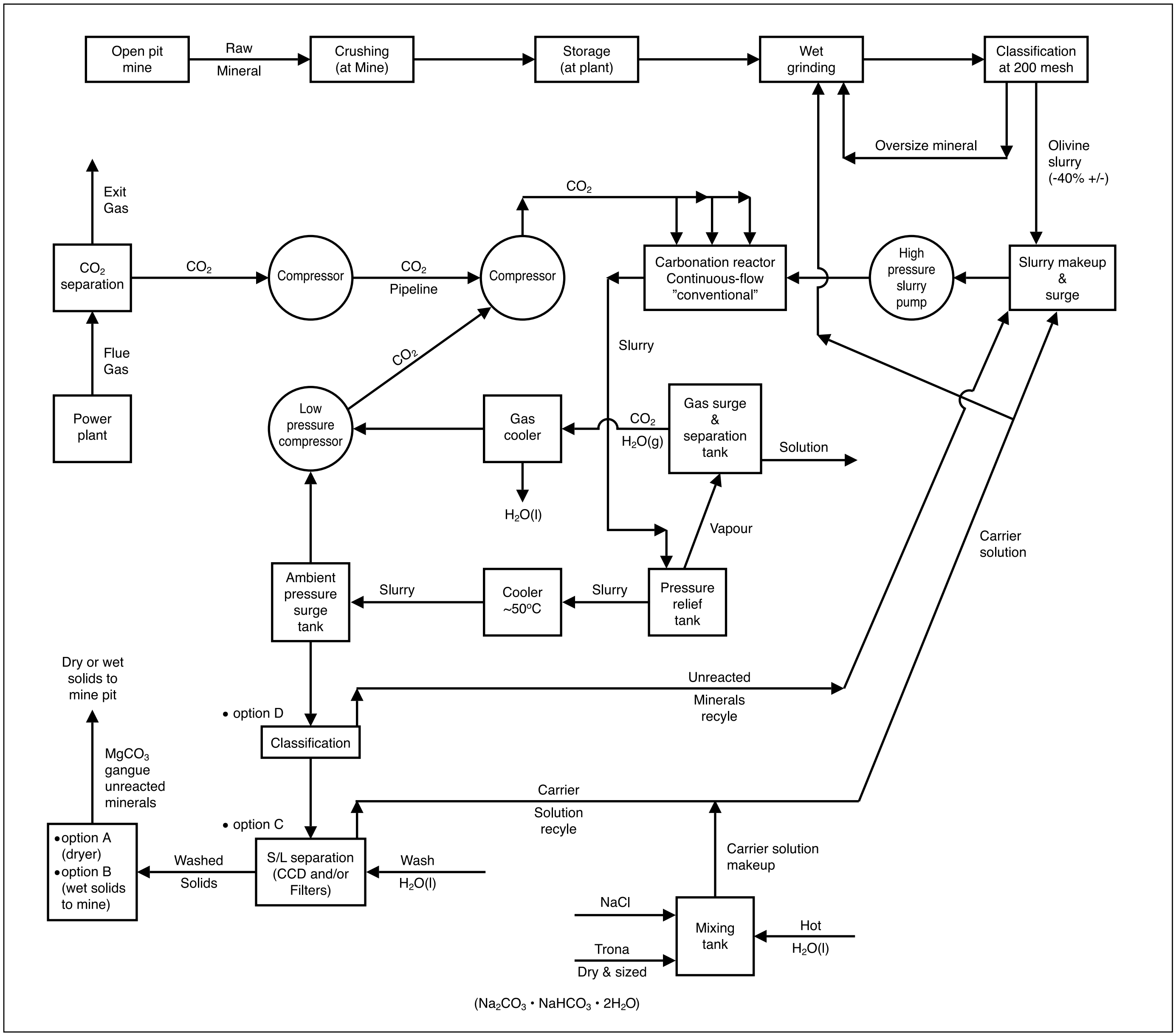

Figure 7.3 Process scheme of the single-step mineral carbonation of olivine in aqueous solution (Courtesy Albany Research Centre). 'Single-step' indicates that mineral dissolution and carbonate precipitation take place simultaneously in the same carbonation reactor, whereas more steps are of course needed for the whole process, including preparation of the reactants and separation of the products.

precipitated upon CO_2 addition. Acetic acid remains in solution as either calcium or magnesium acetate or free acid and can be recycled. The process has only been demonstrated for wollastonite. Experimental conversion levels of the wollastonite have not exceeded 20% (Kakizawa *et al*., 2001).

7.2.4.5 A worked out example: single-step carbonation

Figure 7.3 illustrates the single step wet mineral carbonation process that can be applied to natural silicates as well as to industrial residues, for example steel slag (Huijgen *et al*., 2004). The figure refers to the carbonation of olivine, whereby the mineral is ground first. Subsequently it is dissolved in an aqueous solution of sodium chloride (NaCl, 1 mol L^{-1}) and sodium bicarbonate ($NaHCO_3$, 0.64 mol L^{-1}) in contact with high pressure CO_2 and carbonated therein (O'Connor *et al*., 2002; O'Connor *et al*., 2005). The additives are easily recovered upon filtration of the solid particles, since the sodium and chloride ions do not participate in the reaction and remain in solution, whereas the bicarbonate ion is replenished by contacting the solution in the carbonation reactor with the CO_2 atmosphere. A maximum conversion of 81% in one hour was obtained with an olivine of 37 μm particle size, at a temperature of 185°C and a CO_2 partial pressure of 15 MPa. An important element of the process scheme in Figure 7.3 is the classification (sieving) that allows separating the carbonate and silica products from the olivine that has to be recycled. This is possible since non-reacted olivine minerals are coarse, whereas the carbonate and silica consist of finer particles (O'Connor *et al*., 2002). An additional difficulty of single-step carbonation is when, upon extraction of the metal oxide from the solid particles, a silica layer forms or a carbonate layer precipitates on the particles themselves, thus hindering further dissolution. Experimental evidence indicates that this does not occur in the case of olivine (O'Connor *et al*., 2002), whereas it does occur in the case of steel slag (Huijgen *et al*., 2004).

Using the process scheme illustrated in Figure 7.3, it is possible to calculate the material balances by considering that the molecular mass of carbon dioxide is 44.0 g mol^{-1}, of magnesium carbonate is 84.3 g mol^{-1}, of silica is 60.1 g mol^{-1} and of olivine is 140.7 g mol^{-1}. For the sake of simplicity only two assumptions are made, namely the degree of conversion in the carbonation reactor – the fraction of olivine fed to the reactor that is converted to carbonate in a single pass – and the fraction of non-reacted mineral in the classifier that is not recycled, but ends up with the material for disposal. Based on the stoichiometry of the carbonation reaction, 1.6 tonnes of olivine would be needed to fix one tonne of CO_2, thus producing 2.6 tonnes of solid material for disposal. Assuming 90% carbonation conversion and 10% losses in the classifier, 1.62 tonnes of olivine would be needed and 2.62 tonnes of solids per tonne of CO_2 mineralized would be for disposal. Assuming only 50% conversion and 20% losses, for one tonne of CO_2 stored, 1.87 tonnes of olivine would be needed and 2.87 tonnes would be disposed of. In the latter case however the carbonation reactor would be twice as big as in the former case.

Olivine has the highest concentration of reactive magnesium oxide among the natural minerals (57% by weight). Other minerals in general contain a lower concentration. For pure serpentine the magnesium oxide concentration is about 44% and for typical ores about 50% of that of the pure mineral. Therefore, the mineral feedstock required to fix 1 tonne of CO_2 in carbonates is between 1.6 and 3.7 tonnes and the process yields between 2.6 and 4.7 tonnes of products to be handled. The carbonation process consumes energy and thus causes CO_2 emissions that reduce the net storage of CO_2 accordingly. For the olivine carbonation process, having the lowest unit cost among those described in Box 7.1, the energy requirement is 1.1 GJ/tCO_2. If this is provided by the same coal derived electricity it would cause CO_2 emissions equal to 30% of the fixed CO_2.

7.2.5 *Product handling and disposal*

Disposal options for mineral carbonates are determined by the mass of the resulting material (see Figure 7.2). It is not cost-effective to ship the bulk of these materials over long distances. As a result the obvious disposal location is at the mine site. As in any large-scale mining operation, the logistics of mining a site and reclaiming it after refilling it with the tailings is substantial, but it does not pose novel problems (Newall *et al.,* 2000). The amount of material to be disposed of is between 50 and 100% by volume more than that originally mined. These volumes are comparable to volumes commonly handled in mining operations and are subject to standard mine reclamation practice (Lackner *et al*., 1997; Newall *et al.,* 2000).

The fine grinding of the mineral ore might allow for the extraction of valuable mineral constituents. Serpentine and olivine mines could provide iron ore that either would be removed as magnetite by magnetic separation or result from chemical precipitation during magnesium extraction, yielding concentrated iron oxide or hydroxide (Park and Fan, 2004). Peridotite rocks may contain chromite, elements like nickel and manganese and also elements in the platinum group, but how these can be recovered has still to be studied (Goff and Lackner, 1998). It has been suggested, that magnesium carbonate and silica may find uses as soil enhancers, roadfill or filler for mining operations. Eventually mineral carbonation would have to operate at scales that would saturate any product or byproduct market, but products and byproducts, when usable, could help make a demonstration of the process more viable (Lackner *et al.,* 1997; Goff and Lackner, 1998).

7.2.6 *Environmental impact*

The central environmental issue of mineral carbonation is the associated large-scale mining, ore preparation and waste-product disposal (Goff and Lackner, 1998). It can directly lead to land clearing and to the potential pollution of soil, water and air in surrounding areas. It may also indirectly result in habitat degradation. An environmental impact assessment would be required to identify and prevent or minimize air emissions, solid waste disposal, wastewater discharges, water use, as well as social disturbances. As for many other mining activities, the preventing and mitigating practices are relatively basic and well developed.

Land clearing: The amount of material required to store CO_2 involves extensive land clearing and the subsequent displacement of millions of tonnes of earth, rock and soil, increasing the potential for erosion, sedimentation and habitat loss in the area. Access roads would also lead to clearing of vegetation and soil. Standard practices recommended to minimize these impacts include storage of topsoil removed for use in future reclamation activities, use of existing tracks when constructing access roads and pipelines and use of drainage and sediment collection systems to catch runoff or divert surface water, minimizing erosion.

Air quality: Mining activities like blasting, drilling, earth moving and grading can generate dust and fine particulate matter that affect visibility and respiration and pollute local streams and vegetation. Dust prevention measures are widely applied at mining operations today, but if not properly controlled, dust can threaten human respiratory health. This is particularly important in serpentine mining because serpentine often contains chrysotile, a natural form of asbestos. Even though chrysotile is not as hazardous as amphibole asbestos (tremolite, actinolite) (Hume and Rimstidt, 1992), the presence of chrysotile requires covering of exposed veins and monitoring of air quality (Nichols, 2000). On the other hand, mineral carbonation products are asbestos free, as the reaction destroys chrysotile, which reacts faster than other serpentines, even if conversion of the starting material is not complete. This makes mineral carbonation a potentially effective method for the remediation of asbestos in serpentine tailing (O'Connor *et al*., 2000). The resulting mineral carbonates are inert, but large volumes of powders would also have to be controlled, for example by cementing them together to avoid contamination of soil and vegetation, as well as habitat destruction.

Tailings: Tailings consist of finely ground particles, including ground-up ore and process byproducts. Tailings management systems should be designed and implemented from the earliest stages of the project. Usually tailings are stored in tailings impoundments designed to hold tailings behind earth-fill dams (Newall *et al*., 2000). Other control measures depend on whether tailings are dry or wet, on particle size and chemical reactivity.

Leaching of metals: Although the low acidity of the resulting byproducts reduces the possibility of leaching, certainty about leaching can only be obtained by conducting tests. If necessary, a lining system would prevent ground water contamination. Leaching containment is also possible without lining where underlying rock has been shown to be impermeable.

Reclamation: To minimize water contamination, restore wildlife habitat and ecosystem health and improve the aesthetics of the landscape, a comprehensive reclamation programme has to be designed during the planning phase of the mining project and be implemented concurrently throughout operations. Concurrent incorporation of reclamation with the mining of the site reduces waste early, prevents clean-up costs and decreases potential liabilities. Land rehabilitation will involve the re-shaping of landform, because the volume of tailings will be larger than the mined rock. The main environmental concern regarding reclamation is major soil movements by erosion or landslides. This can be controlled by adequate vegetation cover and by covering the soil with protective mulch, by maintaining moisture in the soil, or by constructing windbreaks to protect the landform from exposure to high winds.

7.2.7 *Life Cycle Assessment and costs*

At the current stage of development, mineral carbonation consumes additional energy and produces additional CO_2 compared to other storage options. This is shown in Figure 7.1 and is why a Life Cycle Assessment of the specific process routes is particularly important. The potential of mineral carbonation depends on the trade-off between costs associated with the energy consuming steps (mining, pre-processing of the mineral ore, its subsequent disposal and mine reclamation) and benefits (the large potential capacity due to the vast availability of natural metal oxide bearing silicates and the permanence of CO_2 storage).

A life cycle analysis of the mining, size reduction process, waste disposal and site restoration calculated additional annual CO_2 emissions of 0.05 tCO_2/tCO_2 stored (Newall *et al*., 2000). This included grinding of the rock to particle sizes less than 100 microns; a ratio of 2.6 tonnes of serpentine per tonne of CO_2 was assumed. The cost was assessed to be about 14 US\$/tCO_2 stored; the capital cost being about 20% of the total. All cost estimates were based on OECD Western labour costs and regulations. The conversion factor from electrical energy to CO_2 emissions was 0.83 tCO_2/MWh electricity. Costs were calculated on the basis of an electricity price of US\$ 0.05 kWh^{-1} electricity. Results from other studies were converted using these values (Newall *et al*., 2000). Other estimates of these costs are between 6 and 10 US\$/tCO_2 stored, with 2% additional emissions (Lackner *et al*., 1997).

As far as the scale of mining and disposal is concerned – about 1.6 to 3.7 tonnes of silicate and 2.6 to 4.7 tonnes of disposable materials per tonne of CO_2 fixed in carbonates, as reported in Section 7.2.4 – this is of course a major operation. When considering that one tonne of carbon dioxide corresponds to 0.27 tonnes of carbon only in theory, but in practice to about 2 tonnes of raw mineral due to the overburden, it follows that mineral carbonation to store the CO_2 produced by burning coal would require the installation of a mining industry of a scale comparable to the coal industry itself. Such large mining operations are significant, but placing them in the context of the operations needed for the use of fossil fuels and geological or ocean storage, the volumes are comparable.

The energy requirements and the costs of the carbonation reaction are very much process dependent and more difficult to estimate, due to scarcity of data. The most detailed study has been carried out for the process where the silicates are dissolved in a magnesium chloride melt (Newall *et al*., 2000). An overall cost (including the operations mentioned in the previous paragraph) of 80 US\$/tCO_2 stored was obtained, with 27.5% additional CO_2 emissions, thus leading to 110 US\$/tCO_2 avoided. In the case of the two-step acetic acid process, an overall cost of 27 US\$/tCO_2 avoided has been reported, but the assumptions are based on a rather limited set of experimental data (Kakizawa *et al.*, 2001). A comprehensive energy and economic evaluation of the single step wet carbonation process illustrated in Figure 7.3 has been recently reported (O'Connor *et al.*, 2005) and is discussed in detail in Box 7.1. This study calculates storage costs between 50 and 100 US\$/tCO_2 stored, with between 30% and 50% of the energy produced needed as input to the mineral carbonation step, i.e. a corresponding reduction of power plant efficiency from 35% for instance to 25% and 18%, respectively. This implies that a full CCS system with mineral carbonation would need 60-180% more energy than a power plant with equivalent output without CCS, when the 10-40% energy penalty in the capture plant is accounted too. No similar economic evaluation is available for either dry mineral carbonation or carbonation using industrial residues. However, it is worth pointing out that the carbonation of toxic wastes may lead to stabilized materials with reduced leaching of heavy metals. Therefore these materials might be disposed of more easily or even used for applications such as in construction work (see Figure 7.2) (Venhuis and Reardon, 2001; Meima *et al.*, 2002).

Once the carbon has been stored through mineral carbonation, there are virtually no emissions of CO_2 due to leakage. To the extent that weathering at the disposal site occurs and leaches out magnesium carbonate from the carbonation products, additional CO_2 would be bound in the transformation of solid magnesium carbonate to dissolved magnesium bicarbonate (Lackner, 2002). It can therefore be concluded that the fraction of carbon dioxide stored through mineral carbonation that is retained after 1000 years is virtually certain to be 100%. As a consequence, the need for monitoring the disposal sites will be limited in the case of mineral carbonation.

7.2.8 Future scope

7.2.8.1 Public acceptance

Public acceptance of mineral carbonation is contingent on the broader acceptance of CCS. Acceptance might be enhanced by the fact that this method of storage is highly verifiable and unquestionably permanent. On the downside, mineral carbonation involves large-scale mining and associated environmental concerns: terrain changes, dust pollution exacerbated by potential asbestos contamination and potential trace element mobilization. Generally, public acceptance will require a demonstration that everything possible is done to minimize secondary impacts on the environment.

7.2.8.2 Gap analysis

Mineral carbonation technology must reduce costs and reduce the energy requirements associated with mineral pretreatment by exploiting the exothermic nature of the reaction. Mineral carbonation will always be more expensive than most applications of geological storage, but in contrast has a virtually unlimited permanence and minimal monitoring requirements. Research towards reducing costs for the application of mineral carbonation to both natural silicates and industrial wastes, where the kinetics of the reaction is believed to be more favourable, is ongoing. Moreover, an evaluation is needed to determine the fraction of the natural reserves of silicates, which greatly exceed the needs, that can be effectively exploited for mineral carbonation. This will require thorough study, mapping the resources and matching sources and sinks, as in O'Connor *et al.* (2005). The actual size of the resource base will be significantly influenced by the legal and societal constraints at a specific location. Integrating power generation, mining, carbonation reaction, carbonates' disposal and the associated transport of materials and energy needs to be optimized in a site-specific manner. A final important gap in mineral carbonation is the lack of a demonstration plant.

7.3 Industrial uses of carbon dioxide and its emission reduction potential

7.3.1 Introduction

As an alternative to storing captured CO_2 in geological formations (see Chapter 5), in the oceans (see Chapter 6), or in mineral form as carbonates (see Section 7.2), this section of the report assesses the potential for reducing net CO_2 emissions to the atmosphere by using CO_2 either directly or as a feedstock in chemical processes that produce valuable carbon containing products. The utilization of CO_2 establishes an inventory of stored CO_2, the so-called carbon chemical pool, primarily in the form of carbon-containing fuels, chemicals and other products (Xiaoding and Moulijn, 1996). The production and use of these products involve a variety of different 'life cycles' (i.e., the chain of processes required to manufacture a product from raw materials, to use the product for its intended purpose and ultimately to dispose of it or to reuse it in some fashion). Depending on the product life-cycle, CO_2 is stored for varying periods of time and in varying amounts. As long as the recycled carbon remains in use, this carbon pool successfully stores carbon. Withdrawal from this pool, by decay or by disposal typically re-injects this carbon into the atmospheric pool.

CO_2 that has been captured using one of the options described in Chapter 3 could reduce net CO_2 emissions to the atmosphere if used in industrial processes as a source of carbon, only if the following criteria are met:

1. The use of captured CO_2 must not simply replace a source of CO_2 that would then be vented to the atmosphere. Replacement of CO_2 derived from a lime kiln or a fermentation process would not lead to a net reduction in CO_2 emissions, while on the other hand replacement of CO_2 derived from natural geological deposits, which would thus be left undisturbed, would lead to a net reduction of CO_2 emissions. This would apply to the majority of the CO_2 used for enhanced oil recovery in the USA (see Section 5.3.2)

that is currently provided from natural geological deposits (Audus et Oonk, 1997).

2. The compounds produced using captured CO_2 must have a long lifetime before the CO_2 is liberated by combustion or other degradation processes.
3. When considering the use of captured CO_2 in an industrial process, the overall system boundary must be carefully defined to include all materials, fossil fuels, energy flows, emissions and products in the full chain of processes used to produce a unit of product in order to correctly determine the overall (net) CO_2 avoided.

CO_2 reductions solely due to energy efficiency improvements are not within the scope of this report, which is focused on capture and storage rather than efficiency improvements. Similarly while environmental benefits like those obtained in replacing organic solvents with supercritical CO_2 may slightly increase the carbon chemical pool, these primary drivers are not discussed in this report. Similarly, this report specifically excludes all uses of captured CO_2 to replace other chemicals that are released into the atmosphere and that have high greenhouse-gas potential, fluorocarbons for example. This area is covered by the IPCC/TEAP Special Report on Safeguarding the Ozone Layer and the Global Climate System: issues related to Hydrofluorocarbons and Perfluorocarbons (IPCC/TEAP, 2005).

The third point is especially important in any effort to estimate the potential for net CO_2 reductions from the substitution of a CO_2-utilizing process for alternative routes to manufacturing a desired product. In particular, it is essential that the system boundary encompasses all 'upstream' processes in the overall life cycle and does not focus solely on the final production process of interest. The appropriate system boundary is shown schematically in Figure. 7.4 This is an extension of the system boundary diagrams shown earlier in Section 7.2 (Figure 7.1) and in Chapter 1 (Figure 1.4) in the context of a CO_2 capture and storage system. The inputs include all fossil fuels together with all other materials used within the system. The fossil fuel input provides energy to the power or industrial plant, including the CO_2 capture system, as well as the elemental carbon used as building blocks for the new chemical compound. Flows of CO_2, energy and materials pass from the primary fuel-consuming processes to the industrial process that utilizes the captured CO_2. This produces a desired product (containing carbon derived from captured CO_2) together with other products (such as useful energy from the power plant) and environmental emissions that may include CO_2 plus other gaseous, liquid or solid residuals.

Once the overall system has been defined and analyzed in this way, it can also be compared to an alternative system that does not involve the use of captured CO_2. Using basic mass and energy balances, the overall avoided CO_2 can then be assessed as the difference in net emissions associated with the production of a desired product. In general, the difference could be either positive or negative, thus meaning that utilization of CO_2 could result in either a decrease or increase in net CO_2 emissions, depending on the details of the processes being compared. Note that only fossil fuels as a primary energy source are considered in this framework. Renewable energy sources and nuclear power are specifically excluded, as their availability would have implications well beyond the analysis of CO_2 utilization options (see Chapter 8 for further discussion). Note too that other emissions from the process may include toxic or harmful materials, whose flows also could be either reduced or increased by the adoption of a CO_2-based process.

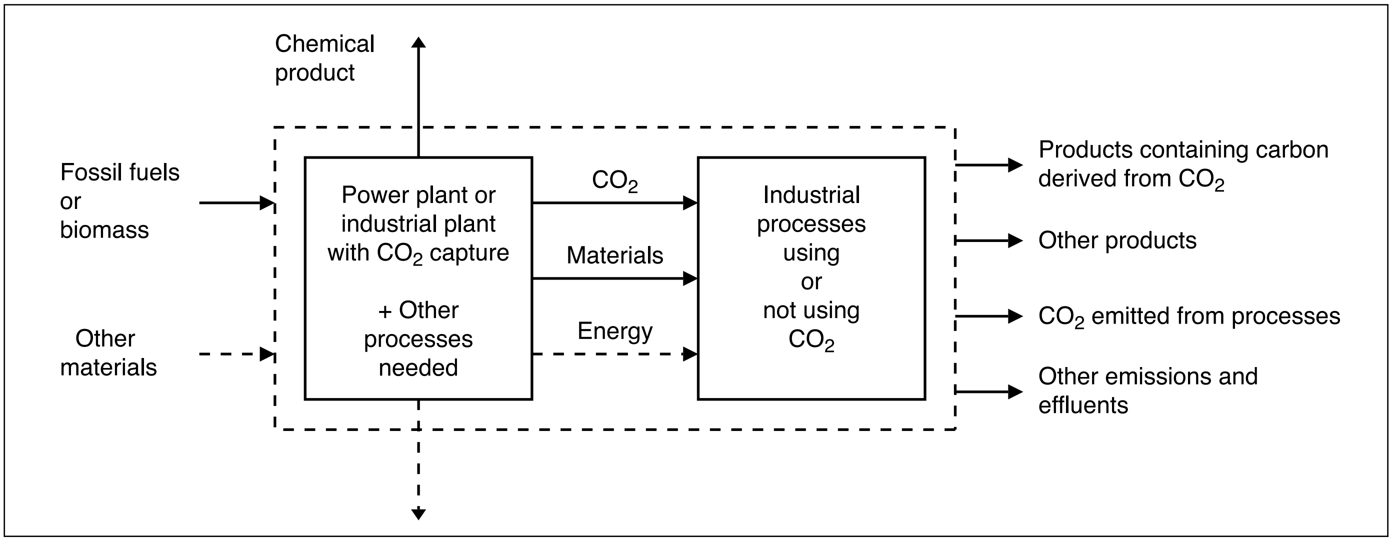

Figure 7.4 Material and energy balances through the system boundaries for a power plant or an industrial plant with CO_2 capture, followed by an industrial process using CO_2. The inputs include all fossil fuels together with all other materials used within the system. The fossil fuel input provides energy to the power or industrial plant, including the CO_2 capture system, as well as the elemental carbon used as building blocks for the new chemical compound. From the primary fuel-consuming processes, flows of CO_2, energy and materials pass to the industrial process, which utilizes the captured CO_2. This produces a desired product (containing carbon, derived from captured CO_2) together with other products (such as useful energy from the power plant) and environmental emissions that may include CO_2 plus other gaseous, liquid or solid residuals.

The application of this framework to the assessment of CO_2 utilization processes is discussed in more detail later in this chapter. First, however, we will examine current uses of CO_2 in industrial processes and their potential for long-term CO_2 storage.

7.3.2 *Present industrial uses of carbon dioxide*

Carbon dioxide is a valuable industrial gas with a large number of uses that include production of chemicals, for example urea, refrigeration systems, inert agent for food packaging, beverages, welding systems, fire extinguishers, water treatment processes, horticulture, precipitated calcium carbonate for the paper industry and many other smaller-scale applications. Large quantities of carbon dioxide are also used for enhanced oil recovery, particularly in the United States (see Section 5.3.2). Accordingly, there is extensive technical literature dealing with CO_2 uses in industry and active research groups are exploring new or improved CO_2 utilization processes.

Much of the carbon dioxide used commercially is recovered from synthetic fertilizer and hydrogen plants, using either a chemical or physical solvent scrubbing system (see Section 3.5.2). Other industrial sources of CO_2 include the fermentation of sugar (dextrose) used to produce ethyl alcohol:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \qquad (3)$$

Industrial CO_2 is also produced from limekilns, such as those used in the production of sodium carbonate and in the Kraft wood pulping process. This involves the heating (calcining) of a raw material such as limestone:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (4)$$

In some parts of the world, such as the United States, Italy, Norway and Japan, some CO_2 is extracted from natural CO_2 wells. It is also recovered during the production and treatment of raw natural gas that often contains CO_2 as an impurity (see Chapter 2 for more details about CO_2 sources).

A large proportion of all CO_2 recovered is used at the point of production to make further chemicals of commercial importance, chiefly urea and methanol. The CO_2 recovered for other commercial uses is purified, liquefied, delivered and stored mostly as a liquid, typically at 20 bar and –18°C (Pierantozzi, 2003).

Table 7.2 shows the worldwide production and CO_2 usage rates for the major chemical or industrial applications currently using CO_2 (excluding enhanced oil recovery, which is dealt with in Chapter 5). The approximate lifetime of stored carbon before it is degraded to CO_2 that is emitted to the atmosphere is also shown. Such values mean that the fraction of the CO_2 used to produce the compounds in the different chemical classes or for the different applications, which is still stored after the period of time indicated in the last column of Table 7.2 drops to zero.

7.3.3 *New processes for CO_2 abatement*

7.3.3.1 *Organic chemicals and polymers*

A number of possible new process routes for the production of chemicals and polymers have been considered in which CO_2 is used as a substitute for other C_1 building blocks, such as carbon monoxide, methane and methanol. The use of CO_2, an inert gas whose carbon is in a highly oxidized state, requires development of efficient catalytic systems and, in general, the use of additional energy for CO_2 reduction. Chemicals that have been considered include polyurethanes and polycarbonates, where the motivation has primarily been to avoid the use of phosgene because of its extreme toxicity, rather than to find a sink for CO_2. The proposed processes can have a lower overall energy consumption than the current phosgene-based routes leading to further CO_2 emission reductions. Current world consumption of polycarbonates is about 2.7 Mt yr^{-1}. If all polycarbonate production was converted to CO_2-based processes the direct consumption of CO_2 would be about 0.6 $MtCO_2yr^{-1}$. Some CO_2

Table 7.2 Industrial applications of CO_2 (only products or applications at the Mtonne-scale): yearly market, amount of CO_2 used, its source, and product lifetime (Aresta and Tommasi, 1997; Hallman and Steinberg, 1999; Pelc et al., 2005). The figures in the table are associated with a large uncertainty.

Chemical product class or application	Yearly market (Mt yr^{-1})	Amount of CO_2 used per Mt product ($MtCO_2$)	Source of CO_2	Lifetime[b]
Urea	90	65	Industrial	Six months
Methanol (additive to CO)	24	<8	Industrial	Six months
Inorganic carbonates	8	3	Industrial, Natural[a]	Decades to centuries
Organic carbonates	2.6	0.2	Industrial, Natural[a]	Decades to centuries
Polyurethanes	10	<10	Industrial, Natural[a]	Decades to centuries
Technological	10	10	Industrial, Natural[a]	Days to years
Food	8	8	Industrial, Natural[a]	Months to years

[a] Natural sources include both geological wells and fermentation.

[b] The fraction of used CO_2 that is still stored after the indicated period of time drops to zero.

savings that are difficult to quantify from current published data are claimed for energy/materials changes in the process.

Similarly, if all world polyurethane production was converted, then direct CO_2 consumption would be about 2.7 $MtCO_2$/yr. However, little progress in commercial application of CO_2-based production has been reported. And as indicated earlier, these possible CO_2 applications directly affect only a very small fraction of the anthropogenic CO_2 emitted to the atmosphere. The net savings in CO_2 would be even smaller or could be negative, as the energy that was available in the hydrocarbon resource is missing in the CO_2 feedstock and unless compensated for by improved process efficiency it would have to be made up by additional energy supplies and their associated CO_2 emissions.

7.3.3.2 *Fuel production using carbon dioxide*

Liquid carbon-based fuels, gasoline and methanol for example, are attractive because of their high energy density and convenience of use, which is founded in part on a well-established infrastructure. Carbon dioxide could become the raw material for producing carbon-based fuels with the help of additional energy. Since energy is conserved, this cannot provide a net reduction in carbon dioxide emissions as long as the underlying energy source is fossil carbon. If a unit of energy from a primary resource produces a certain amount of CO_2, then producing a fuel from CO_2 will recycle CO_2 but release an equivalent amount of CO_2 to provide the necessary energy for the conversion. Since all these conversion processes involve energy losses, the total CO_2 generated during fuel synthesis tends to exceed the CO_2 converted, which once used up, is also emitted.

Production of liquid carbon-based fuels from CO_2 only reduces CO_2 emissions if the underlying energy infrastructure is not based on fossil energy. For example, one could still use gasoline or methanol rather than converting the transport sector to hydrogen, by using hydrogen and CO_2 as feedstocks for producing gasoline or methanol. The hydrogen would be produced from water, using hydropower, nuclear energy, solar energy or wind energy. As long as some power generation using fossil fuels remains, carbon dioxide for this conversion will be available (Eliasson, 1994). Alternatively, it might be possible to create a closed cycle with CO_2 being retrieved from the atmosphere by biological or chemical means. Such cycles would rely on the availability of cheap, clean and abundant non-fossil energy, as would the hydrogen economy, and as such they are beyond the scope of this report.

Methanol production is an example of the synthesis of liquid fuels from CO_2 and hydrogen. Today a mixture of CO, CO_2 and hydrogen is produced through reforming or partial oxidation or auto thermal reforming of fossil fuels, mainly natural gas. The methanol producing reactions, which are exothermic, take place over a copper/zinc/alumina catalyst at about 260°C (Inui, 1996; Arakawa, 1998; Ushikoshi *et al*., 1998; Halmann and Steinberg, 1999):

$$CO + 2H_2 \rightarrow CH_3OH \qquad (5)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad (6)$$

Alternatively one could exploit only reaction (6), by using captured CO_2 and hydrogen from water hydrolysis powered for instance by solar energy (Sano *et al*., 1998).

7.3.3.3 *Capture of CO_2 in biomass*

Biomass production of fuels also falls into the category of generating fuels from CO_2. With the help of photosynthesis, solar energy can convert water and CO_2 into energetic organic compounds like starch. These in turn can be converted into industrial fuels like methane, methanol, hydrogen or bio-diesel (Larson, 1993). Biomass can be produced in natural or agricultural settings, or in industrial settings, where elevated concentrations of CO_2 from the off-gas of a power plant would feed micro-algae designed to convert CO_2 into useful chemicals (Benemann, 1997). Since biological processes collect their own CO_2, they actually perform CO_2 capture (Dyson, 1976). If the biomass is put to good use, they also recycle carbon by returning it to its energetic state. Biomass production eliminates the need for fossil fuels, because it creates a new generation of biomass-based carbonaceous fuels. As a replacement for fossil energy it is outside the scope of this report. As a CO_2 capture technology, biomass production is ultimately limited by the efficiency of converting light into chemically stored energy. Currently solar energy conversion efficiencies in agricultural biomass production are typically below 1% (300 GJ ha^{-1} yr^{-1} or 1 W m^{-2} (Larson, 1993)). Micro-algae production is operating at slightly higher rates of 1 to 2% derived by converting photon utilization efficiency into a ratio of chemical energy per unit of solar energy (Melis *et al*., 1998; Richmond and Zou, 1999). Hence the solar energy collection required for micro-algae to capture a power plant's CO_2 output is about one hundred times larger than the power plant's electricity output. At an average of 200 W m^{-2} solar irradiation, a 100 MW power plant would require a solar collection area in the order of 50 km^2.

7.3.4 *Assessment of the mitigation potential of CO_2 utilization*

This final section aims at clarifying the following points: (i) to what extent the carbon chemical pool stores CO_2; (ii) how long CO_2 is stored in the carbon chemical pool; (iii) how large the contribution of the carbon chemical pool is to emission mitigation.

To consider the first point, the extent of CO_2 storage provided by the carbon chemical pool, it is worth referring again to Table 7.2. As reported there, total industrial CO_2 use is approximately 115 $MtCO_2$ yr^1. Production of urea is the largest consumer of CO_2, accounting for over 60% of that total. To put it in perspective, the total is only 0.5% of total anthropogenic CO_2 emissions – about 24 $GtCO_2$ yr^1. However, it is essential to realize that these figures represent only the yearly CO_2 flux in and out of the carbon chemical pool, and not the actual size of the pool, which is controlled by marketing and product distribution considerations and might be rather smaller than the total yearly CO_2 consumption. Moreover, the contribution to the storage of carbon – on a yearly basis for instance – does not correspond to the size of the pool, but to its size variation on a yearly basis, or in general on its rate of change that might be positive (increase of carbon storage and reduction of CO_2 emissions) or negative (decrease of carbon storage and increase of CO_2 emissions) depending on the evolution of the markets and of the distribution systems (see also Box 7.2 for a quantitative example). Data on the amount of carbon stored as inventory of these materials in the supply chain and on the rate of change of this amount is not available, but the figures in Table 7.2 and the analysis above indicate that the quantity of captured carbon that could be stored is very small compared with total anthropogenic carbon emissions. Thus, the use of captured CO_2 in industrial processes could have only a minute (if any) effect on reduction of net CO_2 emissions.

As to the second point, the duration of CO_2 storage in the carbon chemical pool and typical lifetime of the CO_2 consuming chemicals when in use before being degraded to CO_2 that is emitted to the atmosphere, are given in the last column of Table 7.2 Rather broad ranges are associated with classes of compounds consisting of a variety of different chemicals. The lifetime of the materials produced that could use captured CO_2 could vary from a few hours for a fuel such as methanol, to a few months for urea fertilizer, to decades for materials such as plastics and laminates, particularly those materials used in the construction industry. This indicates that even when there is a net storage of CO_2 as discussed in the previous paragraph, the duration of such storage is limited.

As to the last point, the extent of emission mitigation provided by the use of captured CO_2 to produce the compounds in the carbon chemical pool. Replacing carbon derived from a fossil fuel in a chemical process, for example a hydrocarbon, with captured CO_2 is sometimes possible, but does not affect the overall carbon budget, thus CO_2 does not replace the fossil fuel feedstock. The hydrocarbon has in fact two functions – it provides energy and it provides carbon as a building block. The CO_2 fails to provide energy, since it is at a lower energy level than the hydrocarbon (see Box 7.3). The energy of the hydrocarbon is often needed in the chemical process and, as in the production of most plastics, it is embodied in the end product. Alternatively, the energy of the hydrocarbon is available and likely to be utilized in other parts of the process, purification, pretreatment for example, or in other processes within the same plant. If this energy is missing, since CO_2 is used as carbon source, it has to be replaced somehow to close the energy balance of the plant. As long as the replacement energy is provided from fossil fuels, net CO_2 emissions will remain unchanged. It is worth noting that an economy with large non-fossil energy resources could consider CO_2 feedstocks to replace hydrocarbons in chemical synthesis. Such approaches are not covered here, since they are specific examples of converting to non-fossil energy and as such are driven by the merits of the new energy source rather than by the need for capture and storage of CO_2.

7.3.5 *Future scope*

The scale of the use of captured CO_2 in industrial processes is too small, the storage times too short and the energy balance too unfavourable for industrial uses of CO_2 to become significant as a means of mitigating climate change. There is a lack of data available to adequately assess the possible overall CO_2 inventory of processes that involve CO_2 substitution with associated energy balances and the effects of changes in other feedstocks

Box 7.2 Carbon chemical pool.

The carbon chemical pool is the ensemble of anthropogenic carbon containing organic chemicals. This box aims to provide criteria for measuring the quantitative impact on carbon mitigation of such a pool. If this impact were significant, using carbon from CO_2 could be an attractive storage option for captured CO_2.

Considering a specific chemical A, whose present worldwide production is 12 Mt yr^{-1}, whose worldwide inventory is 1 Mt – the monthly production – and whose lifetime before degradation to CO_2 and release to the atmosphere is less than one year. If next year production and inventory of A do not change, the contribution to CO_2 storage of this member of the chemical pool will be null. If production increased by a factor ten to 120 Mt yr^{-1}, whereas inventory were still 1 Mt, again the contribution of A to CO_2 storage would be null.

If on the contrary next year production increases and inventory also increases, for example to 3 Mt, to cope with increased market demand, the contribution of A to CO_2 storage over the year will be equivalent to the amount of CO_2 stoichiometrically needed to produce 2 Mt of A. However, if due to better distribution policies and despite increased production, the worldwide inventory of A decreased to 0.7 Mt, then A would yield a negative contribution to CO_2 storage, thus over the year the amount of CO_2 stoichiometrically needed to produce 0.3 Mt of A would be additionally emitted to the atmosphere.

Therefore, the impact on carbon dioxide mitigation of the carbon chemical pool does not depend on the amounts of carbon containing chemical products produced; there is CO_2 emission reduction in a certain time only if the pool has grown during that time. With increasing production, such impact can be positive or negative, as shown above. It is clear that since this would be a second or third order effect with respect to the overall production of carbon containing chemicals – itself much smaller in terms of fossil fuel consumption than fossil fuel combustion – this impact will be insignificant compared with the scale of the challenge that carbon dioxide capture and storage technologies have to confront.

Box 7.3. Energy gain or penalty in using CO_2 as a feedstock instead of carbon.

CO_2 can be used as a provider of carbon atoms for chemical synthesis, as an alternative to standard processes where the carbon atom source is fossil carbon, as coal or methane or other. This includes processes where the carbon atom in the CO_2 molecule is either reduced by providing energy, for example methanol synthesis, or does not change its oxidation state and does not need energy, synthesis of polycarbonates for example.

For the sake of simplicity let us consider a reaction from carbon to an organic final product A (containing n carbon atoms) that takes place in a chemical plant (standard process):

$$nC \rightarrow A \qquad (7)$$

Let us also consider the alternative route whereby CO_2 captured from the power plant where carbon has been burnt is used in the chemical plant where the synthesis of A is carried out. In this case the sequence of reactions would be:

$$nC \rightarrow nCO_2 \rightarrow A \qquad (8)$$

The overall energy change upon transformation of C into A, ΔH, is the same in both cases. The difference between the two cases is that in case (8) this overall energy change is split into two parts – $\Delta H = \Delta H_{com} + \Delta H_{syn}$ – one for combustion in the power plant and the other for the synthesis of A from CO_2 in the chemical plant (ΔH_{com} will be –400 which means 400 are made available by the combustion of carbon). If ΔH is negative, that means an overall exothermic reaction (1), then ΔH_{syn} will be either negative or even positive. If ΔH is positive, that means an overall endothermic reaction (7), then ΔH_{syn} will be even more positive. In both cases, exothermic or endothermic reaction, the chemical plant will lack 400 kJ/molC energy in case (2) with respect to case (1). This energy has already been exploited in the power plant and is no longer available in the chemical plant. It is worth noting that large-scale chemical plants (these are those of interest for the purpose of carbon dioxide emission mitigation) make the best possible use of their energy by applying so-called heat integration, for example by optimizing energy use through the whole plant and not just for individual processes. In case (1) chemical plants make good use of the 400 kJ/molC that are made available by the reaction (7) in excess of the second step of reaction (8).

Therefore, in terms of energy there is no benefit in choosing path (8) rather than path (7). In terms of efficiency of the whole chemical process there might be a potential improvement, but there might also be a potential disadvantage, since route (7) integrates the heat generation associated with the oxidation of carbon and the conversion to product A. These effects are of second order importance and have to be evaluated on a case-by-case basis. Nevertheless, the scale of the reduction in CO_2 emissions would be rather small, since it would be even smaller than the scale of the production of the chemicals that might be impacted by the technology change, that is by the change from path (7) to path (8) (Audus and Oonk, 1997).

and emissions. However, the analysis above demonstrates that, although the precise figures are difficult to estimate and even their sign is questionable, the contribution of these technologies to CO_2 storage is negligible. Research is continuing on the use of CO_2 in organic chemical polymer and plastics production, but the drivers are generally cost, elimination of hazardous chemical intermediates and the elimination of toxic wastes, rather than the storage of CO_2.

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