23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

DISSOLUTION STUDIES OF BRAZILIAN SERPENTINITE ROCKS APPLIED TO MINERAL CARBONATION PROCESSES

Kely Regina Maximo Vieira
UNESP - Univ Estadual Paulista, Faculty of Engineering at Guaratinguetá.
kely_eng@hotmail.com

Gretta Larisa Aurora Arce Ferrufino
National Institute for Space Research, combustion and propulsion associated Laboratory.
gretta@lcp.inpe.br

Ivonete Ávila
UNESP - Univ Estadual Paulista, Faculty of Engineering at Guaratinguetá.
iavila@feg.unesp.br

Vitor Oliveira Facio
UNESP - Univ Estadual Paulista, Faculty of Engineering at Guaratinguetá.
vitorfacio@hotmail.com

João Andrade de Carvalho Jr.
UNESP - Univ Estadual Paulista, Faculty of Engineering at Guaratinguetá.
jcarlos@lcp.inpe.br

Turibio Gomes Soares Neto
National Institute for Space Research, combustion and propulsion associated Laboratory.
turibio@lcp.inpe.br

Abstract. *The actual demand of energy leads to an increase in fossil fuel consumption, which causes the need of insertion of carbon capture and sequestration (CCS) technologies and together with other forms of mitigation of carbon dioxide (CO2) can reduce the environmental impact related to the use of fossil fuels. The mineral carbonation is a CCS technology that fixes CO2 in form of insoluble carbonates. These carbonates could be used as raw material in others industrial sectors. Among all the mineral carbonation processes, the indirect mineral carbonation involves the acid dissolution stage. In this process, metals such as Mg, Ca and Fe are extracted from the raw material, to further react with CO2. The serpentinite rocks is known for having considerable concentrations of Ca, Mg and Fe within its structure and is one of the raw materials used in this process, whereas these rocks are found in considerable amounts in Brazil. The aim of this study is to obtain the highest percentage of Mg extraction in acid dissolution stage of serpentinite rocks, since minor extractions may invalidate this technology economically. In this study it was used the brazilian serpentinite from the Minas Gerais state (S-MG). The acid dissolution consists of two stages. In the first stage involves the dissolution reaction to extract magnesium from the serpentinite rock using hydrochloric acid* ($Mg_3Si_2O_5(OH)_4 + 6HCl = 5H_2O + 2SiO_2 + 3MgCl_2$)*. In the second stage the carbonation reaction is performed by injecting CO2 in the MgCl2 solution and to stabilize the hydrogen potential (pH) a sodium hydroxide (NaOH) aqueous solution is used* ($5MgCl_2 + 10Na(OH) + 4CO_2 = 3NaCl + Mg_5(OH)_2(CO_3)_4.4H_2O$)*. Design of experiments (DOE) is used, which considers factors that influence the reaction, such as temperature, hydrochloric acid concentration and particle size of the raw material. The analysis identifies the levels of factors that presented highest percentage of Mg extraction in this process. The results can help on development of the indirect mineral carbonation applied to carbon capture and sequestration.*

Keywords: *Carbon dioxide, Serpentinite, Mineral Carbonation, Acid dissolution, Carbon Capture.*

1. INTRODUCTION

The increase in population brings with it the intensification of production, an increasing demand for energy generation and related environmental impacts.

Fossil fuels have an existing structure and a low cost in the energy sector (Ávila et al., 2013), and will remain the main source of energy for a long period (Alves et al., 2013).

The CO_2 is one of greenhouse gases, and Brazil part of estimated emissions of CO_2 (net emissions to the atmosphere) from fossil fuel combustion in the energy sector in 2005 represented 19 % of the totality of CO_2 emissions and obtained an increased variation in 74 % compared to emissions from the base year of 1990 (Brazil, 2010).

In 2015 the global carbon dioxide concentration in the atmosphere reached 400 parts per million (ppm) for the first time since the 1958 data, an increase of about 24 % (NOAA, 2014).

The intensification of the greenhouse effect caused by high CO_2 emissions in the atmosphere can induce more frequent extreme events until the end of the century (PBMC, 2014).

Forms of mitigating climate change due to the energy production processes are necessary, such as the use of natural resources in a rational way, the use of alternative sources for energy generation and the insertion of new technologies.

Researches are carried out to mitigate CO_2 concentration in the atmosphere, such as carbon capture and sequestration technologies (CCS).

There are a number of CCS technologies, however, the ones that aim at the chemical conversion of CO_2 into a stable product, both thermodynamically and environmentally, are receiving more attention (Sipilä et al., 2008).

Although controlling the reaction conditions is very important for mineral carbonation, the choice of a suitable material is crucial to increase CO_2 capture efficiency (Chang et al., 2011).

Many researches chose the serpentinite as a raw material in their experiments because of its abundance and availability. In this context, the availability becomes a decisive factor for the use of the raw material (Alexander et al., 2007).

The mineral sequestration technology, through a carbonation reaction, alloy CO_2 with the alkali metal present in the silicate rocks to form solid inorganic carbonates (Sipilä et al., 2008).

According to Sipilä et al. (2008), a variety of elements such as calcium (Ca), iron (Fe), magnesium (Mg), potassium (K) and sodium (Na) can be carbonated, but alkaline earth metals such as Ca and Mg are the most promising because of its insolubility after the carbonation process.

The amount of Si in the raw material may influence the dissolution reaction due to pore blockage of Mg extraction processes (Geerling et al., 2013), the problems of formation of silica gel are conventionally associated with the dissolution of serpentinite (Dutrizac and Chen, 2000), as the Mg removal of the silica layer will be a limiting step in the dissolution process (Teir et al., 2007).

Barnes et al. (1950) reported that the use of hydrochloric acid dissolves most of the Mg in the serpentinite, but the silica gel formed substantially difficult to magnesium chloride removal ($MgCl_2$).

In the acid extraction process, the leaching agent should provide easy recovery (Lackner et al., 1995). Although sulfuric acid gives better Mg extraction results (Teir et al., 2007a), its boiling point is higher than that of hydrochloric acid which would require more energy for the evaporation and condensation of the acid on the recycling process (Teir et al., 2007b).

The carbonation reaction is an exothermic reaction, where energy could be exploited (Lackner et al., 1995; Teir et al., 2007a; Teir et al., 2007b; IPCC, 2005) and the products generated in this process could be sent to industrial sectors to stimulate and reduce its costs (Hemmatite et al., 2014).

Indirect mineral carbonation presents two stages, which in the first stage of the dissolution reaction occurs the extraction of Mg from the serpentine rock using hydrochloric acid as shown in Eq. (1).

In the second stage the carbonation reaction is carried out by CO_2 injection into the $MgCl_2$ solution. To stabilize the hydrogen potential (pH) it is used sodium hydroxide (NaOH) as shown in Eq. (2) (Sipilä et al. 2008).

$$Mg_3Si_2O_5(OH)_4 + 6HCl = 5H_2O + 2SiO_2 + 3MgCl_2 \tag{1}$$

$$5MgCl_2 + 10Na(OH) + 4CO_2 = 3NaCl + Mg_5(OH)_2(CO_3)_4.4H_2O \tag{2}$$

The acid concentration, temperature and grain size are the key factors that may influence the reaction rate in the dissolution of Mg and the formation of silica gel, when it is used hydrochloric acid for the dissolution of serpentinite (Barnes et al., 1950).

Various authors used hydrochloric acid as leaching agent for the Mg extraction of serpentine rocks (Park et al., 2004; Teir et al., 2007a; Teir et al., 2007b; Hemmati et al., 2014).

The use of the design of experiments can increase the productivity of the processes, favouring the study of chemical reactions, optimizing systems, maximizing or minimizing response that will subsequently be analyzed and visualise the relationship between factors and responses, since one of the specific objectives of the method Taguchi are characterized to determine the factor levels which results on the closest responses of values considered ideal for the system (Barros et al., 1995).

The objective of this paper is to identify the levels of the factors that have the highest percentage of Mg extraction, applying the L9 Taguchi matrix to the experimental design, to maximize the response variable, to study the process of mineral carbonation by acid dissolution to capture and storage of CO_2.

2. MATERIALS AND METHODS

The serpentinite (SERP-MG) ($Mg_3Si_2O_5(OH)_4$), utilized has been provided by Mineradora Pedras Congonhas Ltda., located Belo Horizonte/MG, extracted from the mine Nova Lima/MG. The raw material passed by milling and sieving process, for determining the particle size utilized. The chemical composition of serpentinite was obtained by Optical Atomic Emission Spectrometer with Inductively Coupled Plasma (ICP OES, Radial) of Spectro brand, model Arcos. It was assumed as determining factors in the reaction presented in Eq. (1), the temperature, acid concentration and particle size. In the dissolution experiments the serpentinite mass values and volume of HCl used was related to stoichiometric values.

Figure 1. Filtrated.

The amounts of serpentinite used for the nine experiments were equivalent to 9.4 g for the experiments using 1M, 18.8 g for the experiments using 2 M and 37.6 g for experiments using 4 M. The amount HCl used for all the experiments fixed at 180 ml. A time of 2 hours reaction for all experiments, after this time the filtered solutions was established. Figure 1 presents the final solutions all experiments.

2.1 Methodology experimental design by Taguchi Method

As pointed out by Barnes et al. (1950), the determining factors that could influence the performance of serpentinite with HCl dissolution reaction are: temperature (T), the concentration of HCl (C_{HCl}) and the size of particle (Φ). To assess the extraction efficiency of Mg (Yi) by varying the experimental conditions we used an exploratory Taguchi matrix (L9). However, it was considered three levels for each factor, as follows: low (1), intermediate (2) and high (3). These factors and their respective levels are shown in Tab. 1.

Table 1. Factors and levels to the acidic dissolution.

Factors	Level		
	low (1)	intermediate (2)	high (3)
A - Temperature (T [ºC])	30	50	70
B - Acid Concentration (C_{HCl} [M])	1	2	4
C - Size of particle (Φ [µm])	64	115	256

Determined factors and their respective levels: Low, intermediate and high, these were arranged in the L9 orthogonal matrix presented in Tab. 2. As observed, this orthogonal arrangement considers nine experiments.

Table 2. L9 Orthogonal arrangement for the experimental design.

	Codified factors			Variable response
$N°_E$	A	B	C	Yi
1°	1	1	1	Y1
2°	1	2	2	Y2
3°	1	3	3	Y3
4°	2	1	2	Y4
5°	2	2	3	Y5
6°	2	3	1	Y6
7°	3	1	3	Y7
8°	3	2	1	Y8
9°	3	3	2	Y9

After performing the experimental tests, we need to determine the Mg extraction (%). To this is used to Eq. (3).

$$X_i = \frac{(C_i * V_i)}{M_i} \tag{3}$$

Where, "X_i" extraction of the element i (%), "C_i" the concentration of the element i (ppm), "V_i" the final solution the (L), "M_i" the initial mass of the element in the i mineral. To calculate the effects of variable factors on the response was used Eq. (4). With, y1, y2, y3.y4, y5, y6, y7, y8, y9 values of the response variable.

$$M\ j, i = \frac{\sum (y_i)}{n} \tag{4}$$

Where "M" is the media of the factor, "j" is the factor, "i" the factor level "y" the variable response "n" the number of times that the level "i" is repeated in the factor "j ".

3. RESULTS AND DISCUSSION

Table 3 shows the chemical composition of SERP-MG obtained by ICP-OES analysis. As observed the SERP-MG presents a equivalent composition of Mg, Ca and Fe equal to 17.69; 0.70; 3.66 %, respectively. but also it has much of the element Si (silicon) equivalent to 15.36 %.

Tabela 3. Chemical composition of SERP-MG obtained by ICP-OES (%m/m.)

Material	Mg	Ca	Fe	Si
S – MG	17,69	0,70	3,66	15,36

The results indicate that the SERP-MG is suitable for mineral carbonation because of the contents Ca,Mg and Fe.

Table 4 shows the variable response in Mg extraction obtained from the ICP-OES analysis.

The global average calculated by the average of Mg extraction values is equal to 18.21 and the knowledge of the interference level of each factor, we calculated the effect for each factor, obtaining results presented in Tab. 4.

Figure 2 presents the graphic with the values of the effect of each factor on the overall average. The factors combined with the conditions that have the greatest significance are higher than the value of the global average.

Table 4. Matrix and the variable response values.

Experiment	T [ºC]	C_{HCl} [M]	Φ [µm]	Solution final	C_{Mg} (ppm)	Y_{Mg} %	Average factors	
1	30	1	64	SF1	120	2	m_{A1}	4,73
2	30	2	115	SF2	581	4	m_{A2}	14,09
3	30	4	256	SF3	2190	8	m_{A3}	35,82
4	50	1	115	SF4	642	10	m_{B1}	12,87
5	50	2	256	SF5	1785	13	m_{B2}	16,64
6	50	4	64	SF6	5273	20	m_{B3}	25,13
7	70	1	256	SF7	1845	27	m_{C1}	17,90
8	70	2	64	SF8	4374	32	m_{C2}	20,52
9	70	4	115	SF9	12888	48	m_{C3}	16,22

The condition of best adjustment is equivalent to $A_3B_3C_2$, which was addressed in the experimental matrix used in this work as the experiment number nine and showed the highest percentage Mg extraction equal to 48 %.

Tabela 5. The best condition found by the methodology Taguchi.

Best Condition	A T	B C_{HCl}	C Φ	T [ºC]	C_{HCl} [M]	Φ [µm]	Y_{Mg}
9	3	3	2	70	4	115	48%

Consequently, a larger Mg extraction, the temperature factor equivalent the factor A should to be used on the high level, the factor B equivalent to acid concentration should to be used at the higher level and the factor C equivalent to size of particle at the intermediate level (Table 5).

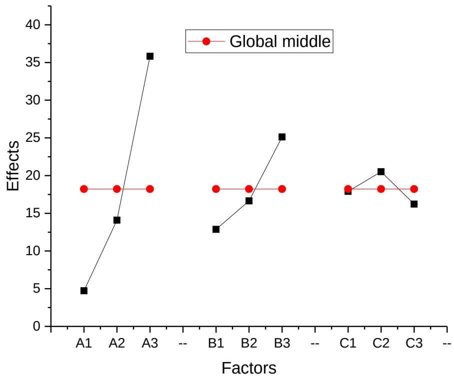

Figure 2. Effects of each factor on the average.

Therefore, the size of particle did not show significance of Mg extraction process.

After obtaining the best reaction conditions for the acidic dissolution of serpentinite, SERP-MG, it was compared to other studies in the literature. The Table 6 shows the chemical amounts in percentage of Mg, Ca, Fe and Si, the reaction conditions of the experiments and percentage Mg extraction in the literature using HCl acid concentration of 4 M as leaching agent.

Table 6. Resulted literature.

Author	Temperature (ºC)	Size of particle (µm)	Reaction time (h)	% Mg	% Ca	% Fe	% Si	Serpentinite (g)	HCl (ml)	Mg extraction (%)
Teir et al.,2007a	20	74-125	1	21,8	10,1	0,34	11,6	1	50	24
Alves et al., 2013	70	75-150	2	22,4	11,8	0,20	24,7	1	50	80
This work	70	115	2	17,95	0,70	3,81	14,87	37,6	180	48

In the literature Teir et al. (2007a) and Alves et al. (2013) conducted experiments using the same amount of sample serpentinite and the same amount of HCl, referring to 1 g and 50 ml respectively, it is emphasized that these amounts do not represent stoichiometric values because they present excess acid percentages.

Teir et al. (2007a) obtained in 1 hour and room temperature Mg extraction percentage equal to 24 %, and Alves et al. (2013) that performed work based on Teir et al. (2007a) obtained extract equivalent to 80 % in two hours with reaction temperature of 70 ° C. In conditions of excess acid, requires higher percentage of water used for the preparation of reagents and stoichiometric conditions need to be evaluated for comparison experiments with excess amounts of acid. In our work used was concentration of 4 M, temperature of 70 °C and mean particle size of 115 µm and 2-hour reaction, the obtained higher value extraction equal 48 %, by not operating a excess HCl in the experiments.

4. CONCLUSIONS

From this study presented in this work can be demonstrated the employability of the experimental design with orthogonal matrix of L9 Taguchi. The elemental composition of serpentinite Minas Gerais presented percentages of magnesium, calcium and iron which enable the use of this raw material for capture and storage of CO_2 processes. The highest percentage extraction of magnesium found in the experiments is equal to 48 % using 4M HCl concentration, temperature of 70 °C and size of particle equal to 115 µm in a reaction of 2 hours. The results from the literature that show the best extraction Mg values in these conditions were carried out with HCl larger values than the stoichiometric condition, so for our subsequent studies of comparisons the excess acid conditions should be subject for higher percentages of Mg extraction be achieved with a smaller amount of excess acid.

5. ACKNOWLEDGEMENTS

The authors would like to thank FAPESP for post-doctoral project number 2013/21244-5, regular research project number 2011/19920-7, the CNPQ for project number 150894/2014-7 and CAPES for masters scholarship. They would also like to thank the person in the laboratories: LCP/INPE in Cachoeira Paulista, Dr. José Augusto Jorge Rodrigues, Sayuri Okamoto. They would also like to thank the companies that provided material for the study: Mineradora Pedras Congonhas Ltda.

6. REFERENCES

Alexander, G.; Maroto-Valer, M.M.; Gafarova-Aksoy, P.,2007. "Evaluation of reaction variables in the dissolution of serpentine for mineral carbonation". *Fuel*.Vol. 86, p. 1–2.

Alves, N.; Xavier, C.; Dullius, J.; Ligabue, R.; Ketzer, J.M.; Seferin, M.; Einloft, S., 2013. "Potencial uso de serpentinito no armazenamento mineral do CO_2". *Quím. Nova*, Vol. 36, n. 6, p. 773–777.

Ávila, I., Carvalho JR., J.A.; Arce, G.L.A.F.; Santos, J.C.; Facio, V.O.; Santos, A.S., 2013. "Evaluation of the potential of a brazilian serpentine as CO_2 sorbent applied to carbon sequestration by mineral carbonation". In: *International Congress of Mechanical Engineering (COBEM 2013)*, 22., Ribeirão Preto, Brazil.

Barnes, V. E., Shock D. A. and Cunningham, W. A. 1950."Utilization of Texas Serpentine," The University of Texas, No. 5020, *Bureau of Economic Geology*.

Barros, N.; Bruns, R.E.; Scarminio, I. S., 1995. "Otimização e planejamento de Experimentos". *Editora da Unicamp*, p.291. Campinas.

Brasil."Segunda Comunicação Nacional do Brasil à Convenção-Quadro das Nações Unidas sobre Mudança do Clima". 2010. *Coodenação-Geral de Mudanças Globais do Clima – Ministério da Ciência e Tecnologia. Brasília.* <http://www.mct.gov.br>

Chang, E; Chen, C; Chen. Y; Pan, S; Chiang, P., 2011. "Performance evaluation for carbonation of steel making slags in slurry reactor". Journal of Hazardous Materials. v. 186, p. 558-564.

Dutrizac, J.E., Chen, T.T., and White, C.W., 2000."Fundamentals of serpentine leaching in hydrochloric acid media". *Magnesium technology 2000.*

Geerlings, H.; Zevenhoven, R., 2013. "CO_2 Mineralization—Bridge Between Storage and Utilization of CO_2". *Annual Review of Chemical and Biomolecular Engineering*.Vol. 4, p. 103-117.

Hemmati, J. Shayegan, J. Bu, T.Y. Yeo, P. Sharratt, 2014. "Process optimization for mineral carbonation in aqueous phase" *Int. J. Miner. Process.* 130, p. 20– 27.

IPCC. Intergovernamental Panel on Climate Change., 2005. <http://www.ipcc.ch/index.htm>.

Lackner, K.S. et al., 1995. "Carbon dioxide disposal in carbonate minerals".*Energy*, 20,1153-1170.

NOAA (2014). National Oceanic and Atmospheric Administration. <http://www.esrl.noaa.gov>.

Park, A-H. A.; Fan, L.-S., 2004."CO_2 mineral sequestration: physically activated dissolution of serpentine and pH swing process". *Chemical Engineering Science*. Vol. 59, p. 5241-5247.

PBMC, 2014: "Base científica das mudanças climáticas. Contribuição do Grupo de Trabalho 1 do Painel Brasileiro de Mudanças Climáticas ao Primeiro Relatório da Avaliação Nacional sobre Mudanças Climáticas". *COPPE. Universidade Federal do Rio de Janeiro*, Rio de Janeiro, RJ, Brasil. < http://www.pbmc.coppe.ufrj.br>.

Sipilä, J.; Teir, S.; Zevenhoven, R., 2008. "Carbon dioxide sequestration by mineral carbonation Literature review update 2005-2007". *Åbo Akademi University Faculty of Technology Heat Engineering Laboratory*.

Teir, S.; Revitzer, H.; Eloneva, S.; Fogelholm, C.-J.; Zevenhoven, R.. 2007a. "Dissolution of natural serpentinite in mineral and organic acids". *International Journal of Mineral Processing*, Vol. 83, p. 36-46, 2007a.

Teir, S., Kuusik, R., Fogelholm, C.-J., Zevenhoven, R., 2007b. "Production of magnesium carbonates from serpentinite for long-term storage of CO_2", *Int. J. Miner. Process.* Vol. 85, p. 1–15.

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.