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Chemical fixation of CO_2 in carbonates: Routes to valuable products and long-term storage

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Abstract

Carbon dioxide emissions to the atmosphere can be reduced by chemical fixation in organic or inorganic carbonates. Many compounds can be commercially produced on an industrial scale using CO_2, allowing for turning a (nowadays problematic) waste gas into economic profit. Besides this, the carbonation of magnesium silicates and calcium silicates is an option for long-term storage of CO_2 at a capacity that exceeds that of other options for CO_2 storage by several orders of magnitude, with the inherent benefit that post-storage monitoring of the stored CO_2 is not necessary. The first part of this paper gives an overview of commercial carbonate chemical production routes that do (or in a near future can) make use of the CO_2 that is produced at a large scale from human activities. The second part addresses the process technology, market potential and other aspects of mineral carbonation for long-term CO_2 storage as an alternative for, for example, storage in underground aquifers.

Keywords: Carbon dioxide; Organic carbonates; Inorganic carbonates; Mineral carbonation; Fixation; Storage

1. Introduction

Avoiding the currently ongoing climate change caused by CO_2 and other greenhouse gases requires the long-term or permanent storage of several gigatonnes (Gt) of CO_2 annually. Using CO_2 as a chemical feedstock gives only a marginal yet not irrelevant contribution to the CO_2 mitigation. The size of the markets of the products produced using industrially produced CO_2 and their lifetime before again releasing the fixed CO_2 are limited, being of the order of 120 megatonnes (Mt) annually at the moment (urea stands for 60% of this!) and 100 years (for polyurethanes used in building insulation), respectively.

Nonetheless, financial, legal, social and environmental factors promote the development of markets and technologies that make use of industrially produced (more generally: antrophogenic) CO_2 as a chemical feedstock. Since the 1990s increasing amounts of fuels, polymers and other organic products, and inorganic products have been produced using new or alternative routes. Besides a small contribution to CO_2 emissions reduction, such processes often have the benefit of higher energy efficiency, lower fossil fuel consumption, less pollution or the use of less toxic chemicals [1–3]. This paper will address one group of possible products, namely organic and inorganic carbonate chemical materials. The main organic carbonate products are dimethyl carbonate (DMC) and the polymer polycarbonate (PC), while for the inorganic carbonates, primarily the (earth-) alkali carbonates are addressed.

Finally, the option of long-term CO_2 storage based on the carbonation of mineral silicates is addressed, a technology that – provided that it can be developed into mature, large-scale process technology – has the capacity to store all fossil-bound carbon on earth as environmentally benign magnesium carbonate [4].

As this ‘‘mini-review’’ paper is based on a presentation at the ICCDU-VIII conference special reference is made to work presented at the previous, ICCDU-VII conference.

2. Organic carbonate products

The organic carbonate products, produced by oxidative carboxylation by CO_2, can be divided into: (1) dimethyl and diethyl carbonate (DMC, DEC), (2) polycarbonates (PC) and (3) other, primarily cyclic, organic carbonates. As CO_2 is an oxidised form of carbon, the conversion reactions will require

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energy to be brought in externally or via reactants with a high free energy content. Very important is also the role of homogeneous or heterogeneous catalysis and one of the bottlenecks for large-scale process development is to find heterogeneous catalysts to replace homogeneous catalysts for reasons of product separation, catalyst recovery and costs [5].

2.1. Dimethyl carbonate (and diethyl carbonate)

Dimethyl carbonate (DMC) is used for the production of polycarbonate, polyurethane and other chemicals. Also, DMC is of interest as an additive to gasoline or fuel oil, increasing the octane number and reducing particulate emissions from diesel engines [1,6]. Total global DMC production capacity was estimated at 0.1 Mt/yr in 1993 [1], in 1997 [6] it was estimated at less than 1000 bbl/day, i.e. around 0.06 Mt/yr, noting that a large US refinery would need 5–10 times that amount if DMC is to be added to gasoline on a large scale. This and other uses for DMC would then yield a market volume of 2000 Mt annually, as anticipated in Ref. [7]; more recently [8] a market potential of 30 Mt/yr for DMC use as gasoline additive was reported. Although exact numbers can hardly be given (for example several plants have been/are being erected in China), current DMC production capacity can be estimated to be 0.1–0.5 Mt/yr.

DMC is commercially produced from methanol and (toxic) phosgene ($COCl_2$), and alternative routes are being developed based on the carboxylation of methanol as summarised in Table 1. A review on (catalysis in) DMC production and its chemistry was published by Ono in 1997 [10]; more recently the chemistry of DMC, a non-toxic and biodegradable ‘‘green reactant’’ was presented by Tundo and Selva [11].

Several papers at the ICCDU-VII conference addressed the heterogeneous catalysis of DMC synthesis. Sun reported methanol conversions to DMC of more than 50% for a route with urea (urea conversion near 100%), with a ZnO-based catalyst. For the more difficult route from methanol and CO_2, which suffers from thermodynamic limitations, the best results (11% methanol conversion) were obtained with supercritical CO_2 (9.3 MPa) [5]. Wei et al. have obtained near 100% conversion of methanol with propylene carbonate to DMC with specially prepared (‘‘pugged’’) CaO/C catalyst [12]. For the production of DMC from CO_2 and methanol, Han et al. [13] proposed $Ce_{1-x}Zr_xO_2$ composite oxides as the best catalysts. Urea methanolysis in two steps (via methyl carbamate) was analysed by Wang et al. [14], showing that ZnO gave the highest DMC yield (37%), as also found by Sun [5]. Aresta et al. reported on homogeneous catalysis of carbamate and carbonate production from urea with methanol (to DMC) and ethanol (to DEC) [15]. Promising results were found for triazine ligands of $ZnCl_2$ and $NiCl_2$.

Other recent developments on DMC synthesis from methanol, mainly aiming at catalyst activity, stability and recovery involve highly dispersed Cu on SiO_2 catalysts [16], Cu + X zeolite [17], zirconia catalysts with a primarily monoclinic surface [18] and organo-tin catalysis [19].

As for the energy efficiency of the phosgene-free routes, it was shown that the route via methanolation of urea might yield lower overall CO_2 emissions, yet the opposite may be true for a badly optimised process especially when using coal or oil as the energy source. A high DMC yield, minimisation of loss of catalyst and, less importantly, minimisation of losses of ammonia and methanol must be achieved. Very important is to minimise the amount of excess methanol used [7]. Audus and Oonk [20] discuss the feasibility of alternative processes using CO_2 that intend to have a CO_2 mitigation effect.

2.2. Polycarbonate

Polycarbonate (PC), which has excellent mechanical properties and good UV light resistance, is widely used in optical media, in the automotive sector and as glazing. Annual production capacity of PC resin was around 0.15 Mt in 1979, 1 Mt in 1996 [3] and 2.6 Mt in 2002 [9] with General Electric and Bayer as the largest producers. Commercial production was initially based on reacting phenol with phosgene, giving diphenyl carbonate that was reacted with bisphenol A (BPA) to give the PC polymer and recoverable phenol. Current processing mostly implies interfacial polymerisation via reaction between alkali salts of BPA and phosgene. Driven by concerns about phosgene toxicity and the economics of converting the chlorine from phosgene to sodium chloride led to the development of an alternative route where diphenyl carbonate is produced from phenol and DMC. The diphenyl carbonate then yields PC via two-stage transesterification with BPA [6,9]. Currently this route stands for around 15% of global PC production capacity. The future aim is to produce diphenyl carbonate from CO_2 and phenol, circumventing the use of DMC [9].

After Inoue and co-workers discovered in 1969 that a $ZnEt_2/H_2O$ catalyst could catalyse co-polymerisation of propylene oxide (a relatively cheap feedstock) and CO_2, a large worldwide effort was made to develop better catalysts. Depending on catalyst, feedstock and process conditions mixtures of monomers, polymers and cyclic carbonates were obtained. The production of polypropylene carbonate is attractive since this can be applied as a mid-segment in polyurethanes. Darensbourg and Holtcamp [21] gave a review for the situation

Table 1
Non-phosgene routes to DMC

Reactants	Products	Catalyst	Reference
Methanol + urea	DMC + NH_3	Pd/C, $Mn(Ac)_2$	[6,9]
Methanol + NO	DMC (via methyl nitrite intermediate)	Pd/C	[6,9]
Methanol + ethylene carbonate[a]	DMC + ethylene glycol	Div. acid–base	[6,9]
Methanol + CO + O_2	DMC	CuCl, Cu/C	[6,9]

[a] Produced from CO_2 + ethylene oxide.

at the mid-1990s. By then, work on ring-opening polymerisation of cyclic carbonates showed that six-membered cyclic carbonate can give pure high molecular weight polymer polycarbonate, while five-membered cyclic carbonates require higher temperatures and results in poly ether carbonate plus CO_2. Very recently the literature on CO_2 and epoxide coupling was reviewed by Coates and Moore [22], mentioning that catalysts for epoxide/CO_2 coupling that have both sufficient activity and thermal stability are based on Cr, Co and Zn. One challenge is the production of aliphatic polycarbonates without at the same time producing significant amounts of cyclic carbonates.

At ICCDU-VII, Kim et al. reported on the production of aliphatic PC by co-polymerisation of cyclohexene with CO_2 using a homogeneous catalyst based on metal cyanide and zinc chloride. Multi metal cyanide (MMC) catalysts appeared much more reactive than double metal cyanide catalysts [23].

Recent work by Coates and co-workers showed that Co-based (salcy)complexes have a high selectivity towards polycarbonate, despite being only half as active as Cr and Zn catalysts [24]; similar findings were reported by Lu and Wang [25]. Darensbourg and Yarbourgh, also aiming at minimising cyclic carbonate formation studied a (salen) Cr(III)Cl complex and effectively produced poly cyclohexenylene carbonate from cyclohexene oxide [26]. Beta diimine (BDI) ligands, converted into (BDI) ZnX complexes show ‘‘unprecedented polymerisation activity’’ for CO_2 and epoxides [27].

2.3. Cyclic and other organic (carbonate) products

The routes to linear and cyclic organic carbonates have been summarised by Halmann and Steinberg [3], see also Refs. [1,21,22]. Ethylene and propylene can react with CO_2 at ~750 K under triethylamine and $CaCl_2$ catalysis to yield ethylene carbonate and propylene carbonate, respectively, which are used as petrochemical solvents. Unsaturated organic carbonate compounds including pyrones and lactones can be formed from alkynes and CO_2 [1], or from dienes and CO_2, using a Pd-based catalyst [28]. Cyclic organic carbonates can be produced from epoxides and CO_2 as well—these products have many applications as high boiling point solvents and can react with ammonia or amines to form carbamates. Eventually, carbamates can be further converted into polyurethane polymer, a very versatile material for which a very large market exists [1,6,29].

Sun stated at ICCDU-VII that five-membered cyclic carbonates have many synthetic uses and reported that (cyclic) propylene carbonate could be produced from urea and propylene glycol using heterogeneous catalysis (such as ZnO, PbO, MgO). Also, using a heterogeneous KI-based catalyst ethylene carbonate and propylene carbonate were produced from CO_2 and epoxide (see also Ref. [6]), at 99% selectivity and 100% epoxide conversion [5]. Also at ICCDU-VII, Aresta et al. [30] showed that vanadium and niobium-based (homogeneous) catalysts give good results for the trans-esterification of ethylene carbonate with methanol, ethanol and allyl alcohol. Park et al. [31] showed that ionic liquids (based on methyl imidazolium with anions Cl^-, BF_4^- or PF_6^-) catalyse the synthesis of propylene carbonate from propylene oxide and CO_2. Also Li et al. [32] investigated the synthesis of propylene carbonate, be it via alcoholysis of urea with propylene glycol, finding propylene carbonate product yields above 90% for ZnO, PbO and MgO, similar to findings by Sun [5] mentioned above.

Recent work by Yasuda et al. suggests that lanthanide oxychloride efficiently catalyses propylene carbonate synthesis from supercritical CO_2 and epoxide [33]. More recent work from that team reports on the catalytic effect of (tetra-alkyl salts of transition-)metal-substituted polyoxometalates for the same cyclic carbonate synthesis [34]; Kim et al. found that this synthesis is catalysed by imidazolium zinc tetrahalides [35]. Sun et al. briefly reviewed the use of ionic liquids (plus some added Lewis acidic compounds) as catalyst and/or reaction medium for cyclic carbonate synthesis from carbon dioxide, with the benefit that product separation and catalyst recovery will be simpler [36].

A very recent paper on styrene carbonate [37] from CO_2 and styrene gives a route that avoids the synthesis (and isolation) of styrene oxide.

2.4. Markets for organic carbonates

Based on data from the open literature, a table on product market volumes for a few organic carbonates could be compiled—see Table 2. (Unfortunately, data can hardly be found in the public domain.)

3. Inorganic carbonate products

3.1. Sodium carbonate (‘‘soda ash’’) and bicarbonate

Sodium carbonate (also referred to as ‘‘soda ash’’) and bicarbonate are the most important inorganic carbonates

Table 2
Market volumes for organic carbonates

Product	Year	Market (Mt/yr)	CO_2 fixed (Mt/yr)	CO_2 source	Reference
DMC	1993	0.1	<0.1	Industrial and natural	[1]
	1997	0.06	<0.1		[6]
	2005	0.1–0.15	<0.1		[a]
Polycarbonate	1979	0.15	<0.1	Industrial and natural	[3]
	1996	1.0	~0.15		[3]
	2002	2.6	~0.4		[9]

[a] Assumption based on scattered information.

produced, primarily from mined trona ($Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$) or sodium carbonate-containing brines, while a major part is produced via the Solvay process for which the necessary CO_2 usually comes from limestone ($CaCO_3$). The (bi)carbonate is widely used in glass industry, soaps and detergents, pulp and paper processing, and many costumer commodities. Worldwide production of ''soda ash'' was estimated at around 35–40 Mt in 2003, of which the amount of bicarbonate produced is typically 10–15% [38].

3.2. Calcium carbonate, precipitated calcium carbonate (PCC)

Calcium carbonate or limestone, is the major component of so-called ''crushed stone'' (other major components dolomite, i.e. magnesium calcium carbonate) which is mined at several Gt/yr: 1.6 Gt was mined in 2004 in the USA alone [39]. Much of this is used as aggregate in road construction. Also a significant portion is used for the production of cement clinker: worldwide cement production was around 2000 Mt in 2004, half of this in China and India [40]. Also it is used in the paper industry for coating and as filler, in Finland for example 0.7 and 0.3 Mt/yr, respectively in 2004 [41].

Some calcium carbonate is used to produce synthetic, so-called precipitated calcium carbonate (PCC), for which the worldwide production was more than 7 Mt in 2003 [42]. Most PCC is produced from lime (produced by calcining limestone) by carbonating a slurry of slaked lime, $Ca(OH)_2$, using an industrial (in a few cases natural) CO_2 source. About 75% of the produced PCC is used in the paper industry [41]. An alternative route to calcium carbonate (aiming at CO_2 sequestration) was suggested by Kakizawa et al. [43], based on extraction of calcium from wollastonite ($CaSiO_3$) mineral using acetic acid. Teir et al. expanded this idea to PCC [41] and showed that PCC production via the conventional route will give CO_2 emissions of the order of 0.21 kg/kg PCC (assuming oil combustion for lime calcination) against a net fixation of 0.34 kg CO_2/kg PCC via the acetic acid route using wollastonite. Fig. 1 shows the simplified process schematics for conventional PCC production and when applying the acetic acid route to PCC production. More recently, the use of slags from iron and steel industry, with calcium contents of the order of 40 wt.% CaO have become interesting for PCC production via this process route [44,45].

3.3. Other inorganic carbonates

Potassium carbonate and (bi)carbonate are used to increase the strength of glass, in batteries, photochemicals, pharmaceutics, rubber manufacturing catalysts, fire extinguishers and food products, and in applications where its use is preferred over sodium (bi)carbonate. It is produced by carbonating KOH brine that is produced from electrolysis of KCl brine. Data from producers suggest a total market volume of 0.1–0.2 Mt annually (about 5% as bicarbonate) which implies a CO_2 fixation of around 0.03–0.06 Mt/yr.

Magnesium carbonate is primarily produced from mined rock, especially dolomites, and is used in rubber processing, cosmetics, medicine and pharmaceutics. World production is estimated at 3.5 Mt/yr in 2004, with a small part produced by carbonation [46,47].

Barium carbonate is used in leaded glass and ceramics and is produced by carbonation of barite (barium sulphate) [48]. World production is estimated at 10–20 kt (kilotonnes).

Strontium carbonate is used in glass (monitor screens), batteries, photochemicals and catalysts. It is produced at 0.3–0.4 Mt/yr, primarily from celestine (strontium sulphate) mineral by carbonation using coal (black ash method) or soda ash (soda ash method), which implies a CO_2 fixation of ~0.1 Mt/yr [49].

Lithium carbonate is used primarily in lithium batteries, aluminum industry and in the production of glass, ceramics and synthetic rubber. Worldwide production is around 10–20 kilotonnes (kt) annually, produced from lithium brines [50].

For other important inorganic carbonates such for example lead carbonate ($PbCO_3$), used in pigment as ''white lead'', no production data is available in the public domain. Moreover,

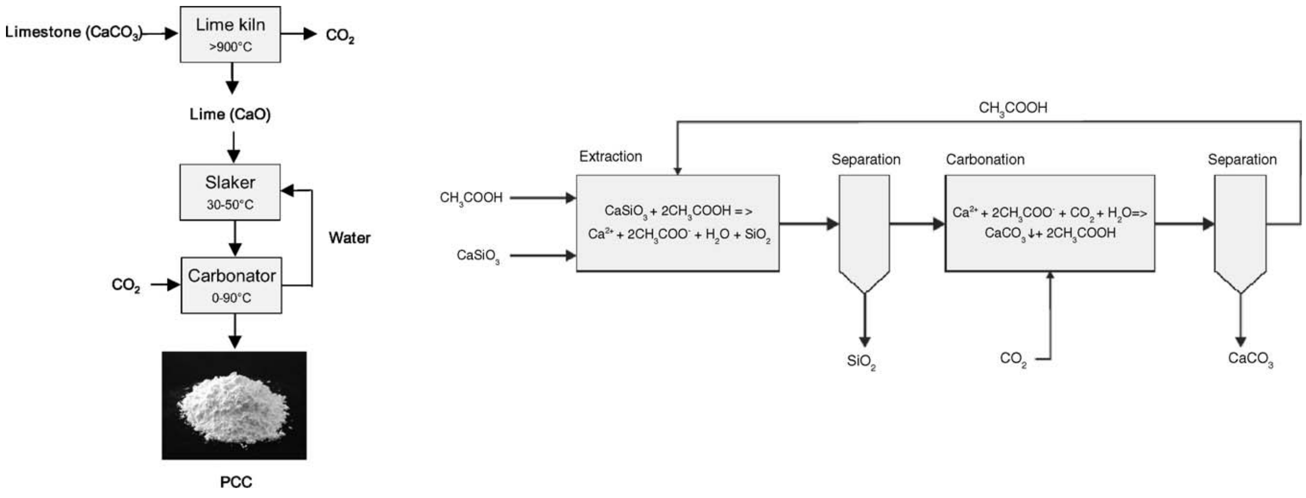

Fig. 1. Precipitated calcium carbonate (PCC) production process schematics according to the conventional route (left) and an alternative, acetic acid route [44,45].

Table 3
Market volumes for inorganic carbonates (Mt/yr)

Product	Year	Market (Mt/yr)	CO_2 fixed (Mt/yr)	CO_2 source	Reference
Na-carbonate	2003	35, ~25% is mined	~15	Partly from limestone	[38]
Na-bicarbonate	2003	5			[a]
Ca-carbonate	2005	Several 1000	Mainly mined		[39]
Ca-carbonate PCC	2003	>7	>3.5	Industrial (or natural)	[41]
K-carbonate	2005	0.1–0.2	0.03–0.05	Industrial (or natural)	[a]
K-bicarbonate	2005	<0.01	<0.01		[a]
Mg-carbonate	2005	3.5	Mainly mined		[46,47]
Ba-carbonate	2005	0.02–0.03[a]	~0.01		[48]
Li-carbonate	2003	0.01–0.02	~0.01		[50]
Sr-carbonate	2003	0.3–0.4	~0.1	Soda or coal	[49]

[a] Assumption based on scattered information.

toxic or otherwise hazardous carbonates materials like lead carbonate are also subject to waste recovery and recycling.

3.4. Markets for inorganic carbonates

Based on data from the open literature, a table on product market volumes for inorganic carbonates could be compiled—see Table 3.

4. Mineral carbonation for long-term CO_2 storage

4.1. Mineral carbonation

As an alternative to geological storage in underground aquifers, depleted oil and gas fields or coal formations, or the more disputable option of ocean storage, long-term storage of CO_2 may be achieved by mineral carbonation. This implies the process of converting CO_2 using naturally occurring minerals such as magnesium- and calcium-based silicates into permanent carbonate minerals. The chemistry for the CO_2 fixation can be summarised as

$$x\mathrm{MgO}\cdot y\mathrm{SiO_2}\cdot z\mathrm{H_2O(s)} \Leftrightarrow x\mathrm{MgO(s)} + y\mathrm{SiO_2(s)} + z\mathrm{H_2O} \quad \text{(R1)}$$

$$\mathrm{MgO(s)} + \mathrm{CO_2} \Leftrightarrow \mathrm{MgCO_3(s)} \quad \text{(R2)}$$

Thermodynamics puts restraints on the stability of $MgCO_3$: at CO_2 pressures of 1 bar $MgCO_3$ is stable up to temperatures of around 400 °C; at 35 bar $MgCO_3$ is stable up to around 550 °C. For mineral carbonation the use of magnesium oxide-based silicates, $x\mathrm{MgO}\cdot y\mathrm{SiO_2}\cdot z\mathrm{H_2O}$ is favoured because they are worldwide available in huge amounts. These natural resources may be capable of binding all fossil fuel-bound carbon [4,51] as illustrated by Fig. 2. Also, the product is a stable solid material that is environmentally inert and hence requires no post-storage monitoring.

Magnesium silicates can be divided into several subgroups: the largest quantities are olivine, $(Mg, Fe)SiO_4$, and serpentine, $Mg_3Si_2O_5(OH)_4$. Some other suitable minerals exist in smaller amounts. The overall carbonation reaction ((R1) + (R2)) is exothermal: the heat effect is of the order of +50 ~ +100 kJ/mol $MgCO_3$ formed. Large-scale sequestration of CO_2 from flue gases as mineral carbonates will, however, require enormous amounts of mineral: 1 kg of CO_2 may require 2 kg of serpentine for disposal, which certainly results in significant environmental impact at the disposal site.

4.2. Wet versus dry mineral carbonation

Only a few laboratories are looking into technical solutions to perform the carbonation of magnesium silicate with carbon dioxide on a large scale. Most important results are reported from the USA. Recent achievements using wet systems report 81% conversion within 1 h for 37 μm olivine mineral particles at 185 °C, 115 bar in an aqueous solution with 0.64 mol/l $NaHCO_3$ and 1 mol/l NaCl [52,53]. Careful control of solution chemistry, heat treatment and grinding is needed, which is mineral specific as well [52] and this makes the economics of the process unattractive [54]. Further improvement is needed and that work is ongoing.

Whilst the research in the USA is concentrating increasingly on wet methods using aqueous solutions, research that started in

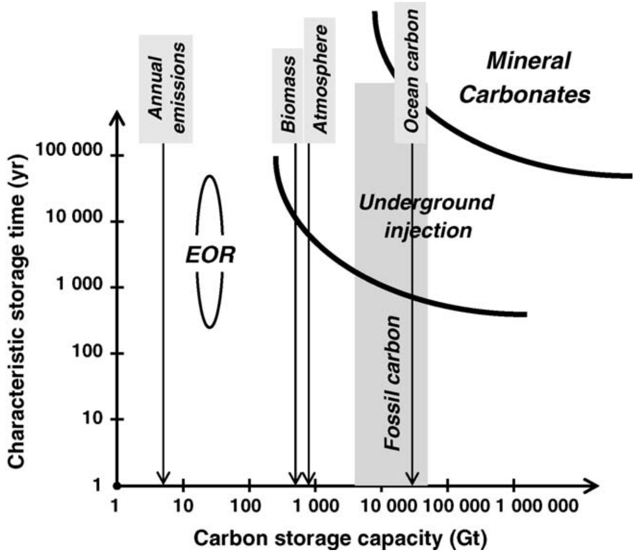

Fig. 2. Estimated storage capacities and storage times for various CO_2 sequestration methods (after Ref. [4]).

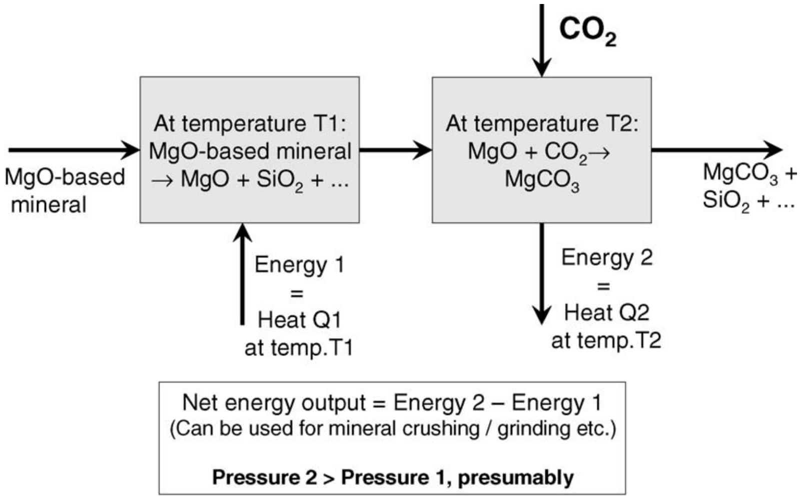

Fig. 3. A process schematic for two-stage MgO-based mineral carbonation (from Ref. [55]).

year 2000 at Helsinki University of Technology (HUT) also addresses dry, gas/solid carbonation methods. The latter shows slower reaction kinetics than the wet process (for example, at 510 °C, 35 bar, with 99 vol.% CO_2 + 1 vol.% H_2O in a pressurised thermobalance with 75–125 μm $Mg(OH)_2$ particles (95% pure), 3% conversion was achieved after 4 h, calculated from thermobalance data) and needs significant improvement on that part. Our kinetics evaluation tests using a pressurised thermogravimetric reactor showed that $Mg(OH)_2$ could be carbonated faster than MgO. This suggests that the mineral carbonation process has to involve the release or activation of the mineral's MgO content, preferably as $Mg(OH)_2$ before the reaction with CO_2 to $MgCO_3$ can take place, which could imply a two-stage process as shown in Fig. 3 [55]. Still to be optimised are the issues of total gas pressure and the effect of other gases, like water and sulphur compounds.

Gas–solid carbonation tests with a $Mg(OH)_2$ material in a fluidised bed reactor indicated that the product of carbonate material that builds up on the reacting particles, eventually slowing the chemical conversion, is removed from the particles as fines by attrition and abrasion. These fines are entrained from the reactor with the exit gas flow, which facilitates their removal from the reactor [56].

The dry process has the potential of producing high temperature steam or electricity while converting CO_2 into carbonates [55–58]. Process integration with mining activities may be very advantageous from cost and energy economy points of view, possibly allowing for, e.g., higher valuable metal extraction rates as well [59].

4.3. *Other carbonation processes for CO_2 sequestration or material stabilisation*

Several other carbonation processes are or have been developed for the fixation of CO_2 or for the stabilisation of materials. For example cementitious wastes can be carbonated as to reduce the leachability of contaminants such as heavy metals or other trace elements [60], an approach that can also be applied to ashes [61]. Alternatively, concrete waste [62] or slags from iron and steel industry [44,45,63] can be carbonated for the purpose of CO_2 sequestration as well. Recently a techno-economical assessment on concrete waste and steel slag carbonation was reported [64]. It must be noted that the amounts of waste materials that can be carbonated limit this approach to CO_2 greenhouse gas mitigation to several 100 Mt/yr; iron and steel slags alone have an capacity of 60–80 Mt/yr CO_2 fixation at the moment.

5. Conclusions

An overview was given on organic and inorganic carbonate products produced using industrially generated CO_2. For the organic products, a lot of developments in the field of catalysis will allow for capacity and markets for DMC, polycarbonate and also polyurethane to grow significantly. The inorganic market is mainly determined by (bi)carbonates of sodium and calcium, with synthetic calcium carbonate (PCC) showing potential for production based on industrially generated CO_2. Finally, mineral carbonation for long-term (or permanent) CO_2 storage is addressed, which has the potential to store more anthropogenic CO_2 than fossil fuel combustion can produce, but suffers from chemical kinetics, thermodynamics and other process engineering limitations. Its development certainly benefits from other progress in the field of carbonate production engineering.

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References

[1] X. Xiaoding, J.A. Moulijn, Energy Fuels 10 (1996) 305.
[2] M. Aresta, I. Tommasi, Energy Convers. Manage. 38 (Suppl.) (1997) S373.
[3] M.M. Halmann, M. Steinberg, Greenhouse Gas Carbon Dioxide Mitigation, Lewis Publish., Boca Raton, 1999 (Chapter 9).
[4] K.S. Lackner, Science 300 (2003) 1677.

[5] Y. Sun, Studies in surface science and catalysis, in: Proceedings of the Seventh Int. Conf. on Carbon Dioxide Utilization, vol. 153, Seoul, Korea, October 2003, Elsevier, Amsterdam, 2004, p. 9.

[6] M.A. Pachero, C.L. Marshall, Energy Fuels 11 (1997) 2.

[7] F. Bertilsson, H.T. Karlsson, Energy Convers. Manage. 37 (1996) 1733.

[8] M. Aresta, A. Dibenedetto, Catal. Today 98 (2004) 455.

[9] Developments in non-phosgene polycarbonate technology, ChemSystems Process Evaluation/Research Planning (PERP) Report 02/03S8, October 2003. Nexant Inc., White Plains, NY, USA, 2003. http://www.chemsystems.com/newsletters/perp/Oct03_N02S8.cfm (June 2005).

[10] Y. Ono, Appl. Catal. A 155 (1997) 133.

[11] P. Tundo, M. Selva, Acc. Chem. Res. 35 (2002) 706.

[12] T. Wei, M. Wang, W. Wei, Y. Sun, B. Zhong, Studies in surface science and catalysis, in: Proceedings of the Seventh Int. Conf. on Carbon Dioxide Utilization, vol. 153, Seoul, Korea, October 2003, Elsevier, Amsterdam, 2004, p. 41.

[13] G.B. Han, N.K. Park, J.H. Hun, W.C. Chang, B.G. Lee, B.S. Ahn, S.O. Ryu, J.T. Lee, Studies in surface science and catalysis, in: Proceedings of the Seventh Int. Conf. on Carbon Dioxide Utilization, vol. 153, Seoul, Korea, October 2003, Elsevier, Amsterdam, 2004, p. 181.

[14] M. Wang, N. Zhao, W. Wei, Y. Sun, Studies in surface science and catalysis, in: Proceedings of the Seventh Int. Conf. on Carbon Dioxide Utilization, vol. 153, Seoul, Korea, October 2003, Elsevier, Amsterdam, 2004, p. 197.

[15] M. Aresta, A. Dibenedetto, C. Devita, O.A. Bourova, O.N. Chapahkin, Studies in surface science and catalysis, in: Proceedings of the Seventh Int. Conf. on Carbon Dioxide Utilization, vol. 153, Seoul, Korea, October 2003, Elsevier, Amsterdam, 2004, p. 213.

[16] I.J. Drake, K.L. Fujdala, A.T. Bell, T.D. Tilley, J. Catal. 230 (2005) 14.

[17] S.A. Anderson, T.W. Root, J. Catal. 217 (2003) 396.

[18] K. Tomishige, Y. Ikeda, T. Sakaihori, K. Fujimoto, J. Catal. 192 (2000) 355.

[19] T. Sakakura, J.-C. Choi, Y. Saito, T. Sako, Polyhedron 19 (2000) 573.

[20] H. Audus, H. Oonk, Energy Convers. Manage. 38 (Suppl.) (1997) S409.

[21] D.J. Darensbourg, M.W. Holtcamp, Coord. Chem. Rev. 153 (1996) 155.

[22] G.W. Coates, D.R. Moore, Angew. Chem. Int. Ed. 43 (2004) 6618.

[23] I. Kim, M.J. Yi, S.H. Pyun, D.W. Park, C.-K. Ha, Studies in surface science and catalysis, in: Proceedings of the Seventh Int. Conf. on Carbon Dioxide Utilization, vol. 153, Seoul, Korea, October 2003, Elsevier, Amsterdam, 2004, p. 239.

[24] Z. Qin, C.M. Thomas, S. Lee, G.W. Coates, Angew. Chem. Int. Ed. 42 (2003) 5484.

[25] X.-B. Lu, Y. Wang, Angew. Chem. Int. Ed. 43 (2004) 3574.

[26] D.J. Darensbourg, J.C. Yarbourgh, J. Am. Chem. Soc. 124 (2005) 6335.

[27] M. Cheng, D.R. Moore, J.J. Reczek, B.M. Chamberlain, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 8738.

[28] W. Leitner, Coord. Chem. Rev. 153 (1996) 257.

[29] Y. Ono, Catal. Today 35 (1997) 15.

[30] M. Aresta, A. Dibenedetto, C. Pastore, Studies in surface science and catalysis, in: Proceedings of the Seventh Int. Conf. on Carbon Dioxide Utilization, vol. 153, Seoul, Korea, October 2003, Elsevier, Amsterdam, 2004, p. 221.

[31] D.-W. Park, J.-H. Hur, E.-S. Jeong, S.-W. Park, I. Kim, Studies in surface science and catalysis, in: Proceedings of the Seventh Int. Conf. on Carbon Dioxide Utilization, vol. 153, Seoul, Korea, October 2003, Elsevier, Amsterdam, 2004, p. 267.

[32] Q. Li, N. Zhao, W. Wei, Y. Sun, Studies in surface science and catalysis, in: Proceedings of the Seventh Int. Conf. on Carbon Dioxide Utilization, vol. 153, Seoul, Korea, October 2003, Elsevier, Amsterdam, 2004, p. 573.

[33] H. Yasuda, L.-N. He, T. Sakakura, J. Catal. 209 (2002) 547.

[34] H. Yasuda, L.-N. He, T. Sakakura, C. Hu, J. Catal. 233 (2005) 119.

[35] H.S. Kim, J.J. Kim, H. Kim, H.G. Jang, J. Catal. 220 (2003) 44.

[36] J. Sun, S.-i. Fujita, M. Arai, J. Organometall. Chem. 690 (2005) 3490.

[37] J. Sun, S.-i. Fujita, F. Zhao, M. Hasegawa, M. Arai, J. Catal. 230 (2005) 398.

[38] US Geological Survey, Mineral Commodity Summaries, US Geological Survey, Reston, VA, USA, January 2005, p. 152.

[39] US Geological Survey, Mineral Commodity Summaries, US Geological Survey, Reston, VA, USA, January 2005, p. 156.

[40] US Geological Survey, Mineral Commodity Summaries, US Geological Survey, Reston, VA, USA, January 2005, p. 42.

[41] S. Teir, S. Eloneva, R. Zevenhoven, Energy Convers. Manage. 46 (2005) 2954.

[42] The Economics of Precipitated Calcium Carbonate, Roskill Information Services Ltd., West Hartford, CT, USA, 2003.

[43] M. Kakizawa, A. Yamasaki, Y. Yanagisawa, Energy 26 (2001) 341.

[44] S. Teir, S. Eloneva, R. Zevenhoven, in: Proceedings of PRES'05, vol. 2, Giardini di Naxos/Messina, Italy, May 15–18, (2005), p. 571.

[45] S. Teir, S. Eloneva, R. Zevenhoven, in: Proceedings of ECOS'2005, vol. 2, Trondheim, Norway, June 20–23, (2005), p. 749.

[46] US Geological Survey, Mineral Commodity Summaries, US Geological Survey, Reston, VA, USA, January 2005, p. 100.

[47] US Geological Survey Minerals Yearbook 2003, US Geological Survey, Reston, VA, USA, 2003, p. 47.1.

[48] US Geological Survey Minerals Yearbook 2003, US Geological Survey, Reston, VA, USA, 2003, p. 9.1.

[49] US Geological Survey Minerals Yearbook 2003, US Geological Survey, Reston, VA, USA, 2003, p. 73.1.

[50] US Geological Survey Minerals Yearbook 2003, US Geological Survey, Reston, VA, USA, 2003, p. 45.1.

[51] K.S. Lackner, D.P. Butt, C.H. Wendt, Energy Convers. Manage. 38 (Suppl.) (1997) S259.

[52] W.K. O'Connor, D.C. Dahlin, G.E. Rush, S.J. Gerdemann, L.R. Penner, D.N. Nilsen, Interim Report Aqueous Mineral Carbonation, DOE/ARC-TR-04-002, US DOE, Albany Research Center, September 2004.

[53] W.K. O'Connor, D.C. Dahlin, D.N. Nilsen, S.J. Gerdeman, G.E. Rush, L.R. Penner, R.P. Walters, P.C. Turner, in: Proceedings of the 27th Int. Conf. on Coal Utilization and Fuel Systems, Clearwater, FL, (March 2002), p. 819.

[54] H. Herzog, Carbon Sequestration via Mineral Carbonation: Overview and Assessment, MIT Laboratory for Energy and the Environment, MIT, MA, USA, 2002.

[55] R. Zevenhoven, S. Teir, in: Proceedings of the Third Ann. Conf. on Carbon Capture and Sequestration, Alexandria, VA, May 2004, 11 pp.

[56] S. Teir, T. Raiski, I. Kavaliauskaite, G. Denafas, R. Zevenhoven, in: Proceedings of the 29th Int. Conf. on Coal Utilization and Fuel Systems, Clearwater, FL, (April 2004), p. 127.

[57] R. Zevenhoven, I. Kavaliauskaite, Int. J. Thermodyn. 7 (2004) 23.

[58] R. Zevenhoven, J. Kohlmann, A.B. Mukherjee, in: Proceedings of the 27th Int. Conf. on Coal Utilization and Fuel Systems, Clearwater, FL, (March 2002), p. 743.

[59] J. Kohlmann, R. Zevenhoven, in: Proceedings of the 29th Int. Conf. on Coal Utilization and Fuel Systems, Clearwater, FL, (April 2004), p. 56.

[60] M.A. Venhuis, E.J. Reardon, Environ. Sci. Technol. 35 (2001) 4120.

[61] J.A. Meima, R.D. van der Weijden, T.T. Eighmy, R.N.J. Comans, Appl. Geochem. 17 (2002) 1503.

[62] A. Iizuka, M. Fujii, A. Yamasaki, Y. Yanagisawa, Ind. Eng. Res. 43 (2003) 7880.

[63] W. Huijgen, G.-J. Witkamp, R. Comans, in: Proceedings of the Seventh Int. Conf. on Greenhouse Gas Control Technologies (GHGT-7), Vancouver, Canada, September 2004.

[64] J.K. Stolaroff, G.V. Lowry, D.W. Keith, Energy Convers. Manage. 46 (2005) 687.