AN EXERGY ANALYSIS FOR MINERAL CARBONATION
Ekserģijas analīze minerālu karbonizācijai

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Abstract

Magnesium oxide-based minerals such as serpentine and olivine may be used for long-term storage of CO_2, from combustion of fossil fuels or industrial processes such as steel works, 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 the mineral carbonation process can be evaluated using exergy analysis, which will allow for comparing different mineral deposits that are characterised by different composition and quality. Other factors that play a role are the temperature and pressure, the presence of other gases besides CO_2 and the degree of magnesium carbonation that is reached. Important for the analysis is the calculation of the standard chemical exergy of the chemical species involved.

Keywords: *carbon dioxide, mineral carbonation, exergy analysis.*

Introduction

For the year 2001 the total emissions of carbon dioxide from combustion of fossil fuels and peat in Finland were around 60 million tones [1]. This is less than the value for year 1996 (61 million tones) but still 11% higher than the 54 million tones that were emitted in 1990.

The only option for Finland to reach efficient CO_2 sequestration is mineral carbonation, which implies storage of carbon dioxide in the form of magnesium carbonate (magnesite)[2].

For mineral carbonation the use of magnesium oxide- based silicates, $xMgO \cdot ySiO_2 \cdot zH_2O$ is favored because they are worldwide available in huge amounts. These natural resources may be capable of binding all fossil fuel-bound carbon [3, 4]. 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 chemistry for the CO_2 fixation can be summarized as:

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

$$MgO \ (s) + CO_2 <=> MgCO_3 \ (s) \quad\quad\quad (R2)$$
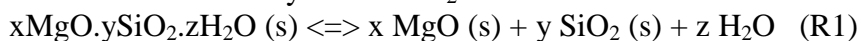
Whilst the research in the USA is concentrating increasingly on wet methods using aqueous solutions, our research (started mid-2000) [5,6] (still) aims at dry methods. The reaction kinetics of mineral carbonation with and without catalytically active contaminants as well as the effects of gas composition and pressure were analyzed 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.

Our current research concentrates on reaction kinetics and large-scale integrated processing based on direct, dry carbonation of MgO-containing mineral with pressurized CO_2

from a separate captures process; the exergy analysis reported below is a part of that.

Exergy analysis of mineral carbonation
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.

Standard exergies

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

$$Ex_{chem}(T, p) = Ex°_{chem} + \Delta Ex_{chem}(T°, p° \rightarrow T, p) \qquad (1)$$

where

$$\Delta Ex_{chem}(T°, p° \rightarrow T, p) = \Delta H(T°, p° \rightarrow T, p) - T° \Delta S(T°, p° \rightarrow T, p) \qquad (2)$$

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 [8]. The chemical exergies of the solids, liquids and gases are assumed independent of pressure, *i.e.* $Ex_{chem}(p,T) = Ex_{chem}(T)$.

Standard chemical exergies, $Ex°_{chem}$, of the compounds are calculated from standard chemical exergies of the elements as listed by Kotas [7] and standard Gibbs' energy of formation $\Delta_f G°$ data [8] using:

$$Ex°_{chem} = \Delta_f G° + \sum_{elements} n_{element} \times Ex°_{chem,element} \qquad (3)$$

[7] 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 1 and 2.

Table 1.

Standard reference exergies of the relevant elements and calculated values for some compounds

Element	Standard chemical exergy (kJ/mol)
Mg	626.71 [7]
O_2	3.97 [7]
Si	803.01 [7]
H_2	238.49 [7]
C	410.82 [7]
Compound	
MgO	59.78
$Mg(OH)_2$	35.55
Mg_2SiO_4	6.49
$Mg_3Si_2O_5(OH)_4$	-56.97
$MgCO_3$	31.30
SiO_2	-49.46

Table 2.

Standard Gibbs' energy of formation of the relevant compounds [8]

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
$MgCO_3$	-1012.19
SiO_2	-856.44

For comparison, data for standard chemical exergies of some of the compounds, listed by Kotas [7] are given in Table 3. Surprisingly large differences between data in [7] and what is calculated using (3) are found for some species. Although this will effect process exergy calculations, the calculated values given in Table 1 are used below.

Table 3.

Standard reference exergies of some relevant compounds as given by Kotas [7]

Compound	Standard chemical exergy (kJ/mol)
MgO	59.17
$Mg(OH)_2$	33.83
Mg_2SiO_4	140.77
$Mg_3Si_2O_5(OH)_4$	No data
$MgCO_3$	13.7
SiO_2	1.86

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. [9] 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

$$Ex_{CO2}(p,T) = Ex_{CO2}(T) - RT \ln(p/p°) \qquad (4)$$

and

$$Ex°_{CO2} = RT° \ln(p°/p°°) = 20.108 \text{ kJ/mol}$$

with R = 8.314 J/molK, using a reference concentration of 0.03 %-vol of CO_2 in the atmosphere ($p°° = 0.0003 \times p°$) although 0.04 %-vol would be a more realistic value nowadays.

A simplified mineral carbonation process

A simple exergy analysis of a mineral carbonation process can be made for the system shown in Figure 1. 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 $T_R+25°C$ and $T°+25°C$, for a chosen

reaction temperature T_R. For the cooling of the reaction and the reaction products, the input and output of the water / steam streams Q_C as well as for Q_D are $T°$ and $T_R-25°C$, respectively. The exergies for these heat flows are calculated as

$$Ex(Q_A) = \left(1 - \frac{T°}{T_R + 25}\right)Q_A \qquad (6)$$
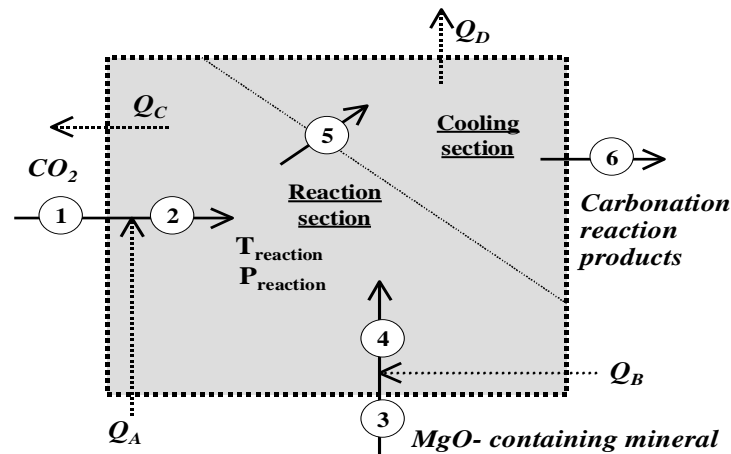
and similar for Q_B, Q_C, Q_D.

Fig.1. System boundary for a mineral carbonationprocess 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

  Thus, the process consumes steam of temperature $T_R+25°C$ but produces steam with temperature $T_R-25°C$. 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 places 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 conversion of the CO_2 to $MgCO_3$ will be assumed, however.

Exergy calculation results

The exergy calculations were made in Microsoft Excel™, using thermodynamic data calculated with and transported from HSC-4 [8]. All calculations were made for a CO_2 stream of 1000 kg/s, entering the process at 15 °C, 75 bar.

Table 4.

Calculated results for 1000 kg/s CO_2, 100% conversion, 350°C, 75 bar, standard chemical exergies from Table 1.

Mineral	$Mg(OH)_2$	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	173	173	173
Input B	378	287	450
Output C	261	789	426
Output D	938	427	886
Net heat input	-1348	-1510	-1389
Exergies MW:			
Stream 1	696	696	696
Stream 2	790	790	790
Stream 3	804	71	-325
Stream 4	1038	248	-156
Stream 5	1290	1370	1743
Stream 6	826	235	89
In: 1+3+A+B	2051	1227	883
Out: C+D+6	2025	1450	1380

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 4 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 1.4 kJ heat per kg CO_2 stored. Also, due to the exergies of some of the products after cooling, the difference exergy$_{out}$ minus exergy$_{in}$ may be negative. This is mainly due to the values for standard chemical exergy for those species.

Conclusions

As a first step, an exergy analysis of was made of a simplified process for MgO-based mineral carbonation for long-term storage of CO_2 in the form of $MgCO_3$. We can conclude 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. 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 also show a negative exergy decrease, which is quite unconventional.

Finally, 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 standardization for solids such as the Mg-species considered here and the definition of "environment".

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