ACID DISSOLUTION STUDIES USING BRAZILIAN SERPENTINITE ROCKS APPLIED MINERAL CARBONATION

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

Carlos Manuel Romero Luna
UNESP - Univ Estadual Paulista, Faculty of Engineering at Guaratinguetá.
c_romeroluna@yahoo.com

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. *Indirect mineral carbonation through pH-swing is an attractive option for Carbon Capture Storage/Sequestrate technology (CCS). This technology can to fix the CO_2 emission into carbonates. Thus, indirect mineral carbonation through pH-swing considers two stage, such as, extraction stage and carbonation stage. The extraction stage involves acid dissolution process of the silicate rocks, such as, serpentinite, in order to extract magnesium (Mg) contains into the rocks. The main aim of this study was investigate the uses of the brazilian serpentinite rocks in indirect mineral carbonation. For this, was used two serpentinite rocks. One serpentinite rock from Goiás state (SERP-GO) and the other from Minas Gerais state (SERP-MG). This samples were undergoes to different characterization tests. For extraction stage was used a Design of experiment (DoE) by Taguchi method, this DoE uses an L9 orthogonal matrix, in order to, evaluate four factors and its levels, such as, temperature process (T °C), HCl concentracion (M), particle size (µm) and HCl excess (E). The choice of these factors and levels is based on their influences in the dissolution process. The results shown that experimental tests using: particle size of 69 µm, temperature of 70 °C, 2 M HCl, and four times the stoichiometric amount resulted in the highest Mg extraction for SERP-GO and SERP-MG. However, the Mg extracted for SERP-GO was more efficient that for SERP-MG, so, 76 % and 29 % of Mg extracted were obtained for SERP-GO and SERP-MG, respectively. The low efficiency on Mg extracted from SERP-MG was probably to the chemical composition, once that, SERP-MG contains 30 percent more of silicon oxide (SiO_2) than SERP-GO. The statistical analysis shown the main factor on dissolution process is the temperature. The worth mentioned that the acid excess was the factor less significant.*

Keywords*: Carbon dioxide capture, Serpentinite rocks, Indirect mineral carbonation, Acid dissolution, Extraction efficiency.*

1. INTRODUCTION

Currently research are developed to mitigate CO_2 emissions in the atmosphere, called Carbon Capture and Storage/Sequestration (CCS) to ensure the continued use of fossil fuels within the context of the reduction of anthropogenic emissions.

Different technologies are under investigation, including geological storage consisting of the CO_2 injection in oil and natural gas, saline formations, the biological storage that is based on increased photosynthesis (Kemache et al. 2016) and the carbonation mineral first mentioned by Seifritz (1990) which consists in studying the natural process of weathering through of precipitation containing dissolved CO_2.

The mineral carbonation process are a variety of elements which can react with CO_2 to form carbonates, alkaline earth metals are the most promising because of its high stability (Sipilä et al. 2008) extracted from silicate minerals containing mostly magnesium or calcium oxide (Kemache et al. 2016).

Mineral carbonation is one method for long-term storage of CO_2. This method consists in the extraction and precipitation mainly of magnesium and its reaction with CO_2, resulting in the production of carbonates (Lavikko and Eklund 2016).

From serpentinite rocks it is possible to extract the elements of interest. The serpentine group is composed of the mineral polymorphs: chrysotile, antigorite and lizardite. The serpentine is an ultramafic rock and can contain one or more minerals serpentine (Kemache et al. 2016), these minerals have different characteristics that affect the application of serpentinite as a feedstock for carbon capture, even if both coils, the chemical composition and structure differ from each other (Lavikko and Eklund 2016).

The study of serpentinite becomes generates knowledge not only to improve and applicability of the carbonation process to reduce emissions of CO_2, as well as the application of other purposes, such as the use of serpentinite as ornamental rocks (Lavikko and Eklund 2016).and the Brazilian case in ground control application.

Another important feature in the raw material to be used in the mineral carbonation is having low silicon content (Si) in its composition due to pore blocking when applied to any type of activation to extract alkaline earth rocks metals (Ghgrlings and Zevenhoven, 2013).

For activation of serpentinite in the mineral carbonation process, an important step in the process is the stage of dissolution, mostly where the Mg is liberated. For improving the dissolution process of some pre-treatment are used as grinding to reduce the particle size, magnetic separation for removal of iron oxides (which recovered can be used in the iron and steel industries) and thermal treatment (Kemache et al., 2016).

Decreasing the particle size influences the dissolution reaction by increasing the Mg value taken when the particle size is reduced to < 75 μm (Teir et al. 2007).

The most usual form of Mg extraction from a silicate matrix is the use hydrochloric acid (HCl), which was proposed by Lackner (Lackner et al. 1997) at the initial stage of mineral sequestration search CO_2 (Olajire 2013). The reaction occurs in two steps: firstly is done of Mg extraction from the feedstock using hydrochloric acid and then makes the injection of CO_2 to form carbonates.

The concentration of HCl, the reaction temperature and the particle size are the main factors that may influence the reaction rate in magnesium dissolution and formation of silica gel (Barnes et al. 1950).

From the application of the Taguchi method to assess the acid dissolution of Brazilian serpentinites in Mg extraction for mineral carbonation is expected to find the best conditions for setting and significance of the variables of influence.

3. MATERIALS AND METHODS

The serpentinite ($Mg_3Si_2O_5(OH)_4$) used are from the Mineradora Pedras Congonhas Ltda., located Belo Horizonte/MG, extracted from the mine Nova Lima/MG and SAMA SA, Miguaçu/GO, extracted from the Cana Brava mine. The SERP-MG is an industrial serpentinite and SERP-GO was obtained after the beneficiation stage of chrysotile and is considered a tailings mining. The raw materials have been through the sieving process for the determination of particle size given in the experimental design. The chemical composition was obtained by analysis of X-ray Fluorescence Spectroscopy (XRF). The X-ray Diffraction (XRD) has been used to identify the compounds presents in the two samples serpentinite.

3.1 Design of experiments

In the dissolution process are identified two final products, a solid residue and a solution. The Inductively Coupled Plasma-Atomic Emission Spectrometry Thermo Scientific iCAP 7000 (ICP-AES) was employed to determine the extraction of magnesium in the final solution from the acid dissolution of serpentinite process.

In the final solution can also be found other extracted elements such as calcium and iron. However this paper aims the extraction of magnesium in the serpentinite for the formation of carbonates because of low calcium content and the possibility of ferro-magnetic separation, which would facilitate production of magnesium carbonates with increased purity.

The experiments were carried out twice in aleatory order. 100 ml of HCl were used for all tests and used as serpentinite mass of the reaction stoichiometry, Eq. (1), whereas the values of all the oxides encountered in XRF analysis. The masses ranged from 4.6 to 18.4 g in a glass reactor with magnetic stirring higher than 600 rpm and a condensation system.

$$Mg_3Si_2O_5(OH)_4 + 6HCl \rightarrow 5H_2O + 2SiO_2 + 3MgCl_2 \quad (1)$$

The Taguchi L9 orthogonal array is employed experimental design with two replicates, considering the variables of temperature, acid concentration, particle size of the raw material and excess.

As from the response variable experimental design can be calculate the Mg extraction for each of the nine tests after the dissolution, found by Eq. (2). The *Ci* is element concentration (ppm), *Vi* the volume of the final solution (L) and *Mi* the mass of the element in material (in nature) before being added in the reactor (mg) (Teir et al. 2007).

$$Y_i = \frac{(C_i * V_i)}{M_i}, \tag{2}$$

To calculate the effects of factors on the response variable was used in Eq. (3), while the average response variables - *j* is the factor (A, B, C) and *k* is the factor level (1, 2, 3). The variable *n* refers to the number of repetitions *k* represented in the level *j* factor.

$$M_{j,k} = \frac{\sum(Y_i)}{n} \tag{3}$$

For the analysis of the results were considered the best adjustment conditions (larger-the-better), the signal-to-noise ratio (S/N) analysis, Eq. (4), and analysis of variance (ANOVA). Given the *y* variables responses and considering the amount of replicas *n*.

$$(S/N) = -10\log\left(\frac{\sum\left(1/y^2\right)}{n}\right) \tag{4}$$

4. RESULTS AND DISCUSSION

The XRF detected that the SERP-MG contains about 30.63 wt% of MgO, 52.09 wt% of SiO_2, 11,82 wt% of Fe_3O_4, 1.66 wt% of CaO and less than 4 wt% of other components such as Al_2O_3, Cr_2O_3, NiO, MnO, SO_3, Co_3O_4 and TiO_2. The SERP-GO contains about 40.43 ± 0.43 wt% of MgO, 39.06 ± 0.84 wt% of SiO_2, 9.18 ± 1.16 wt% of Fe_2O_3, 2.26 ± 0.32 wt% of CaO and less than 10 wt% of Al_2O_3, Cr_2O_3, NiO, MnO, Na_2O, P_2O_5 and CuO detected by XRF.

The serpentine mainly consists in antigorite [$Mg_3Si_2O_5(OH)_4$], actinolite [$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$], chrysotile [$Mg_3Si_2O_5(OH)_4$], akermanita [$Ca_2MgSi_2O_7$], johannsenita [$CaMnSi_2O_6$], lizardite [$Mg_3Si_2O_5(OH)_4$] and talc [$Mg_3Si_4O_{10}(OH)_2$] according to XRD pattern.

In the Table 1 presents the L9 array with the parameters and its codings. The responses refer to Mg extraction of SERP-MG and SERP-GO presenting the result of the extraction average (M) and the signal-to-noise ratio (S/N).

Table 1. The Taguchi L9 orthogonal array and the reponses.

	Parameters				Process parameters				Response (Mg (%))			
									SERP-GO		SERP-MG	
Run	A	B	C	D	T (°C)	C_{HCl} (M)	Φ (μm)	V_{HCl} (mL)	M	S/N	M	S/N
1	1	1	1	1	30	1	69	E	16,37	24,26	1,51	3,51
2	1	2	2	2	30	2	328	2E	14,50	23,23	1,11	0,28
3	1	3	3	3	30	4	550	4E	16,83	24,49	2,90	6,88
4	2	1	2	3	50	1	328	4E	32,45	30,17	3,97	11,97
5	2	2	3	1	50	2	550	E	34,41	30,54	4,04	11,91
6	2	3	1	2	50	4	69	2E	57,30	35,01	15,54	23,80
7	3	1	3	2	70	1	550	2E	62,23	35,87	16,94	24,58
8	3	2	1	3	70	2	69	4E	75,51	37,56	28,52	28,89
9	3	3	2	1	70	4	328	E	68,69	36,73	26,20	28,10

In Figure 1 presents the effects of factors on the medium and on the signal signal-to-noise ratio (S/N).

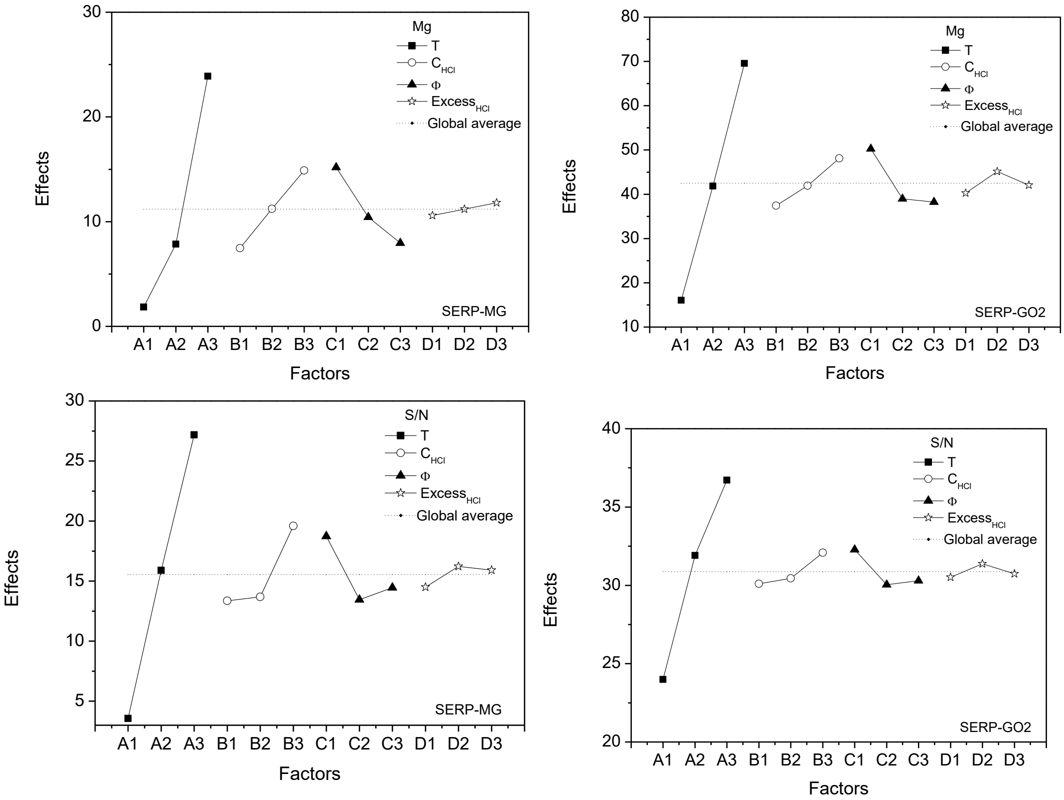

Figure 1. Effect of factors on the average and S/N.

The results shown that using: temperature of 70 °C, 2 M HCl, particle size of 69 µm and four times the stoichiometric amount resulted in the highest Mg extraction for the two of evaluated serpentinites.

The Mg extracted for SERP-GO was more efficient that for SERP-MG, so, 76 % and 29 % of Mg extracted were obtained for SERP-GO and SERP-MG, respectively. The low efficiency on Mg extracted was probably to the percent more of silicon oxide (SiO_2), because is detected that the SERP-MG contains about 52.09 wt% of SiO_2 and the SERP-GO contains about 39.06 ± 0.84 wt% of SiO_2.

Despite the test nine present the highest percentage of Mg extraction, the best condition adjustment by evaluating the media and the S/N ,Fig. 1, occurs with temperature of 70 °C, 4 M HCl, particle size of 69 µm and four times the stoichiometric amount for SERP-MG and twice for SERP-GO. These conditions have not been assessed by the matrix and require confirmation experiments. The smaller particle size is more efficient than others assessed granulometries.

From the Tab. 2 to Tab. 5 the ANOVA is shown for the average and the S/N. Since there is no sufficient degrees of freedom for calculating error, the parameter D related to acid excess replaces the error value because that is the parameter that presented the smallest value in sum of squares.

Table 2. ANOVA table for Mg extration of SERP-MG.

Analysis of variance on Mg extration			Mean 944.9		Result
	SS	DF	MS	F	
Factors	sum of squares	degree of freedom	Mean square	F-ratio	
A	779.3	2	389.6	354	Significant
B	82.4	2	41.2	37	Significant
C	81.0	2	40.5	37	Significant
D	2.2	2	1.1		
Residual error	2.2	2	1.1		

Table 3. ANOVA table for Mg extration of SERP-GO.

Analysis of variance on Mg extration			Mean 4673.6		Result
Factors	SS sum of squares	DF degree of freedom	MS Mean square	F F-ratio	
A	4200.6	2	2100.3	114	Significant
B	169.6	2	84.8	5	Not significant
C	267.2	2	133.6	7	Not significant
D	36.2	2	181		
Residual error	36.2	2	18.1		

Table 4. ANOVA results for signal-to-noise rations for Mg extraction of SERP-MG.

Analysis of variance on S/N ratio (larger-the-better)			Mean 964.35		Result
Factors	SS sum of squares	DF degree of freedom	MS Mean square	F F-ratio	
A	838.1	2	419.0	168	Significant
B	74.0	2	37.0	15	Not significant
C	47.3	2	23.6	9	Not significant
D	5.0	2	2.5		
Residual error	5.0	2	2.5		

Table 5. ANOVA results for signal-to-noise rations for Mg extration of SERP-GO.

Analysis of variance on S/N ratio (larger-the-better)			Mean 264.6		Result
Factors	SS sum of squares	DF degree of freedom	MS Mean square	F F-ratio	
A	247.7	2	123.9	208	Significant
B	6.7	2	3.3	8	Not significant
C	9.0	2	4.5	7	Not significant
D	1.2	2	0.6		
Residual error	1.2	2	0.6		

The statistical analysis shows that for Mg extraction using the SERP-MG all parameters are significant (A, B and C) in relation to average, however for other analyzes (S/N) only the temperature showed significance in the process.

The results showed that for the best low Mg extraction using brazilian serpentinite the temperature, the acid concentration must be used in high level.

The availability of the mineral and composition influence in the applicability as a feedstock for CCS processes. The Brazil consumes and exports mineral silicates like serpentinites. It is known that the serpentines have different composition and structure behaving in different ways in the metal extraction process. Thus, whereas the SERP-GO has a higher percentage of Mg, smaller percentage of Si and better Mg extraction, it can be concluded that the study of the chemical composition collaborates with the acid dissolution tests. Since evaluating the potential of serpentinite for MC processes, higher percentages of Mg in the rock are relevant and with higher extraction conditions would propitiate higher carbonation rates in CO_2 mineralization process.

5. CONCLUSIONS

The conclusion is that the conditions that lead to improved Mg extraction of metals in serpentinite occurs using the temperature and the acid concentration in high level. Smaller particle sizes can provide better results in Mg extraction.

The temperature is variable with increased significance for the acid dissolution process. The serpentinite of Goiás state obtained the highest potential for carbon capture systems by mineral carbonation, from the composition analyzes and the best percentage of Mg extraction.

6. ACKNOWLEDGEMENTS

The authors would like to thank for masters scholarship, the FAPESP for post-doctoral project number 2013/21244-5, regular research project number 2011/19920-7, research project number 2016/15749-5 and the CNPQ for project number 150894/2014-7. They would also like to thank the person in the laboratories: LCP/INPE in Cachoeira Paulista, Dr. José Augusto Jorge Rodrigues and Sayuri Okamoto. They would also like to thank the companies that provided material for the study: Mineradora Pedras Congonhas Ltda and SAMA S.A.

7. REFERENCES

Barnes, V.E., Shock, D.A. and Cunninghan, W.A., 1950. "Utilization of Texas serpentine". The university of Texas, Vol. 5020.

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, pp. 103–17.

Kemache N, Pasquier LC, Mouedhen I, Cecchi E, Blais JF and Mercier G., 2016. "Aqueous mineral carbonation of serpentinite on a pilot scale: The effect of liquid recirculation on CO2 sequestration and carbonate precipitation". Appl Geochemistry. Vol. 67, pp. 21–29.

Lackner, K.S., Butt, D.P. and Wendt, C.H., 1997. "Progress on binding CO_2 in mineral substrates". Energy Conversion and Management, Vol. 38, pp.259–264.

Lavikko, S. and Eklund, O., 2016. "The significance of the serpentinite characteristics in mineral carbonation by "the ÅA Route." International Journal of Mineral Processing, Vol. 152, pp.7–15.

Olajire, A., 2013. "A review of mineral carbonation technology in sequestration of CO_2". Journal of Petroleum Science and Engineering, Vol. 109, pp. 364–392.

Seifritz, W., 1990. "CO_2 disposal by means of silicates". Nature, Vol 345, pp. 489.

Sipilä, J., Teir, S. and Zevenhoven, R., 2008."Carbon dioxide sequestration by mineral carbonation Literature review update 2005 – 2007. Report VT 2008-1.

Teir, S., Rein K., Carl J. F., and Zevenhoven R., 2007. "Production of Magnesium Carbonates from Serpentinite for Long-Term Storage of CO_2." International Journal of Mineral Processing. Vol. 85, pp. 1-15.

8. RESPONSIBILITY NOTICE

The following text, properly adapted to the number of authors, must be included in the last section of the paper: The author(s) is (are) the only responsible for the printed material included in this paper.