

EVALUATION OF MINERAL CARBONATION PROCESSES FOR LONG-TERM CO₂ STORAGE

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Abstract. Carbon dioxide capture and storage (CCS) is considered as one of the main options for reducing atmospheric emissions of CO₂ from human activities. This concept includes capture of CO₂ from large, centralized CO₂ emitters (power plant, metal industry and cement producers). Carbonation of natural silicate minerals is an interesting alternative to geological reservoirs for storage of CO₂. Discussions on mineral carbonation are given: (1) the enormous resources of suitable magnesium silicates found worldwide are more than sufficient for storage of all fossil fuel-bound carbon found on earth, (2) advantage of method from permanent, leakage-free storage is that does not require monitoring (as opposed to the more widely advocated geological storage of CO₂ in underground cavities) since the magnesium carbonate produced is thermodynamically more stable in nature than CO₂. Drawback of the method that have prevented widespread application so far are: (1) the slow kinetics of the carbonation chemistry, and (2) the risk for a significant energy input requirement. For that reason is necessary to evaluate carbonation way different, where, reaction kinetics must be improved, while the net energy requirements of the process must be minimized. In this work assessment three routes of carbonation: (I) dry carbonation (serpentine → MgO → MgCO₃), (II) wet carbonation (Serpentine → Mg(OH)₂ → MgCO₃) and (III) carbonation for Acid digestion (Serpentine → MgCl₂ → Mg₅(OH)₂(CO₃)₄·4H₂O).

Dry carbonation (route I) will require a temperature of ~600°C, 1 bar ($\Delta G < 0$ Kcal and $\Delta H = 60$ Kcal) for production of MgO from serpentine, which is apparently higher than carbonation process of MgO or production of MgCO₃ (below ~400°C, $\Delta H = -30$ Kcal).

Wet carbonation (route III), the carbonation process, Mg(OH)₂ for reaction with CO₂ shown temperature below than 980°C ($\Delta H = -9$ Kcal).

Hydromagnesite formation (Route III) shown that leaching serpentine in aqueous solution of hydrochloric acid (production of MgCl₂) will require a temperature ~75°C, 1 bar ($\Delta G < 0$ Kcal and $\Delta H = 68$ Kcal), and the fixation of CO₂ by precipitation of Hydromagnesite shown temperature range 10 - 1000°C, reaching optimal fixation of CO₂ at 30°C (1 bar) and pH range 7 - 9 ($\Delta H = -62$ Kcal).

In the result shown that hydromagnesite formation (route III) is an preferable and interesting alternative from energy point view; fortunately this routes also appears to show faster carbonation kinetics. (Combustion, fuel and environmental engineering).

Keywords: Serpentine, Mineral Carbonation, Thermodynamics Evaluation.

1. INTRODUCTION

Of all of the energy consumed in the world, 91% comes from combustion of carbon-containing fuels and 80% from the combustion of fossil fuels. The result is the largest single anthropogenic product of the modern era, carbon dioxide. It is estimated that the total world production now exceeds 25 billion tons per annum. Because of the established infrastructure, cost of alternatives, and societal pressure, carbon-containing materials are likely to remain our major source of energy for the near future. However, the production of CO₂ cannot be sustained without risking our future. (VanEssendelft, 2009)

Considering the vital role of fossil fuel to global economy there is a urgent need to developed an effective methodology for carbon management (Fan,2003). Carbon management involves steps including capturing, transporting, and securely storing carbon emitted from sources. The storing of carbon is a process known as carbon sequestration. Any viable system for sequestering carbon will be effective if: The cost is competitive, the storage is stable for long-term, and environmentally benign too.

There is no single solution to decrease the massive carbon emission. That we currently have. The demand for energy is likely to increase as population grows and per capita income increase. If generation and use of energy continues in “business as usual” fashion, anthropogenic CO₂ will at least double in 50 years. One of the basic strategies to reduce CO₂ emissions is capture and storage of the combustion products from the fossil fuels. (Pacala,2004).

Carbon dioxide capture and storage (CCS) is considered as one of the main options for reducing atmospheric emission of CO₂ from industry and power plants (IPCC, 2005). This concept includes separation and compression of CO₂ from industry and power plants, and transportation of CO₂ to a suitable storage site. Of the many ways that CO₂

can be sequestered, mineral carbonation is the only method that can sequester without the chance of leakage and, if done correctly, could be the most benign approach. Mineral carbonation mimics natural weathering phenomena, but with greatly accelerated kinetics. (Van Essendelft, 2009)

2. MINERAL CARBONATION

Carbonation of natural silicates mineral is an interesting alternative to underground geological formations for storage of CO₂ into environmentally benign carbonate products via carbonation reactions. This process occurs naturally as products of hydrothermal alteration and weathering. However the natural processes are slow, generally forming deposits over millions of years. Acceleration of the natural reaction will be very important in helping managing the global CO₂ budget, and hence avoiding any possible climate change problems associated with CO₂ release. (UBC, 2010)

Alkaline- oxides, such as magnesium oxide (MgO) and calcium oxide (CaO), are present in large amounts and high concentrations in naturally occurring silicate minerals (Wei,2003; Lackner, 2003). Carbonation of these minerals traps CO₂ as environmental and thermodynamically stable solid carbonates, which would provide storage capacity on a geological time scale. (Park,2003; Teir, 2007). The most interesting of these rocks for carbonation purposes are the serpentinites, because these consist mainly of serpentine, which may contain about 40% of MgO (Teir, 2009).

Details discussion on mineral carbonation and its potential for long-term CO₂ storage are given elsewhere, To Zevenhoven (2008), the main advantages are: 1) the enormous resources of suitable magnesium silicates found worldwide are more than sufficient for storage of all fossil fuel-bound carbon found on earth, 2) the method benefits from permanent, leakage-free storage that does not require monitoring, since the magnesium carbonate produced is thermodynamically more stable in nature than CO₂ and 3) The overall chemistry is exothermic, allowing in principles for process with a zero or negative overall energy input.

The technologies to achieve this chemistry can be divided in three routes, Zevenhoven (2008) presents two routes important (dry carbonation and wet carbonation) and Teir (2007) present one route (Carbonation for acid digestion).

3. THERMOCHEMISTRY OF THE CHEMICAL REACTION

In the chemical process deals with multiples aspects of chemical engineering (chemical reaction, chemical energetic, and equations/ law of thermodynamics) play an important role in the selection and design chemical reactor.

Chemical equation give the quantitative relationship between the reactants and the product, this quantitative information can be utilized to carry out variety of calculations which are required many a times, to assess the economic viability of the chemical process. These chemical reactions are always associated with energy changes. Quite often, the energy change accompanying a chemical reaction is more significant than the reaction itself.

The thermodynamic potentials are very important to assessment chemical reaction. In order for the reaction occur, the molecules have to leap over an energy barrier that normally exists along the reaction path from initial state to the final state of the reaction, this is a flow of reacting molecules through an activated state required for the reaction to proceed.

When reactions proceed, the amount of energy equivalent to the energy gap dissipates, thereby producing an amount of uncompensated heat and creating an amount of entropy. Usually, the energy diagram of chemical reaction at constant T and P is expressed in terms of free enthalpy (Gibbs energy). Obviously, the Gibbs energy or free enthalpy play role of thermodynamic potentials for irreversible process to occur in isothermal systems at constant P. In general, the Gibbs energy can be used as the thermodynamic potentials to indicate the direction of an irreversible processes to occur under the condition that their respective characteristic variables remain constant (Sato, 2004).

The equation Gibbs energy is understood as fundamental equation of chemical thermodynamic:

$$\Delta H - T\Delta S = \Delta G \quad (1)$$

See that a spontaneous change is accompanied by a decrease in G. the Eq(1) with connection to (q_{rev}-q) shown that when ΔG is negative, the entropy of the universe increases. The free enthalpy gives us a criterion for spontaneous change in which we need look only at properties of our system is the one that chemists most commonly use, and it is a often posed as a measure of competition between an energy effect and randomness effect. In our new expression for tendency:

$$\Delta G < 0 \quad (2)$$

The Eq (2) is made more negative (indicates a spontaneous reaction) by both negative value of ΔH (exothermic reaction) and it is made more negative by a positive value of ΔS (more randomness in the system) (Spratley, 1969). Its can be shown in the table 1.

Table 1- Temperature effect in the spontaneous reactions

ΔH	ΔS	$T\Delta S$	ΔG	Characteristic
-	+	-	Ever negative	Spontaneous to all temperature
+	-	+	Ever positive	No Spontaneous to all temperature, but inverse reaction spontaneous
-	-	+	Negative for less temperature and positive for high temperature	Spontaneous for less T and no spontaneous a high T
+	+	-	Positive for less T and negative for high T	No spontaneous less T, and spontaneous a high T

4 ASSESMENT THERMODYNAMICS OF THE DIFFERENT CARBONATION REACTION

4.1 Route I - Dry Carbonation or carbonation via MgO

In the first step, the producing free MgO in the magnesium silicate carbonation (serpentine), as silicate cannot be carbonated at a sufficient chemical rate directly, this implies the following chemistry:



The second step, followed by carbonation reaction:



For the Dry carbonation (R1 and R2); the thermodynamics are illustrated by Fig. 1a and Figure 1b, giving the ΔG and ΔH values. First ΔG line for R1 (MgO production from serpentine) will require a temperature $\sim 600^\circ\text{C}$ for occur reaction, and MgO production is a endothermic reaction, which will need $\sim 60\text{Kcal}$ of energy. The carbonation reaction (R2 - $MgCO_3$ production) has $\Delta G < 0$ for temperatures below $\sim 400^\circ\text{C}$ under 1 bar CO_2 pressure and this reaction is exothermic and will produce ~ -30 Kcal of energy.

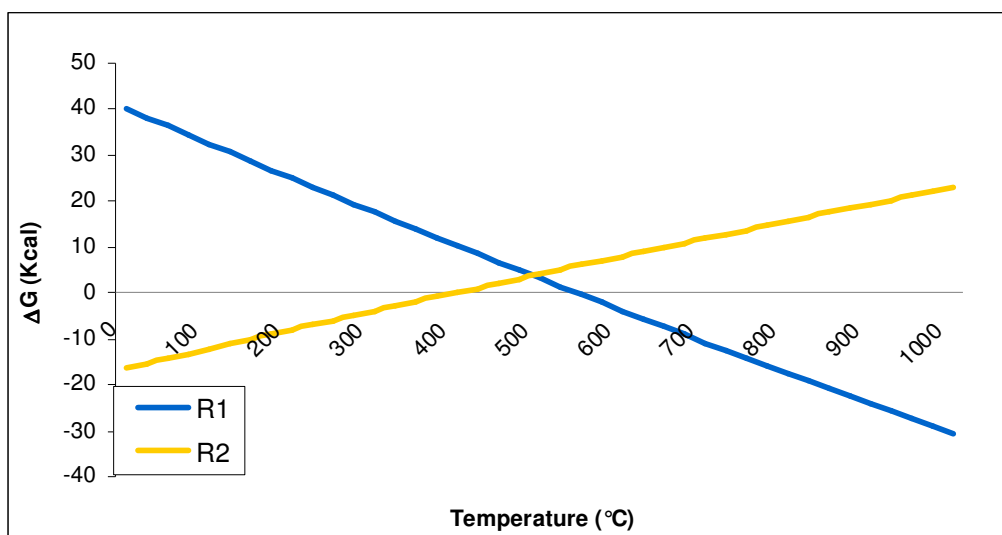


Figure1a – Thermodynamics assessment of free enthalpy ΔG for reaction R1 and R2

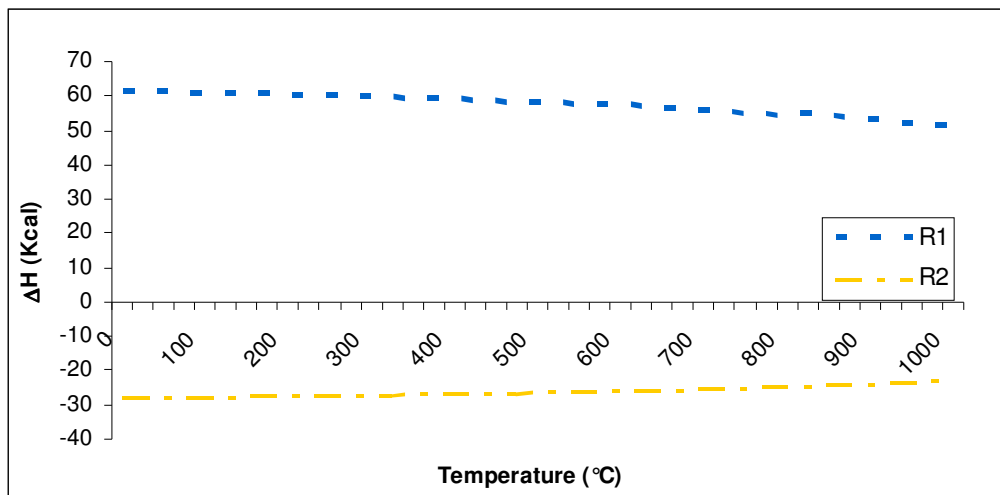


Figure 1b – Thermodynamics assessment of enthalpy ΔH for reaction R1 and R2

4.2 Route II - Wet Carbonation or carbonation via $Mg(OH)_2$

The wet carbonation is realized in three step process: the first step: MgO production (R1) and followed by MgO hydration reaction (second step):



The three and final step is the carbonation reaction:



This route is most fast than route I, yet from a viewpoint of carbonation kinetics the process via $Mg(OH)_2$ would be preferable; moreover, MgO hydration (R3) should not be a problem. The thermodynamic is illustrated in the Fig. 2a. Free enthalpy (ΔG) where the production of magnesium hydroxide is favored has temperature below than $\sim 250^\circ C$ and reaction is exothermic, which the released energy will be 19 Kcal and the carbonation reaction (R4) has spontaneous reaction at temperature below $\sim 980^\circ C$ and the reaction is exothermic too (-9 Kcal). These released energies should compensate the energy required in R1.

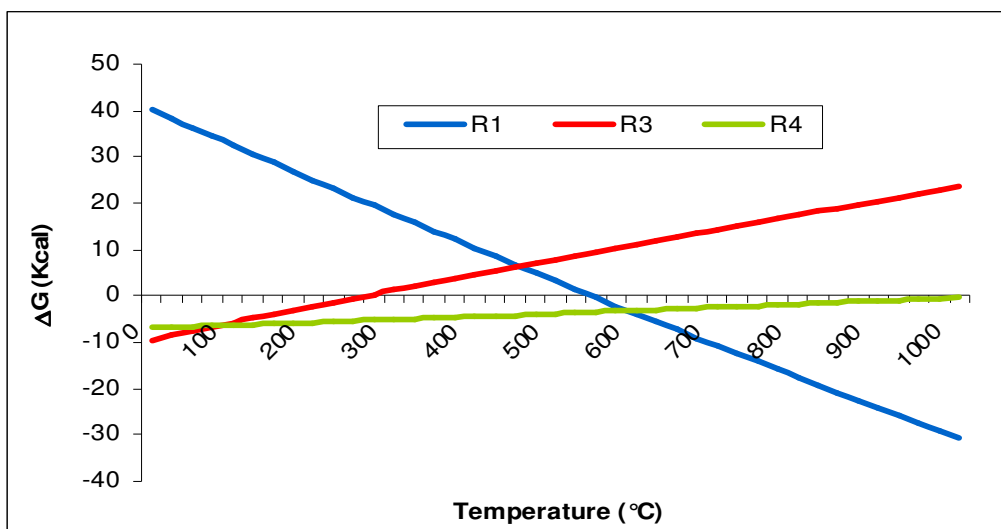


Figure 2a – Thermodynamics assessment of free enthalpy ΔG for reaction R1 R3 and R4

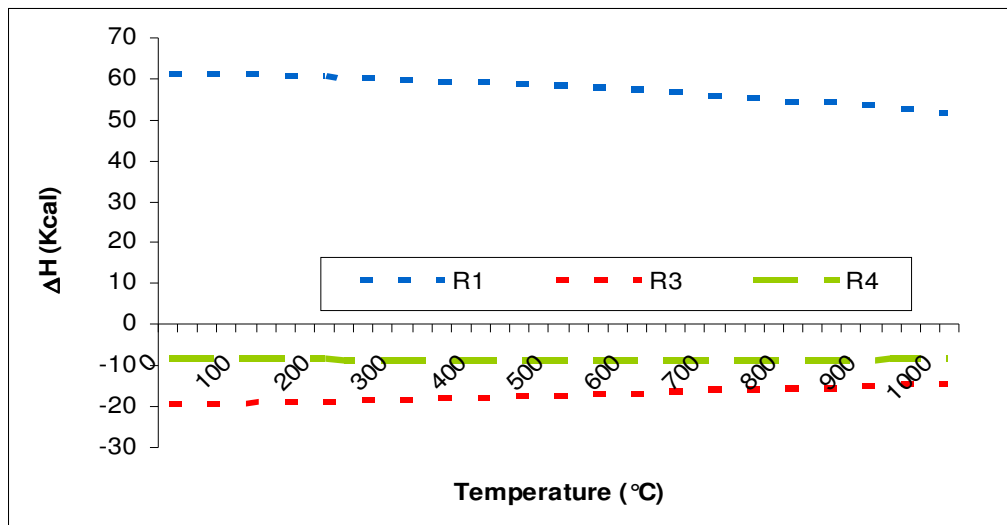
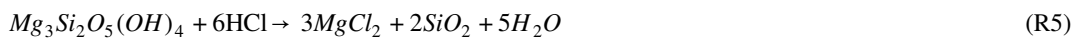


Figure 2b – Thermodynamics assessment of enthalpy ΔH for reaction R1 R3 and R4

4.3 Route III - Carbonation for Acid Digestion

The first step magnesium and iron is extracted from serpentine using acid (In this paper using HCl), the product are salts of magnesium, as well as silicon dioxide in serpentine can be recovered at this stages as highly porous, amorphous silica. The main reaction is (Teir, 2007):



The second step, the carbonation reaction is realized, the salts solution is neutralized with sodium hydroxide (NaOH) and injecting CO₂ gas:



This route is favorable because both reaction R(5) and R(6) are spontaneous for less temperature. The digestion reaction (R5) is spontaneous at temperature below 400°C. The carbonation reaction (R6) occur between 10-1000 °C but exothermic reaction occur only at temperature below 150°C and the enthalpy shown less energy released (10 Kcal), Digestion reaction (R5) is totally exothermic (between -50 Kcal and -2160 Kcal respectively).

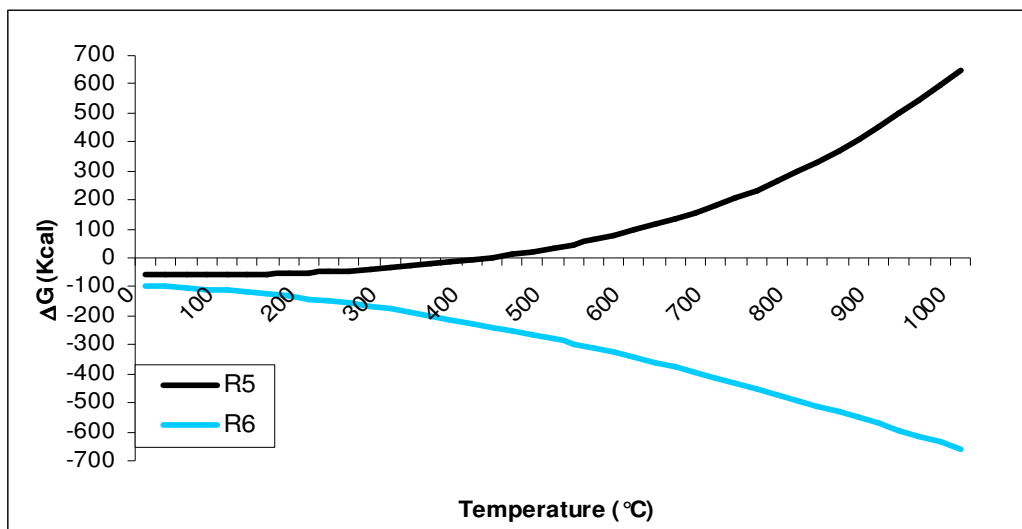


Figure3a – Thermodynamics assessment of free enthalpy ΔG for reaction R5 and R6

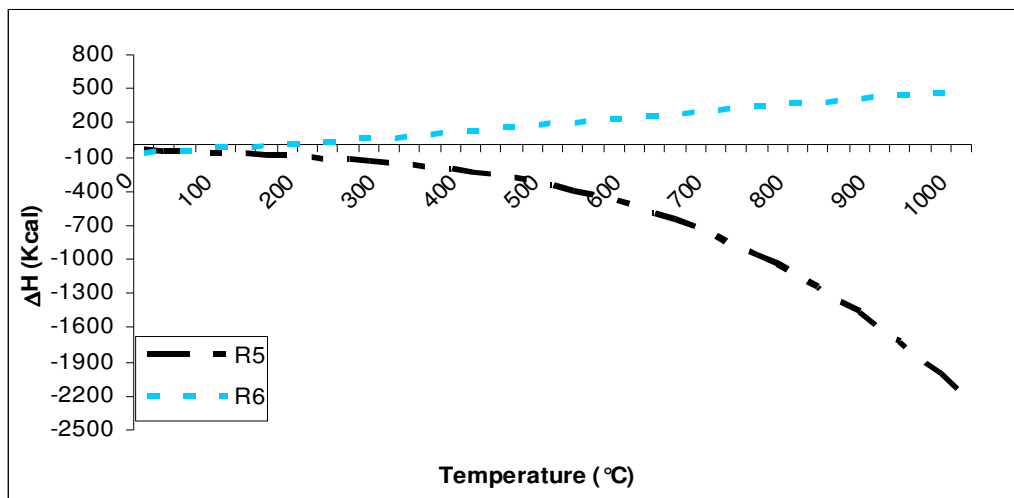


Figure 3b – Thermodynamics assessment of enthalpy ΔH for reaction R5 and R6.

4.3.1 Thermodynamics Stable Solid Carbonates

Despite being the most stable phase, magnesite ($MgCO_3$) proves to be virtually impossible to synthesize at room temperature. As such, Mineral carbonation is theoretically complex because the product will be dominated metastable species, including hydrated (Barringtonite ($MgCO_3 \cdot 2H_2O$), nesquehonite ($MgCO_3 \cdot 3H_2O$) and landsfordite ($MgCO_3 \cdot 5H_2O$)) and basic Mg-carbonates (hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), dypingite ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$) and artinite ($Mg_2(CO_3)(OH)_2 \cdot 3H_2O$)). It is reported that nesquehonite is the most commonly grown mineral in aqueous solutions at near ambient temperature and low pressure; will bring up various basic species. Magnesite has been reported to form only at temperature greater than 60-100 °C and elevated partial pressure (Zhao, 2009).

5. CONCLUSION

Dry carbonation process, is realized by thermal degradation of serpentine to oxide magnesium (R1), this thermal degradation is realized above 600°C (Figure 1a – Blue line), thus needs input energy approximately 60 Kcal (Fig 1b – Blue dotted line).

Next step is carbonation of oxide magnesium (R2) this step is realized at temperatures below 400°C, being more spontaneous reaction at low temperature (Figure 1a – yellow line). However, R2 is exothermic releasing approximately 30Kcal (Figure 1b – Yellow dotted line).

R1 and R2 (Dry carbonation process) are worked 1 bar, however, temperatures condition are different (R1 > 600°C and R2 < 400°C). Other articles were worked with similar temperatures increasing the pressure to attain negative free enthalpies (ΔG), but this process could be increase cost process.

Wet carbonation process, requires to thermal degradation reaction (R1) thereafter this process is realized hydration of magnesium oxide for production magnesium hydroxide (R3) and carbonation of magnesium hydroxide for production Magnesite (R4).

Hydration step (R3), is realized at temperature below 250°C, else the Figure 2a (red line) shows more spontaneous reactions at low temperature.

Carbonation step (R4), is realized at temperature below 980°C, in the Figure 2a (green line) show more spontaneity to low temperature (favorable reaction to products).

Although, kinetic support this process, operational conditions of R3 and R4 are most efficient to low temperature (<100°C), however are very different from R1, which works at temperature above 600°C. Nevertheless, the expenditure energy to increase temperature above 600°C could be wasting energy in cooling process products from R1.

Other option would be increasing pressure of R3 for increase temperature up to 450°C, even Zevenhoven (2008) make similar procedures in R3 and R4 attaining pressure of 75 bar and 10 bar respectively, which generate additional cost.

Acid digestion of serpentine (R5) is performed by chlorhydric acid to obtain magnesium chloride $MgCl_2$ and carbonation reaction (R6) of $MgCl_2$ to produce hydromagnesite. Acid digestion, is perform at temperature below $400^\circ C$, even so the Figure 3a (Black line) shows more spontaneity with low temperature ($75^\circ C$, $\Delta H = -68 Kcal$).

R6, is realized at temperatures range between $10 - 1000^\circ C$ (Figure 3a – Blue line), nevertheless this reaction is exothermic at low temperature ($<150^\circ C$), else the Figure 3b (Blue dotted line) shows more spontaneity with temperature of $30^\circ C$ ($\Delta H = -62 Kcal$).

R5 and R6, both reaction work with similar temperature and pressure, the only problem is the need for additional chemical inputs to carry out the reactions, but the introduction of chemical looping (material recovery) can help to solve problem. The kinetics of R5 present fast behaviors, results reaction time are between 2-3 hours.

Reaction times similar are obtained to dry and wet carbonation. The advantage is low pressure and temperature, which minimize energy required and cost process.

6. ACKNOWLEDGEMENTS

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7. REFERENCE

- Van Essendelft, D.T.; Shobert, H.H. 2009, "Kinetics of the acid digestion of serpentine with concurrent grinding. 1. Initial Investigations", *Ind. Eng. Chem. Res.*, Vol. 48, pp. 2556-2565.
- Park, A.A.; Jadhav, R.; Fan, L.S.; 2003, "Co₂ mineral sequestration: chemically enhanced aqueous carbonation of serpentine", *the Canadian Journal Chemical Engineering*, Vol. 81, pp. 885-890.
- Pacala, S.; Socolow, R. 2004, "Stabilization Wedges: Solving the climate problem from the next 50 years with current technologies", *Science*, Vol 305, pp. 968-972.
- UBC, 2010; "Mineral carbonation", 9 June 2010, <http://www.eos.ubc.ca/research/dipple/UBC_Carbonation/index.htm>.
- Lackner, K.S., 2003, "A guide to CO₂ sequestration", *Science*; Vol. 300, pp. 1677-1678.
- Park, A.A.; Fan, L.S.; 2003; "Carbon dioxide sequestration using alkaline earth metal-bearing mineral", Patent Application Serial N° 60/533,500.
- Wei, X.; 2003, "technological Evaluation of Mineral Sequestration Of CO₂ by Carbonation", Morgantown, West Virginia.
- Teir, S.; Kuusik, R.; Fogelholm, C.J.; Zevenhoven, R.; 2007; "Production of magnesium carbonates from serpentine for long-term storage of CO₂", *Int. J. Process.*, Vol. 85, pp. 1-15.
- Teir, S.; Hannu R.; Eloneva, S.; Fogelholm, C.J.; Zevenhoven R.; 2007; "Dissolution of natural serpentine in mineral and organic acids"; *Int. J. Process.*, vol. 83, pp. 36-46.
- Teir, S.; Eloneva, S.; Fogelholm, C.J.; Zevenhoven, R. 2009; "Fixation carbon dioxide by producing Hydromagnesite from serpentine", *Applied Energy*, Vol. 86, pp. 214-218.
- Zevenhoven, R.; Teir, S.; Elenova, S.; 2008; "Heat optimization of staged gas- solid mineral carbonation process for long-term CO₂ storage", *Energy*, Vol. 33, pp. 362-370.
- Norio Sato, 2004; "Chemical energy and Exergy: an introduction to chemical thermodynamics for engineers"; Elsevier B.V., Hokkaido, Japan, Pg.23-30.
- Pimentel, G.; Spratley, R.D.; 1969; "Understanding Chemical Thermodynamics"; holden-day Inc, San Francisco, California, EE UU, pp. 122-130.
- Zhao, L.; Sang, L.; Chen, J.J.; Teng, H.; 2010; "aqueous Carbonation of natural Brucite: Relevance to CO₂ sequestration"; *Environ. Sci. Technol.*, Vol. 44, pp. 406-411.

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