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Mineral Carbonation for Long-term CO_2 Storage: an Exergy Analysis

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Abstract

Magnesium oxide-based minerals (serpentine, olivine) may be used for long-term storage of CO_2, from combustion of fossil fuels or industrial processes in the form of magnesium carbonate. Large resources of suitable minerals appear to exist in Finland and at many other locations worldwide. The efficiency of mineral carbonation processing can be evaluated using exergy analysis, which will allow for comparing different mineral types characterised by different composition and quality. Other important factors are temperature and pressure and the degree of magnesium carbonation conversion. Important for the analysis is the calculation of the standard chemical exergy of the chemical species involved.

Keywords: Carbon dioxide, mineral carbonation, exergy analysis

1. Introduction

For the year 2002 the total emissions of carbon dioxide from combustion of fossil fuels and peat in Finland were around 63 million tonnes (Statistics Finland, 2003). This is of the same level as the value for year 1996 (61 million tonnes) but still 11% higher than the 54 million tonnes that were emitted in 1990. In order to comply with Finland's commitments to the 1997 Kyoto protocol, Finland aims at reducing the consumption of coal and oil in favour of that of natural gas, peat and wood. And, recently a small majority of Finnish parliament voted for the construction of a fifth nuclear reactor in Finland. Nevertheless, these changes may not prevent that active measures are needed to further reduce Finland's carbon dioxide emissions in the future.

Partly this may be accomplished by CO_2 sequestration, *i.e.* the removal of CO_2 from flue gases followed by long-term storage. Finland appears to have access to large mineral resources that may be carbonated. Finland doesn't have deep oceans or exhausted oil or gas fields; and improved forestry, biofixation and the utilisation of CO_2 will not give enough capacity. Apart from exporting carbon dioxide for storage elsewhere, for example below the seabed at oil and gas fields in the North Sea or the Barents Sea, the only option for Finland appears to be mineral carbonation, which implies storage of carbon dioxide in the form of magnesium carbonate (magnesite) (Koljonen *et al.*, 2004). Very large resources of suitable silicates were found to exist in Central and Northern Finland as natural minerals and as wastes from mining industry.

For mineral carbonation the use of magnesium oxide- based silicates, $xMgO{\cdot}ySiO_2{\cdot}zH_2O$ is favoured because they are worldwide available in huge amounts. These natural resources may be capable of binding all fossil fuel-bound carbon (Ziock, 2000, Lackner and Ziock, 2000). Magnesium silicates can be divided into several subgroups. The largest quantities are olivine, $(Mg,Fe)SiO_4$, and

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serpentine, $Mg_3Si_2O_5(OH)_4$. Some other suitable minerals exist in smaller amounts. The chemistry for the CO_2 fixation can be summarised as

$$xMgO.ySiO_2.zH_2O\ (s) <=> x\ MgO\ (s) + y\ SiO_2\ (s) + z\ H_2O \quad (R1)$$

$$MgO\ (s) + CO_2 <=> MgCO_3\ (s) \quad (R2)$$

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.

Only a few laboratories are looking into technical solutions to perform the carbonation of magnesium with carbon dioxide on a large scale. Most important results are reported from the USA. In 1998 those researchers reported conversion rates such as 40-50% conversion of MgO to $MgCO_3$ after 24 h at 150-250°C, 85-125 bar, with olivine particles of 75-100 μm (Walters *et al.*, 1999, Goldberg *et al.*, 2001). More recent achievements using wet systems report 65% conversion after 1 hour, (Goldberg *et al.*, 2001, O'Connor *et al.*, 2001), followed later by 80% conversion within 30 minutes (O'Connor *et al.*, 2002) mainly as a result of careful control of solution chemistry, heat treatment and finer grinding.

Whilst the research in the USA is concentrating increasingly on wet methods using aqueous solutions, our research which started in year 2000 (Kohlmann *et al.*, 2002, Zevenhoven *et al.*, 2002) (still) aims at dry methods. The reaction kinetics of mineral carbonation with and without catalytically active contaminants as well as the effects of gas composition and pressure were analysed for Finnish $Mg_3Si_2O_9(OH)_4$ (serpentine) and $Mg(OH)_2$ samples. It was concluded that the mineral carbonation process has to involve the release or activation of the mineral's MgO content before the reaction with CO_2 to $MgCO_3$ can take place, which could imply a two-stage process. Temperatures around 350°C and elevated pressures appear to be most suitable when considering chemical kinetics and thermodynamics. Water catalyses the carbonation reaction somewhat, which makes the use of serpentine (its 10-14%-wt crystal water is released) more attractive than other MgO-containing minerals. CO_2 will have to be transported to a suitable mineral deposit since transporting minerals to/from CO_2 emission sources will give unacceptable costs. Process integration with mining activities may be very advantageous from cost and energy consumption points of view, possibly allowing for, *e.g.*, higher valuable metal extraction rates as well.

Our current research concentrates on reaction kinetics and large-scale integrated processing based on direct, dry carbonation of MgO-containing mineral with pressurised CO_2 from a separate capture process; the exergy analysis reported below is a part of that.

2. Exergy Analysis of Mineral Carbonation

2.1 Objectives

The main goal of this work is to study the second-law efficiency of a magnesium oxide-based mineral carbonation, focusing on the effect of mineral type and the level of MgO to $MgCO_3$ conversion. As will be demonstrated below, the latter is very important since the heat generated by the exothermic carbonation reaction contributes significantly to the overall energy consumption of the process.

Below, a simple irreversibility analysis based solely on differences between MgO-containing minerals is followed by an exergy analysis for a process where a (pressurised) gas stream of pure CO_2 is reacting with MgO-containing minerals, with heat exchange. An interesting feature is that CO_2, the exergy reference substance for carbon, is converted to a species that is thermodynamically more stable than gaseous CO_2. Also, the minerals that contain the MgO are part of rock material that is part of the environment which makes system boundary definition somewhat complicated.

2.2 Standard exergies

For given environmental conditions (T° = 298.15 K, p° = 1.01325 bar) the chemical exergies E_{chem} of the compounds are calculated as function of temperature T and pressure p as

$$E_{chem}(T, p)=E^\circ_{chem} + \Delta E_{chem}\ (T^\circ, p^\circ \rightarrow T, p) \quad (1)$$

where

$$\Delta E_{chem}\ (T^\circ, p^\circ \rightarrow T, p) = \Delta H(T^\circ, p^\circ \rightarrow T, p) - T^\circ\ \Delta S(T^\circ, p^\circ \rightarrow T,p) \quad (2)$$

with enthalpy H and entropy S. The values for ΔEx_{chem} were calculated using enthalpy and entropy data transported from HSC-4 software and databank (HSC 1999). The chemical exergies of the solids, liquids and gases are assumed independent of pressure, *i.e.* $E_{chem}(p,T) = E_{chem}(T)$.

Standard chemical exergies, E°_{chem}, of the compounds (at 298.15 K and for the gases, 1.01325 bar partial pressure) are calculated from standard chemical exergies of the elements as listed by Kotas (1995) or Szargut *et al.* (1988), Morris and Szargut (1986), and standard Gibbs energy of formation $\Delta_f G°$ data (HSC, 1999, Robie *et al.*, 1979) using:

$$E^0_{chem} = \Delta_f G^0 + \sum_{elements} n_{element} \times E^0_{chem,\,element} \quad (3)$$

(Szargut *et al.*, 1988) where $n_{element}$ is the number of moles of the element in a mole of a certain compound. Input data for the relevant elements and results are given in TABLES I-II.

TABLE I. STANDARD REFERENCE EXERGIES OF THE RELEVANT ELEMENTS AND CALCULATED VALUES FOR SOME RELEVANT COMPOUNDS

Element	Standard chemical exergy (kJ/mol) (Kotas 1995)	Standard chemical exergy (kJ/mol) (Szargut *et al.* 1988)
Mg	626.71	633.8
O_2	3.97	3.97
Si	803.01	854.60
H_2	238.49	236.09
C	410.82	410.26
Compound	*Calculated using Kotas data*	*Calculated using Szargut et al. data*
MgO	59.78	66.85
$Mg(OH)_2$	35.55	40.25
Mg_2SiO_4	6.49	72.26
$Mg_3Si_2O_5(OH)_4$	-56.97	62.71
$MgCO_3$	31.30	37.87
SiO_2	-49.46	2.13

TABLE II. STANDARD GIBBS ENERGY OF FORMATION OF RELEVANT COMPOUNDS

Compound	Standard Gibbs energy of formation $\Delta_f G°$ (kJ/mol)
MgO	-568.94
$Mg(OH)_2$	-833.62
Mg_2SiO_4	-2057.88
$Mg_3Si_2O_5(OH)_4$	-4037.96
$MgCO_3$	-1113.28
SiO_2	-856.44

For comparison, literature data for standard chemical exergies of some of the compounds are given in TABLE III. Surprisingly large differences are found between reference data by Kotas (1995) and what is calculated (see bottom half of TABLE I) using Equation (3) for some species, especially $MgCO_3$. The explanation for that must be that the reference data from Szargut *et al.* (1988) are for elements as present in the earth's crest, whilst the data found in Kotas (1995) refer to elements as dissolved in seawater. For forsterite (Mg_2SiO_4) Finnveden and Östlund (1997) give a standard chemical exergy of 0.532 kJ/g, *i.e.* 73.58 kJ/mol which agrees well with the data from Szargut *et al.* (1988). We decided to proceed using the reference data as given by Szargut et al. for the elements and our own calculated values for the compounds, for two reasons: the data by Szargut *et al.* appear to be more consistent, as discussed above, and the earth's crest is closer related to a process of mineral carbonation on land than seawater is. (For an exergy analysis of ocean disposal of CO_2 the data by Kotas (1995) may be of use. It is noted that Szargut *et al.* (1988) also give data for the elements as found in seawater.)

TABLE III. STANDARD REFERENCE EXERGIES OF SOME RELEVANT COMPOUNDS AS GIVEN BY KOTAS (1995) AND SZARGUT *ET AL.* (1988)

Compound	Standard chemical exergy (kJ/mol) (Kotas 1995)	Standard chemical exergy (kJ/mol) (Szargut *et al.* 1988)
MgO	59.17	66.8
$Mg(OH)_2$	33.83	40.9
Mg_2SiO_4	140.77	74.9
$Mg_3Si_2O_5(OH)_4$	no data	61.3 (crysolite)
$MgCO_3$	13.7	37.9
SiO_2	1.86	1.9

Thus, the underlined calculated values given in TABLE I, based on the reference data from Szargut *et al.* (1988) are used in the calculations that are given in the remainder of the text.

2.3 Carbon dioxide

It is assumed that the CO_2 is transported by pipeline to the mineral deposit where the carbonation and long-term CO_2 storage as $MgCO_3$ takes place. According to Hamelinck *et al.* (2002) the CO_2 transport should occur at 80 bar entrance pressure, with a maximum pressure drop of 10 bar, at a temperature of 10-20°C, with water contents below 10 ppm in order to prevent corrosion. Thus, the CO_2 is assumed here to arrive at the mineral deposit at 75 bar, 15°C, 100 %-vol CO_2.

In this paper, all gases are considered ideal; the exergy of CO_2 as function of temperature and pressure is calculated as

$$E_{Chem,CO2}\ (p,T) = E_{Chem,CO2}\ (T) - RT \ln(p / p°) \quad (4)$$

$$E\ °_{Chem,CO2} = RT° \ln (p°/p°°) = 19.587 \text{ kJ/mol} \quad (5)$$

with R = 8.314 J/molK, using a reference concentration of 0.0375 %-vol of CO_2 in the dry atmosphere (p°° = 0.000375×p°). This value is used in all calculations given here, representing the current situation. It is expected that the level of 0.04 %-vol atmpospheric CO_2 is reached within a decade. In Kotas (1995) the value 0.03 %-vol CO_2 in air is given, Szargut *et al.* (1988) gives 0.0345 %-vol.

2.4 Irreversibility analysis, comparing minerals

A first impression of the second law efficiency of a mineral carbonation process for long-term storage of CO_2 as $MgCO_3$ can be obtained by comparing the irreversibilities resulting from reactions (R1) + (R2) for different minerals. With entropy difference $\Delta S(T)$ for the carbonation reaction at temperature T, the irreversibility or exergy loss is defined as

$$\Delta E_{loss}(T) = T°\Delta S(T) \quad (6)$$

Normalised to a mole of CO_2 converted to $MgCO_3$, the results of this are given in *Figure 1* for the temperature range up to 500°C.

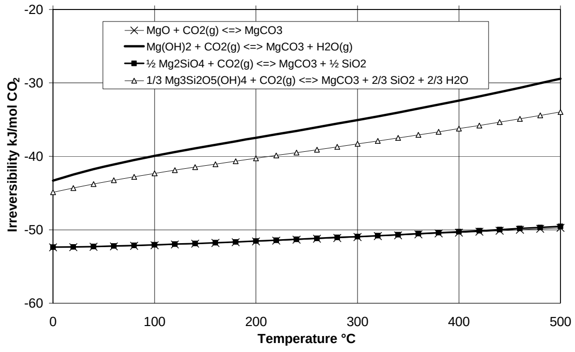

Figure 1. Irreversibility of the reaction of CO_2 with several MgO-containing species, per mol CO_2. (1 bar, 0-500℃)

The results show that the irreversibility is largest when $Mg(OH)_2$ is used; lower, identical values are calculated for MgO (which will not, however, be found free in nature in large amounts) and Mg_2SiO_4 Serpentine $Mg_3Si_2O_5(OH)_4$ gives an intermediate value. All values are negative, which suggests that a carbonation process based on MgO produces excess heat and may allow for power generation. This energy may be used, for example, to pre-treat the mineral (crushing and grinding) or to compensate for pumping losses.

For the chemical carbonation reaction to proceed it is necessary that the Gibbs energy difference $\Delta G = \Delta H\text{-}T\Delta S$ is negative, so a negative value for ΔS must be compensated for by a sufficiently large negative enthalpy difference ΔH.

The chemical exergies for MgO, $Mg(OH)_2$, Mg_2SiO_4, $Mg_3Si_2O_5(OH)_4$ and $MgCO_3$ are given in *Figure 2*, expressed per mol Mg, for 0-500°C. It is seen that the exergies of MgO and $MgCO_3$ decrease with temperature. Comparing the lines for Mg_2SiO_4 and $Mg_3Si_2O_5(OH)_4$ indicates that carbonation of serpentine to $MgCO_3$ will require a smaller energy input (or give a larger output) per mole Mg than a fosterite/olivine type mineral.

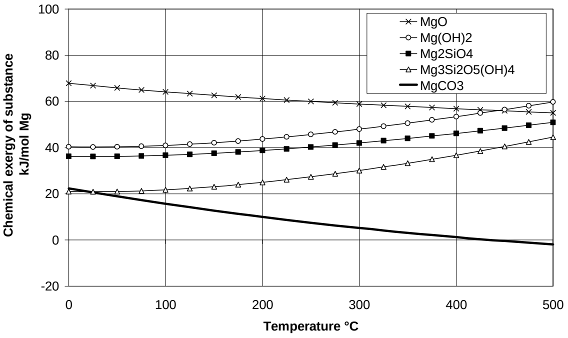

Figure 2. Chemical exergies of MgO, $Mg(OH)_2$, Mg_2SiO_4, $Mg_3Si_2O_5(OH)_4$ and $MgCO_3$, per mol Mg. (0-500℃).

3. A Simplified Mineral Carbonation Process

A simple exergy analysis of a mineral carbonation process can be made for the system shown in *Figure 3*. It is based on a pressurised CO_2 stream (1) which reacts with MgO-containing mineral stream (3) under isothermal conditions. The final $MgCO_3$-containing product released to the environment after cooling is stream (6).

Heat inputs Q_A and Q_B are needed to preheat the incoming streams, respectively; heat outputs Q_C and Q_D result from the need to maintain the isothermal conditions for the carbonation reaction, and to cool the products, respectively. The input and output temperatures of Q_A as well as Q_B are chosen to be T_R+25ºC and Tº+25ºC, for a chosen reaction temperature T_R. For the cooling of the reaction and the

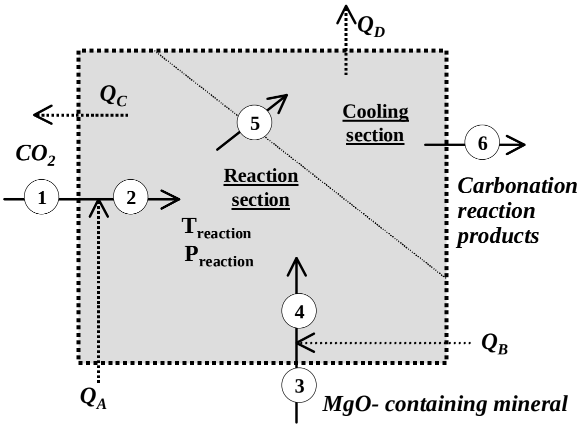

Figure 3 System boundary for a mineral carbonation process based on MgO carbonation reaction and heat exchange

Stream 1	Incoming (pressurised) CO_2
Stream 2	CO_2 preheated to reaction temperature
Stream 3	MgO-containing mineral at environmental conditions
Stream 4	MgO-containing mineral preheated to reaction temperature
Stream 5	Products of carbonation at reaction conditions
Stream 6	Products of carbonation reaction after cooling
Heat Q_A	Heat (enthalpy) input to preheat CO_2
Heat Q_B	Heat (enthalpy) input to preheat the MgO-containing mineral
Heat Q_C	Heat (enthalpy) output to maintain the isothermal carbonation
Heat Q_D	Heat (enthalpy) output to cool the reaction products

reaction products, the input and output of the water / steam streams Q_C as well as for Q_D are T^o and T_R-25ºC, respectively. The exergies for these heat flows are calculated as

$$E\,(Q_A) = \left(1 - \frac{T^o}{T_R + 25}\right) Q_A \qquad (7)$$

and similar for Q_B, Q_C, Q_D.

Thus, the process consumes steam of temperature T_R+25ºC but produces steam with temperature T_R-25ºC. At this point integration of Q_A, Q_B, Q_C and Q_D in a heat exchange network (HEN) is not considered: in practice these may be integrated with other activities, for example metal ore processing at the location of the MgO-containing mineral deposit where the CO_2 is stored.

It is assumed that the carbonation reaction takes place at the pressure at which the CO_2 arrives after transportation, *i.e.* 75 bar.

Apart from comparing minerals, also the degree of conversion, X (in %) of the mineral carbonation will be considered as a variable. For example, 50% conversion of the MgO to $MgCO_3$ implies that a double amount of mineral must be preheated for a given heat effect, that the reaction heat per MgO is only half and that the solid product is a mixture of unreacted mineral and reaction products. A complete (100%) conversion of the CO_2 to $MgCO_3$ will be assumed, however, in most of the calculations.

4. Exergy Calculation Results

The exergy calculations were made in Microsoft Excel™, using thermodynamic data calculated with and transported from HSC-4 (HSC, 1999), with correction for thermodynamic input data for $MgCO_3$ (see Note at the end of this paper). All calculations were made for a CO_2 stream of 1000 kg/s, entering the process at 15 °C, 75 bar.

Since free MgO does hardly occur in nature calculations were only made for $Mg(OH)_2$, (brucite), Mg_2SiO_4 (olivine) and $Mg_3Si_2O_5(OH)_4$ (serpentine). TABLE IV gives the results for carbonation of these three minerals at 350°C, 100% conversion of the Mg to $MgCO_3$, and product disposal to the environment at 50°C. These results show that the net heat input to the process is negative, *i.e.* the overall process is exothermic, producing around 1.5 kJ heat per kg CO_2 stored. Also, due to the exergies of the products after cooling, the difference $exergy_{out}$ minus $exergy_{in}$ is negative. This is mainly due to the values for standard chemical exergy for those species.

TABLE IV. CALCULATED RESULTS FOR 1000 KG/S CO_2, 100% CONVERSION, 350°C, 75 BAR, CALCULATED STANDARD CHEMICAL EXERGIES FROM TABLE I

Mineral	Brucite	Olivine	Serpentine
	Mass in	*kg/s:*	
CO_2	1000	1000	1000
Mineral	1325	1599	2099
	Mass out	*kg/s:*	
$MgCO_3$	1916	1916	1916
SiO_2	0	683	910
H_2O	409	0	273
	Heat	*MW:*	
Input A	321	321	321
Input B	701	532	833
Output C	1539	1908	1176
Output D	1324	276	1183
Net heat input	-1841	-1331	-1205
	Exergies	*MW:*	
Stream 1	684	684	684
Stream 2	779	779	779
Stream 3	911	819	471
Stream 4	1145	996	750
Stream 5	759	557	786
Stream 6	881	912	943
In: 1+3+A+B	2146	1963	1778
Out: C+D+6	2348	2045	2149

4.1 Effect of carbonation temperature

The effect of temperature for the range 300-400°C on $Mg(OH)_2$ carbonation (higher temperatures give unfavourable chemical equilibrium, lower temperatures give too slow reaction kinetics!) is illustrated by *Figure 4*, which gives the exergy flows E 1, E3, E6 and the exergy of the heat flows Q_A, Q_B, Q_C, and Q_D as defined in *Figure 3*. Also the net exergy consumption E in – E out of the process is included.

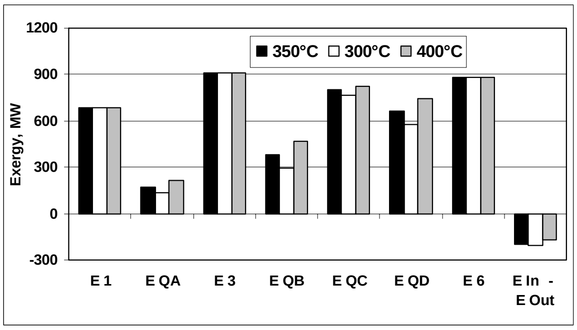

Figure 4. Effect of carbonation reaction temperature on MgO from $Mg(OH)_2$ carbonation process exergies (75 bar, conversion 100%)

The results show that going from 300 to 400 °C the net exergy consumption becomes less negative: the increased exergy input for pre-heating CO_2 and mineral to a higher temperature, $Q_A + Q_B$, is less balanced by the increased exergy output by cooling the exothermal process, Q_C.

4.2 Effect of mineral type

The differences between the three minerals are shown in *Figure 5*. Clearly seen – as also in TABLE IV– are the differences in the exergies for the minerals and differences in the energy needed for heat-up, Q_B, which is relatively high for the olivine. Also important are the differences in the heat of reaction, (which is largest for the olivine) but also important is the cooling heat flow Q_D, which appears small for olivine. For the serpentine the highest negative net exergy difference is found, making this (apparently) the most feasible mineral from an exergy point of view for this process under the given conditions.

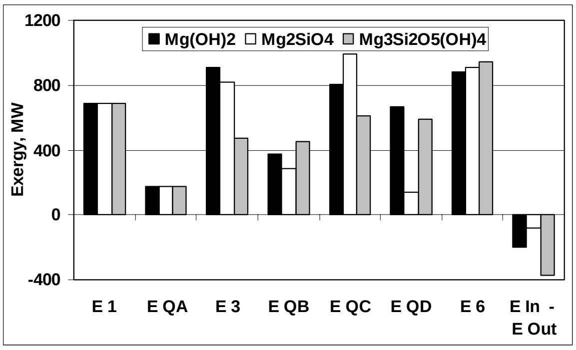

Figure 5. Effect of mineral type on MgO carbonation process exergies (75 bar, 350°C, conversion 100%)

4.3 Effect of degree of conversion

The degree of conversion of mineral-MgO to $MgCO_3$ has a large influence on the exergetic performance of the process, as shown in *Figure6* for 40, 70 and 100 % conversion, respectively.

It is clearly seen that a lower degree of conversion gives a higher net exergy consumption. Not only is much more energy needed to pre-heat the mineral, as reflected by a higher value for exergy Ex 3, also less products (with exergies lower than that of the mineral) are formed. Unfortunately, obtaining high degrees of conversion within acceptable technical time scales is a major bottleneck for this technology (Lackner *et al.*, 1997, Kohlmann *et al.*, 2002).

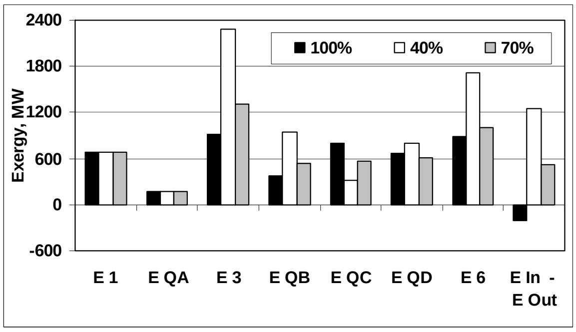

Figure 6. Effect of magnesium conversio degree on MgO from $Mg(OH)_2$ carbonatio process exergies (75 bar, 350°C)

For serpentine and olivine similar results (not given as graphs here) are found. It is noted that processing with serpentine will show negative exergy consumption at conversion levels above 85-90 %, depending on pressure and temperature. For olivine conversion levels close to 100% will be needed for that.

4.4 Effect of pressure of CO_2 and the carbonation reaction

The pressure at which the carbonation reaction is taking place, here assumed (for simplicity) to be equal to the pressure at which the CO_2 is delivered to the process, has a negative effect on the exergy efficiency of the process – see *Figure 7*. A higher pressure corresponds to a higher exergy input to the process which gives no further benefits, since the same non-gaseous products are formed whatever this pressure. Hence, for the heat balance (heat flows Q_A, Q_B, Q_C and Q_D) there is no effect of pressure.

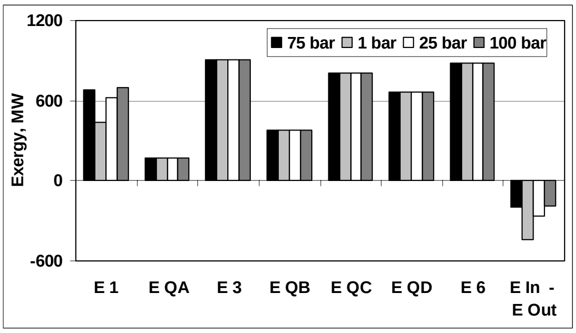

Figure 7. Effect of pressure on $Mg(OH)_2$ carbonation process exergies (350°C, 100% conversion)

However, an increased pressure is needed for reducing the costs for pipeline transport of the CO_2, and the kinetics of the carbonation reaction may benefit from a high pressure as well (allowing for higher carbonation temperature). The exergy of CO_2 pressurisation is lost during the carbonation process. It must be noted that CO_2 may not be treated as an ideal gas at elevated temperatures and pressures – this has not been considered here.

For the carbonation chemistry, pressure is very important. Increasing the pressure of CO_2 raises the temperature at which $MgCO_3$ is stable, allowing for higher temperatures for the carbonation process.

4.5 Effect of reference exergy values

As mentioned above, some remarkable differences were found between calculated standard chemical exergies using equation (3) from Szargut et al. (1988), Moran and Szargut (1986), or from data given by Kotas (1995). For $Mg(OH)_2$ and Mg_2SiO_4 calculations were made using both these sets of data as input; the results are given in *Figure 8*.

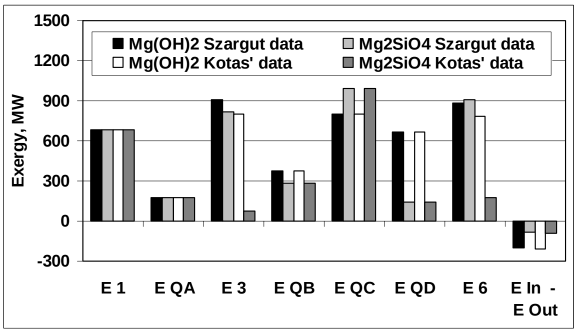

Figure 8. Effect of standard reference exergy values selection on $Mg(OH)_2$ and Mg_2SiO_4 carbonation process exergies (350°C, 75 bar, 100% conversion)

The results are different but similar for the carbonation of $Mg(OH)_2$, apparently due to the small differences between the standard chemical exergies as given in Tables 1 and 3. The total input and output exergies are 2146 MW and 2348 MW, respectively, when using the standard chemical exergy values calculated from data by Szargut *et al.* against 2039 MW and 2248 MW, respectively, when using data by Kotas. This implies a net exergy output of either 220 MW or 186 MW. For the Mg_2SiO_4 (olivine) mineral, also a dependence on reference exergy values was found, as a result of differences for all relevant species Mg_2SiO_4, $MgCO_3$ and SiO_2. For example, for the carbonation of olivine, the calculated standard chemical exergies in Table 1 based on Szargut *et al.* input data give a total exergy input and output of 1963 MW and 2045 MW, respectively, against 1215 MW and 1310 MW, respectively, using data given by Kotas. This implies an exergy production of 80 MW and 95 MW, respectively.

This dependence on reference data makes it difficult to draw conclusions on exergy efficiency or make a comparison between minerals from an exergy point of view. The difference between chosing Mg as ion in seawater (Kotas) or as a component of the earth's crust (Szargut *et al.*) does not explain all differences found.

5. Conclusions

An exergy analysis was made of a simplified process for MgO-based mineral carbonation for long-term storage of CO_2 in the form of $MgCO_3$. It is shown that pressure and temperature are both of less importance in comparison to type of material and the degree of conversion of the mineral. It is found that the process has a net exothermic heat effect, indicating that it may be used to generate 300-350°C steam. (Higher pressures will allow for higher carbonation reaction temperatures, which then yields heat at higher temperatures.). The heat input for pre-heating the CO_2 is relatively small compared to that for mineral pre-heating.

As a result of values for standard chemical exergies for the species, the process may – provided that a sufficiently high degree of conversion is reached - show a negative exergy decrease which is quite unconventional. This is solely the result of the fact that CO_2, the reference species for carbon in exergy calculations, is converted to $MgCO_3$ that has yet a lower exergy. The different values that can be found for standard chemical exergies for the species may in some cases yield enormous differences in process exergy calculations. Clearly, more work is needed on the part of standardisation for solids such as the Mg-species considered here and the definition of "environment". In fact, the only correct reference environment is the region around the mineral deposit that is used.

Notwithstanding the use of thermodynamic analyses like this, the kinetics of MgO-based mineral carbonation is the most urgent problem to be resolved before this technology can be implemented on a large scale. The authors are also engaged with that (see *e.g.* Kohlmann *et al.*, 2002, Zevenhoven *et al.*, 2002, Teir *et al.*, 2004). When the optimum levels for carbonation process temperature, pressure and conversion are known a better exergy analysis can be made. Mineral carbonation conversion levels of 100% will not be achievable, but elevated pressures will allow for temperatures higher than 350°C.

Note

This paper was earlier presented at the ECOS'2003 Conference at Copenhagen, Denmark, June 2003. The numbers and figures and some of the conclusions given here differ slightly after correcting for the fact that thermodynamic data used for $MgCO_3$, as found in the HSC software database are not correct. We are grateful to prof. Klaus Lackner from Columbia University, New York (NY) for bringing this to our attention.

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