EVALUATION OF THE POTENTIAL OF A BRAZILIAN SERPENTINE AS CO2 SORBENT APPLIED TO CARBON SEQUESTRATION BY MINERAL CARBONATION

Ivonete Ávila (iavila@feg.unesp.br)
João A. Carvalho Jr.
Gretta L. A. A. Ferrufino
Vitor O. Facio
Allan S. Santos
UNESP - Univ Estadual Paulista, Faculty of Engineering at Guaratinguetá , Department of Energy, Guaratinguetá, SP, Brazil

José C. dos Santos
Laboratório Associado de Combustão e Propulsão, Instituto Nacional de Pesquisas Espaciais, INPE, Cachoeira Paulista, Brazil

Abstract. Energy is intrinsically linked to the development of countries, and its demand has substantially increased in recent decades. Eighty percent of all energy sources consumed in the world are derived from fossil fuel combustion. In order to stabilize its concentration levels in the atmosphere, the reduction of anthropogenic emissions of carbon dioxide (CO_2) is going to enable the continuous use of fossil fuels in power generation. Several researches have shown that mineral carbonation has a great potential to capture substantial amounts of CO_2. Its thermodynamic analyses have shown that acid dissolution is the most suitable process due to its lower energy consumption. In this process, the carbon dioxide is captured by the sorbent to produce a carbonate (sustainable product), in which mineral silicates, as serpentine [$Mg_3Si_2O_5(OH)_4$], are used. In this paper, it is presented a brief review of the literature on the carbonation process applied to carbon capture. Furthermore, a characterization of a Brazilian serpentine is performed in order to evaluate its potential as a CO_2 sorbent. Literature shows that the particles size is one of the factors that can influence the kinetics of the dissolution reaction. Thus, the sample preparation is carried out to obtain particle sizes that are suitable for being used in the carbonation process. Afterwards, the sample characterization is carried out using the following techniques: porosimetry by N_2 adsorption, X-ray diffraction, scanning electron microscopy, and X-ray fluorescence. The results found that the methodology applied in the sample preparation interfered in the final composition of the material due to contaminations present in the used systems.

Keywords: carbon capture, serpentine, carbonation, carbon dioxide

1. INTRODUCTION

Considering the importance of fossil fuels for the world's economy, there is urgency to develop effective technologies for the management of carbon emissions due to energy generation. Thus, there are some suggestions or technologies to reduce those dioxide carbon emissions, e.g., increasing the energy efficiencies applied to existing technologies, and replacing the fossil fuels by using renewable energy sources (Wall, 2007).

The products that are derived from fossil fuel combustion can be captured and sequestered. On the other hand, technologies and strategies to reduce carbon emissions can be assessed using three criteria: (1) a minimum impact on both, availability and cost, (2) the possibility of a large-scale application and expansion of technology, and (3) a minimum environmental impact (Arce, 2012).

Due to the magnitude of emission reduction required to stabilize CO_2 concentrations in the atmosphere (approximately 1 Gt_C/year for 2025 and 4 1 Gt_C/year for 2050), carbon capture and sequestration is the most promising technology that can comply with the three aforementioned criteria. Furthermore, sequestration is essential to keep on using fossil fuels (O'Connor et al., 2001).

The processes known as carbon sequestration are those used to capture and sequester CO_2 emissions in an environmentally safe manner. The sequestration and fixation through geological, oceanic, and mineral methodologies have been suggested to reduce CO_2 emissions.

The concept of mineral sequestration technology with accelerated kinetics for CO_2 sequestration is commonly called as mineral carbonation (Lackner, 2002; Park et al., 2003; Sipilä et al., 2008). It is a technology based on a natural process of CO_2 sequestration, known as rocks weathering.

The carbon sequestration technology through mineral carbonation allows the formation of solid inorganic carbonates by a reaction between CO_2 and silicate minerals. This process involves a gas-solid reaction between finely ground minerals with CO_2 to form geologically stable carbonates. Magnesium and calcium containing silicate ores are identified to react with CO_2 to form stable carbonates which is given by the generic reaction (Park, 2005):

$$(Mg, Ca)_x Si_y O_{x+2y+z} H_{2z}(s) + xCO_2(g) \leftrightarrow x(Mg, Ca)CO_3(s) + ySiO_2(s) + zH_2O \qquad [1]$$
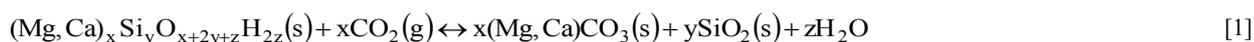
The mineral carbonation applied as a concept of CO$_2$ sequestration was cited for the first time by Seifritz (1990). A few years later, Dunsmore (1992) investigated the carbon sequestration through mineral carbonates by CO$_2$ absorption with minerals of magnesium, calcium and iron. Afterwards, Lackner et al. (1995) further developed the research on mineral carbonation and demonstrated that the thermodynamic processes of dissolution and carbonation are favorable. They proposed the formation of carbonates from metal hydroxides by a carbonation reaction.

This technology has been getting great attention from the scientific community, and many researchers reported the potential of different minerals, such as olivine [(Mg,Fe)$_2$SiO$_4$], serpentine [Mg$_3$Si$_2$O$_5$(OH)$_4$], forsterite [Mg$_2$SiO4] and wollastonite [CaSiO$_3$], as carbon absorbents. Those minerals were identified as optimum natural silicate minerals due to their abundance and low cost (Seifritz, 1990; Sipilä et al., 2008; Van Essendelft and Schobert, 2009a and 2009b).

Park (2005) evaluated the viability of the application of carbonation through the dissolution of minerals with organic acids in a single step reaction by physical activation. In contrast, Teir et al. (2007a) studied the possibility of carbonation with various inorganic acids.

Teir (2008) studied magnesium extraction with various weak and strong acids (H$_2$SO$_4$, HCl, HCO$_3$), and the most efficient extraction was achieved by HSO$_4$, followed by HCl. Compared to H$_2$SO$_4$, the use of HCl has the advantage due to its ease to be recovered. The acid extraction reaction with HCl is shown in Eq. [2]. In the carbonation step, besides the CO$_2$, it is used the NaOH to adjust the pH of the solution, and to accelerate the carbonate precipitation, as presented in Eq. [3].

$$Mg_3Si_2O_5(OH)_4(s) + 6HCl(aq) \rightarrow 3MgCl_2(aq) + 2SiO_2(s) + 5H_2O(l) \qquad [2]$$

$$5MgCl_2(aq) + 10NaOH(aq) + 4CO_2(g) \rightarrow Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O(s) \qquad [3]$$
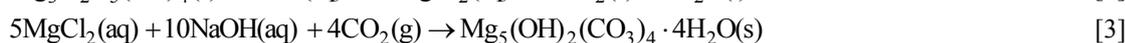
The precipitation of hydro-magnesite, as a carbonate which is stable in the environment through this process, was introduced by Teir (2008). The precipitation reached up to 99% of pure hydro-magnesite from serpentine that was used in the process. However, the acid loss and high amount of NaOH required for the carbonate precipitation has made this process expensive and unattractive. Thus, this process only becomes economic and environmentally viable when there is the recovery of used acids and bases (Sipilä et al. 2008).

Silicates are the most suitable minerals to be used in CO$_2$ sequestration mainly due to their composition that contains large quantities of alkali metal, and because they are present at a much higher proportion than fossil fuels on the Earth's surface.

Serpentine, olivine and forsterite are the most suitable mineral rocks for carbonation due to a large amount of magnesium, calcium and iron that is present in their composition, and also because of their considerable reactivity. Moreover, the mineral quantity required to carbon dioxide capture is small.

The carbonation reaction is exothermic, i.e., no additional energy is required, where the biggest challenge to the use of mineral silicates for CO$_2$ capture is their low conversion to carbonates (Lackner et al., 1997). Therefore, much research has been focused on the identification of rapid kinetic methods, as well as on the application of small-scale experiments to determine the reaction speed, and on the characterization of mineral reagents, and reaction products (Zhang et al., 1999; Park et al., 2003; Maroto-Valer, 2005b; Zevenhoven et al., 2006; Wang and Maroto-Valer, 2011).

Although the required raw material is cheap and the carbonation reaction has an exothermic behavior, the process conditions (pressure and temperature) and additional chemical products used to increase the reaction speed contribute to the expensive costs of the process (Teir, 2008).

Admittedly, the mineral carbonation is theoretically complex because the reaction products are metastable species, (Teir et al., 2007b). The most stable phase of magnesium carbonates is the magnesite (MgCO$_3$). Nevertheless, the magnesite is formed at temperatures above 60° C and at high pressures (Zhao et al., 2010). Even though the production of magnesite can allow a significant rate of CO$_2$ capture per mole of magnesium, the environments of aqueous solutions adopted in carbonation processes are favorable for the formation of hydromagnesite. Teir (2008) investigated the thermal stability of hydromagnesite and concluded that it should be a safe and stable storage medium for CO$_2$ up to 300 ºC. Since the solubility of hydromagnesite in water is lower than that of lansfordite, hydromagnesite seemed to be a suitable material for the long-term storage of CO$_2$.

Considering the importance of the use of CO$_2$ capture technologies, as previously discussed, this research is part of a project of carbon capture by a carbonation process that is being developed by the Energy Department, Faculty of Engineering Guaratinguetá (FEG/UNESP). The first step of this project is to evaluate the potentialities of which raw material to be used as carbon sorbent. This work aims to prepare and characterize the serpentine which is going to be used in the carbonation process. The importance of this step is emphasized because the serpentine is received in its raw form (rock) and it requires a prior preparation for the particle size to be suitable for use. Another aspect that is also important is to assess whether the methodology applied in the sample preparation interferes or not in the final obtained material due to the contamination present in used systems.

2. EXPERIMENTAL AND METHODS

2.1 Serpentine [$Mg_3Si_2O_5(OH)_4$]

The raw material, serpentine, [$Mg_3Si_2O_5(OH)_4$], was collected directly from Cana Brava mine in Minaçu which is located at 510 km from Goiânia, and it was provided by SAMA S.A. Its chemical composition is presented in Tab. 1.

Table 1: Chemical composition of the serpentine extracted from Cana Brava mine (SAMA S.A.)

Composition	Concentration	Composition	Concentration	Composition	Concentration
SiO_2	32.8-40.1%	K_2O	< 0.05%	Zn	18-25 ppm
MgO	39.2-41.1%	P_2O_5	< 0.05%	V	25-61 ppm
Fe_2O_3	3.2-8.5%	TiO_2	< 0.05%	Pb	24-34 ppm
FeO	< 0.01-0.56%	Na_2O	< 0.04%	Rb	7-11 ppm
Al_2O_3	0.42-0.99%	H_2O^+	12.91-15%	Sr	< 5-8 ppm
Cr_2O_3	0.28-84%	H_2O^-	0.4-1.25%	S	< 0.08%
NiO	0.22-0.35%	MnO	< 0.13 ppm	Cu	6-363 ppm
CaO	< 0.11%	Cl	< 20-610 ppm	Co	66-150 ppm

Four samples were received in their natural form (rocks) with a total mass of around 12.5 kg. The greatest measured rocks were approximately 15.5 cm × 31.0 cm large. The raw material was has a dark gray color, lightly green, which is characterized by the mineral absence present in the parent rock. The main constituent is serpentine in which chrysotile is the most abundant (Ferreira Filho, 2013).

In the crushing process of the raw material, a jaw crusher was used. After this process, part of the obtained material was milled using a ball mill. After its crushing, the material presented different sizes from > 100 μm to rocks with sizes of 6.5 cm × 4.0 cm. In order to obtain fine particle sizes, a ball mill was used, followed by a subsequent selection using a set of sieves and a mechanical Shaker.

2.2 Porosimetry by Nitrogen Absorption

The porosity tests were run in a Micromeritics porosimeter (ASAP - 2020). Prior to porosimetry tests, the samples were dried in an oven for approximately 12 h under a temperature of 110 ^{o}C. Samples of (1.0±0.3)g were used in all experiments. In the degas conditions, the sample was heated from a rate of 10°Cmin^{-1} up to 350°C, and submitted to an evacuation rate of 10 mmHgs^{-1} until 10 μmHg, remaining under these conditions for 4 h. In the analysis of the conditions, the samples were immersed in liquid nitrogen, and the isothermal conditions were at -196 ^{o}C, maintained during all experiments. The porosimetry analysis was performed under vacuum at an evacuation rate of 5mmHgs^{-1}until 10 μmHg, remaining under these conditions for 6 min. Then, a P/P_0 programming for 42 points was applied (27 points for adsorption and 15 points for desorption). P/P_0 is the ratio between the applied pressure (P) and the saturation vapor pressure of the adsorbed gas (P0), i.e., nitrogen.

2.3 X-ray diffraction (XRD)

The samples were analyzed by X-ray diffraction – XRD (Rigaku-Rotaflex RU-200B diffractometer) operated in θ-2θ Bragg configuration using Cu (Kα) radiation (λ = 1.4 Å). The voltage was set at 200 kV with a flux of 80 mÅ. Data for θ-2θ experiments were collected in the range of 5° to 100°, using a scan rate of 2.0°min^{-1}.

2.4 Scanning Electron Microscopy (MEV/XEDS)

The morphological structures of the samples were observed by a Scanning Electron Microscope (SEM) in a LEO Electron Microscopy 440 (ZEIZ/LAIKA). The semi-quantitative composition by energy dispersive spectroscopy of X-ray (XEDS) was obtained from a PGT probe which is coupled to MEV.

2.5 X-Ray Fluorescence Spectroscopy (XRF)

A scanning electron microscope, a Zeiss EVO LS-15, equipped with an Oxford INCA X-Act detector (Oxford Instruments) for energy dispersive microanalysis was applied in XRF analysis.

3. RESULTS AND DISCUSSION

The main objectives of this stage are: making a qualitative identification of crystalline compounds; establishing the proportion in which each element is present in the crystalline materials; knowing the amount of elements; evaluating the surface structure of a sample; and assessing whether the methodology used in the sample preparation interferes in the

Ivonete Ávila, João A. Carvalho Jr., Gretta L. A. A. Ferrufino, José C. Santos, Vitor O. Facio and Allan S. Santos
Use of Serpentine as CO$_2$ Sorbent Applied to Dioxide Sequestration

final composition of the material. In this case, three serpentine samples which have gone through different crushing processes were evaluated. The samples were called as SB, SB-323 and SBM-362, as described in Tab. 2.

Table 2: Description of the serpentine samples evaluated.

Sample	Description
SB	Sample with a measurement of 2×0.75×0.15 cm (length, width, and height) obtained after the crushing process. This sample had their faces polished with sandpaper to adapt it to the sample port of the XRF equipment.
SB-323	Sample with an average particle size of 323.5 μm obtained after crushing and a subsequent selection between the two sieves (passing through a 350 μm sieve and retention on 297 μm sieve).
SBM-362	Sample with an average particle size of 362.5 μm obtained after the crushing and milling processes with a subsequent selection between the two sieves. (passing through a 425 μm sieve and retention on a 297 μm sieve)

It is noteworthy that sample SB is the cleanest as possible, and it is contaminant free. Sample SB-323 was prepared in order to assess whether there was contamination after the crushing process and sample SBM-362 will be checked if the contamination occurred after the grinding process.

3.1 Porosimetry Results

The porosimetry technique was applied only for SB-323 and SBM-362 samples. Due to size limitation of the equipment's sample port, it was not possible to apply this technique for SB. Figure 1 shows the adsorption/desorption isotherms and pore size distribution for both samples.

(a)

(b)

(c)
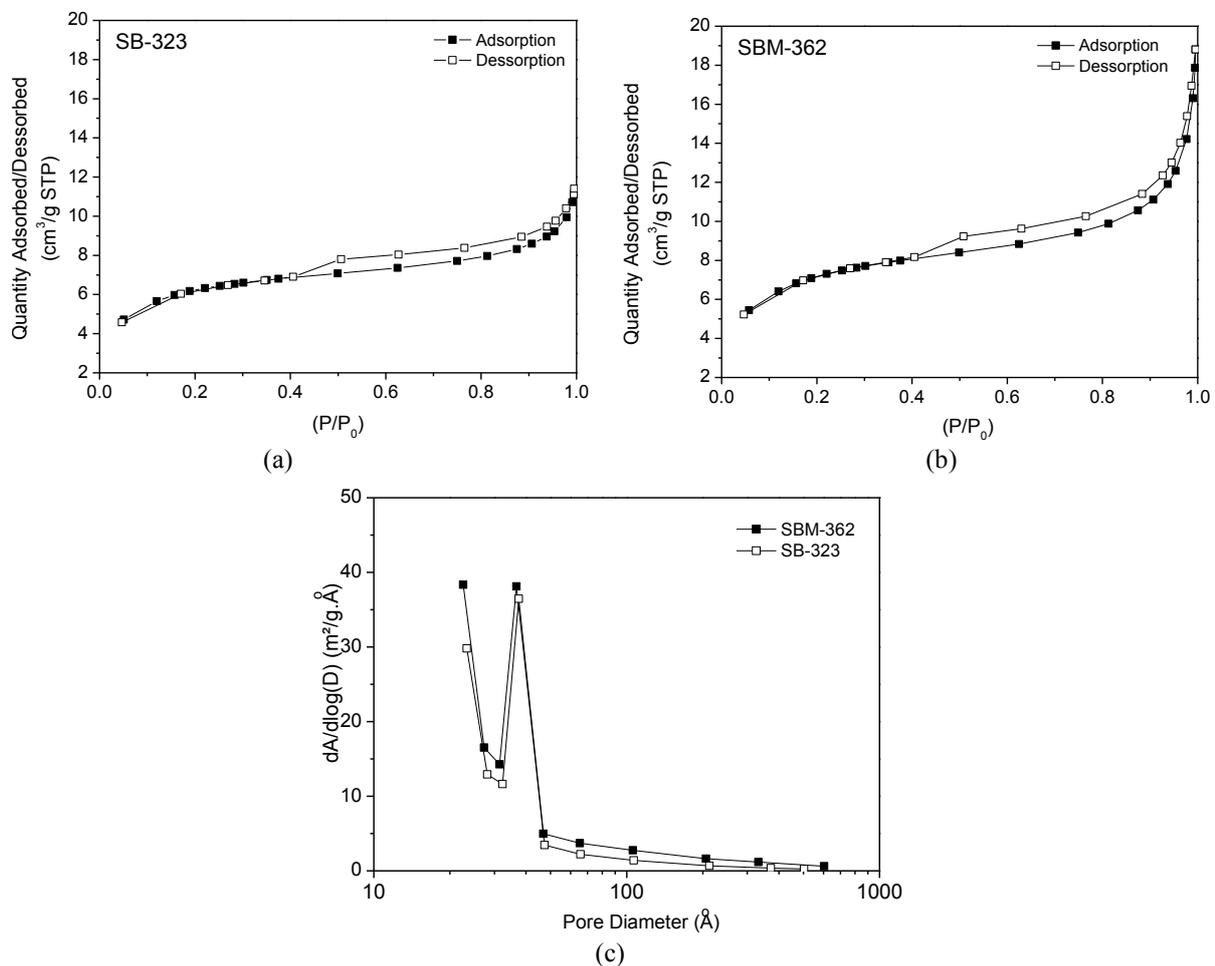
Figure 1: Adsorption and desorption isotherms of natural serpentine samples: (a) SB-323 and (b) SBM-362; (c) Pore size distributions for both natural serpentine samples.

Adsorption isotherms generally follow one of the six forms which characterize the size of the pores of the analyzed material. For the two analyzed samples, adsorption and desorption isotherms have similar shapes, indicating isotherms of type IV and hysteresis loops (when the curve does not coincide with the adsorption desorption). This behavior is typical of mesoporous and macroporous materials, i.e., materials whose pore opening is larger than 2 nm (20 Å). The hysteresis behavior can be classified as type H3. According to the IUPAC, such hysteresis is observed in aggregates of particles with pore-shaped cracks (Greg and Sing, 1982; Rouquerol et al., 1999).

Parameters, such as BET surface area (S_{BET}), average pore volume ($V_{P.Ds}$), and average pore diameter ($D_{P.Ds}$) for both samples, are shown in Tab. 3.

Table 3: Pore characteristics for both SB-323 and SBM-362 serpentine samples.

Parameters	SB-323	SBM-362
S_{BET} (m^2/g) – BET	20.33	23.81
$V_{P.Ds}$ (cm^3/g) – BJH	12.46×10^{-3}	23.63×10^{-3}
$D_{P.Ds}$ (Å) – BJH	54.50	76.39
$Q_{A.\,max}$ (cm³/g CNTP)	11.40	18.80

It is noted, in Tab. 3, that SBM-362 (sample that was crushed and milled) presents S_{BET} and $Q_{A\,max}$ values of 14.6% and 39.4%, respectively, which is higher than SB-323 (sample that was only crushed). These results show that the milling process led to an increase in the porosity of the material. The serpentine has different compounds and, possibly, the milling process released more porous compounds, thereby increasing the S_{BET} and $Q_{A.max}$.

In addition, it was visually observed that SBM-362 had its finest particles clumped in the surface of larger particles and that they were not separated in the selection process. Possibly, this fact also has contributed to the increase in the surface area of this sample.

Figure 1.c shows that both samples have similar pore size distribution in the mesoporous region (pores between 20 Å and 500 Å).

3.2 X-ray diffraction (XRD)

The XRD is one of the main techniques for a microstructural characterization of crystalline materials. The main application of this technique refers to the qualitative identification of crystalline compounds.

The spectra obtained for samples SB-323 and SBM-362 are presented in Fig. 2. It is possible to confirm that the samples have an identical composition. However, the peaks achieved in sample SBM-362 were more intense.

In the first search, it was made a comparative analysis of the sample spectra with inorganic compounds using the database from ICDD (International Center for Diffraction Data).The probable found compounds are shown in Figures 3 and 4, and the serpentine ($Mg_3Si_2O_5(OH)_4$) was identified.
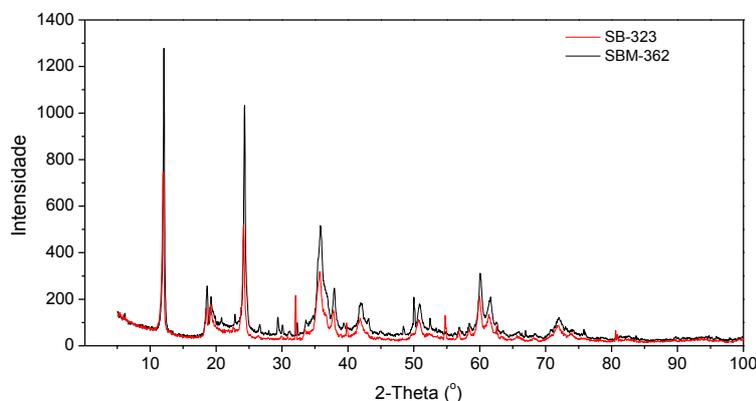
Figure 2: Comparative identification of crystalline compounds obtained from XRD analysis for samples SB-323 and SBM-362.

It is emphasized that this technique is qualitative, requiring an additional analysis to quantify the elements present in the raw material.
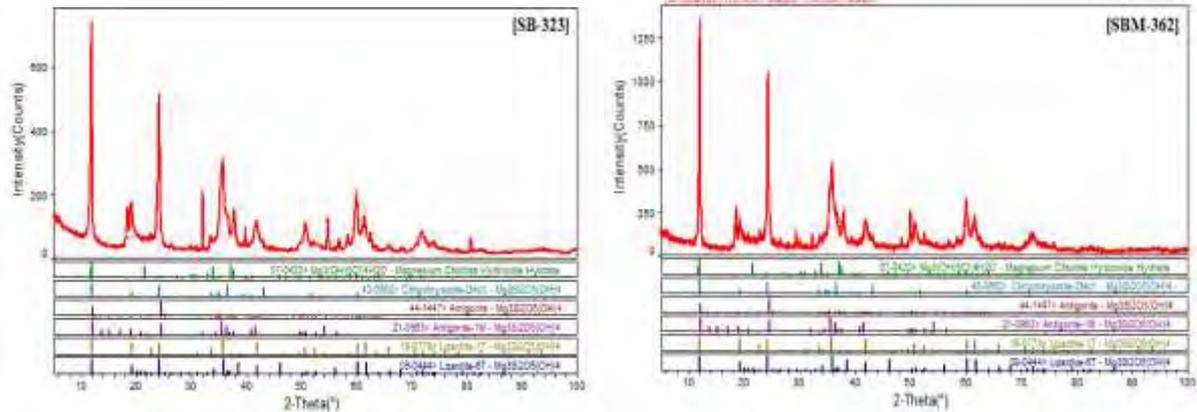
Figure 3: Comparative analysis of the sample spectra with inorganic compounds using the database from ICDD (International Center for Diffraction Data).

3.3 Scanning Electron Microscopy (MEV/XEDS)

The MEV images for both SB-323 and SBM-362 samples with 100X and 1000X magnification are presented in Fig. 4 and Fig. 5, respectively. As it was observed earlier, SBM-362 presented a clump of fine particles on the surface of larger particles. This phenomenon was not observed for SB-323, since it did not pass by the milling process, indicating that the selection methodology of the particle size should be reevaluated.

(a) (b)
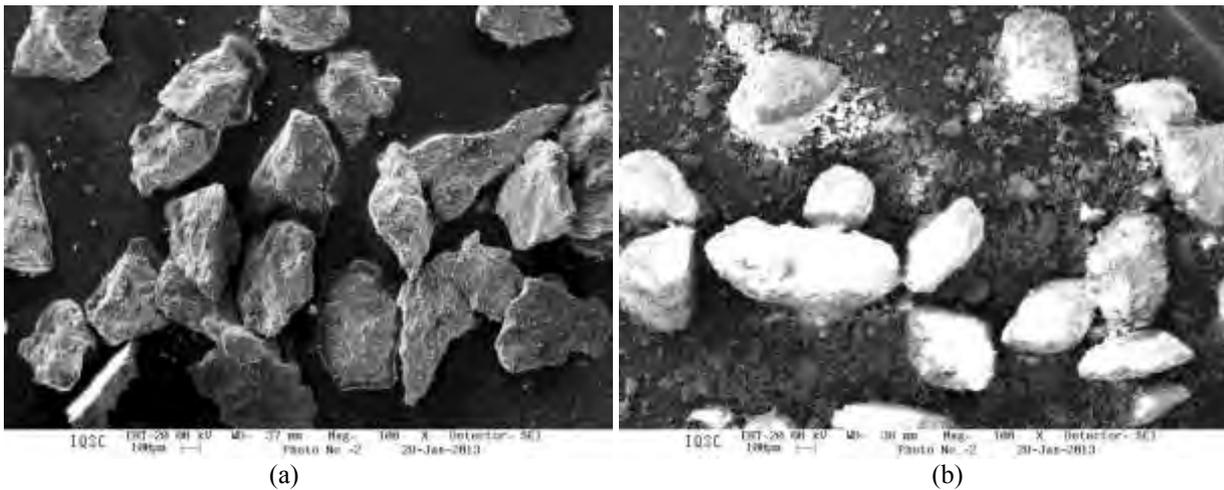
Figure 4: Images obtained by SEM with 500X magnification: (a) SB-323 and (b) SBM-362.

(a) (b)
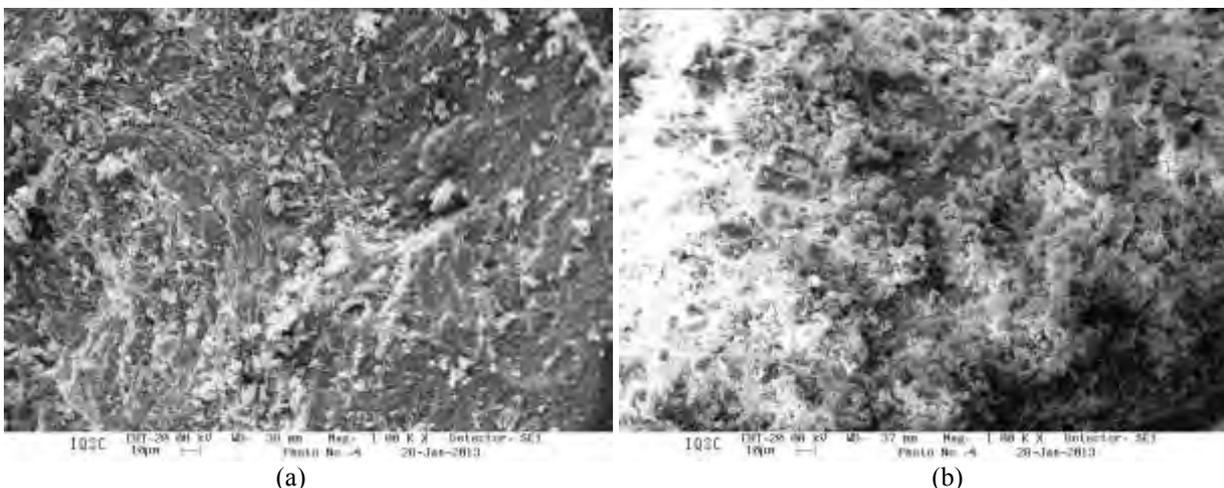
Figure 5: Images obtained by SEM with 10000X magnification: (a) SB-323 and (b) SBM-362.

XEDS analyses were applied in three particles (T1, T2 and T3) of each sample in order to evaluate their composition. The results are presented in Tab. 4.

Table 4: Elemental composition (%m/m) for SB-323 and SBM-362 obtained by XEDS.

Element	SB-323				SBM-362			
	T1	T2	T3	Average	T1	T2	T3	Average
O	55.46	54.85	52.12	54.1±1.5	53.92	51.60	51.30	52.3±1.2
Mg	23.99	22.86	22.73	23.2±0.6	20.69	19.03	21.29	20.3±1.0
Al	0.20*	1.90	0.73	0.9±0.7	1.83	2.18	1.91	2.0±0.1
Si	16.21	17.09	13.91	15.7±1.3	16.32	14.89	17.15	16.1±0.9
Ca	0.09*	-0.01*	0.06*	0.1±0.0*	1.50	1.43	1.08	1.3±0.2
Fe	4.05	3.30	10.45	5.9±3.2	5.74	10.88	7.27	8.0±2.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

(*)Values inside of the range of equipment error

Magnesium (Mg) is the main element of interest in the CO_2 capture process. It is observed that the milled (SBM-362) sample has a lower percentage (1.14%) of this element when compared to the crushed sample (SB-323). Also note that the largest differences were observed for Al, Fe, and Ca that are in greater quantity in the crushed sample (SB-323).

It is noted that the Ca is present only in the SBM-362 sample, indicating that this element is a contaminant of the milling equipment.

3.4 X-Ray Fluorescence Spectroscopy (XRF)

This method allows determining the proportion in which each element is present in crystalline materials, being one of the variants of the XEDS. In addition, this technique enables the obtainment of a distribution map of chemical elements.

In order to obtain the minor influence possible of the equipment used in the sample preparation a serpentine rock (2×0.75×0.15 cm) was compared with SBM-362 in this analysis. The spectra obtained are shown in Fig. 6, and the quantities of elements are shown in Table 5.

(a)   (b)
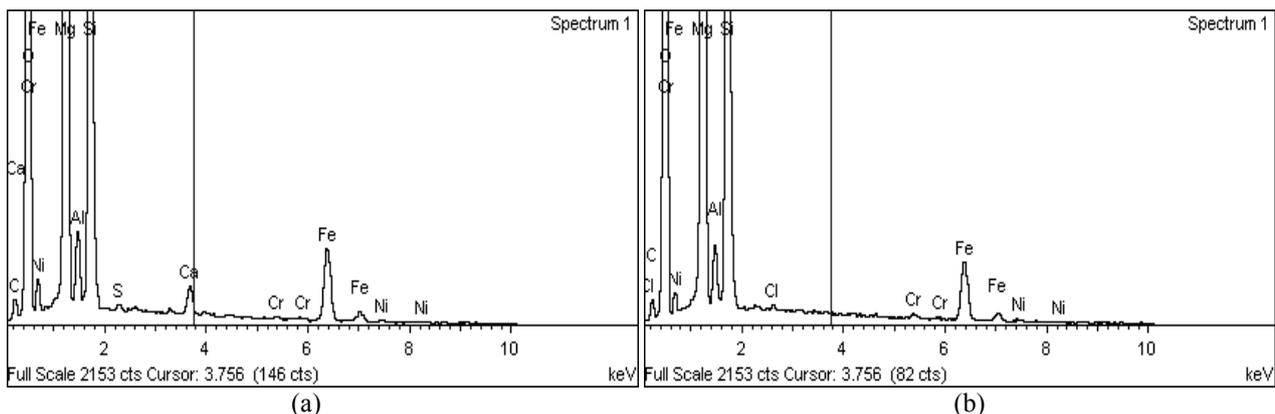
Figure 6: Elemental composition obtained by XRF technique for (a) SBM-362 and (b) SB.

In the evaluation of the element of interest (Mg), it is observed, in Table 5, that excluding (except for) carbon and considering the standard deviation, its composition is identical to that retrieved from the EDX analysis.

It is also observed that Ca and S were not detected in sample SB, and these elements are possibly contaminants of the milling system. Cl was detected only in sample SB that was washed under running water after the polishing process. Possibly, it is a contaminant of the water used in the wash. In order to observe how the elements are distributed in the raw material, the compositional maps are presented in Fig. 7 and Fig. 8 for SBM-362 and SB, respectively.

Ivonete Ávila, João A. Carvalho Jr., Gretta L. A. A. Ferrufino, José C. Santos, Vitor O. Facio and Allan S. Santos
Use of Serpentine as CO$_2$ Sorbent Applied to Dioxide Sequestration

Table 5: Elemental composition (%m/m) for SB-323 and SBM-362 obtained by XRF.

Elements	SBM-362		SB	
	with Carbon	without C	with Carbon	without C
C	3,52	-	3,81	-
O	57,6	57,73	55,46	55,89
Mg	19,67	21,07	21,9	23,55
Al	1,24	1,36	0,93	1,02
Si	12,64	13,77	13,78	15,1
S	0,13	0,14	Nd	Nd
Ca	0,62	0,67	Nd	Nd
Cl	Nd	Nd	0,1	0,11
Cr	0,14	0,15	0,18	0,2
Fe	4,62	4,95	3,68	3,96
Ni	0,16	0,17	0,17	0,18
Total	100	100	100	100

Obs.: Nd – not detected.

The maps show that the elements such as O, Mg, Al, and Si are homogeneously distributed in both samples, while Fe is placed in some regions. Ca is present in the sample that was crushed, but in determinate locals and superficially on the particle surface. Probably, the present Ca is due to contamination from the ball mill system.
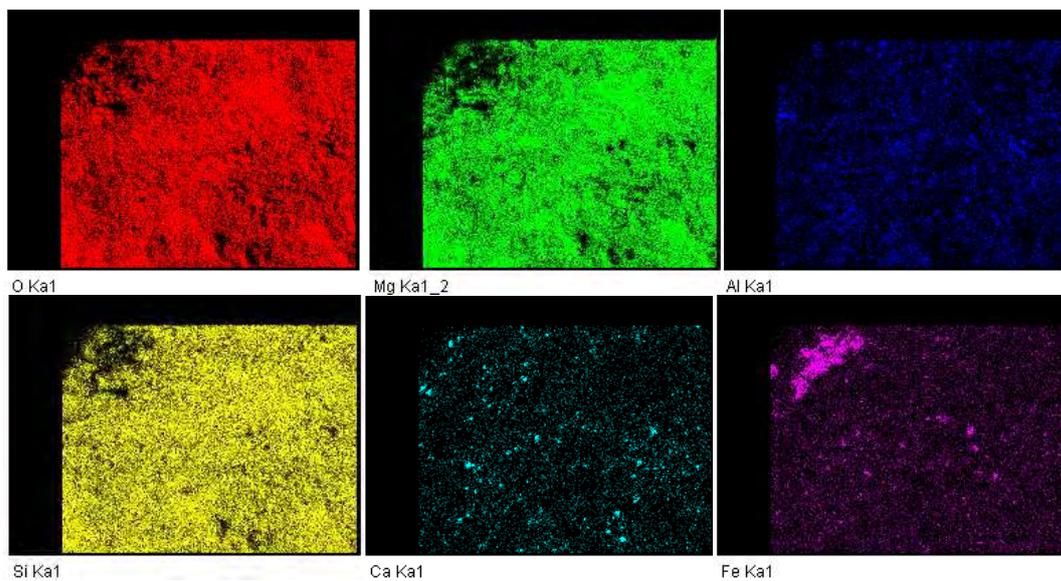
Figure 7: Compositional maps of the main elements for SBM-362.
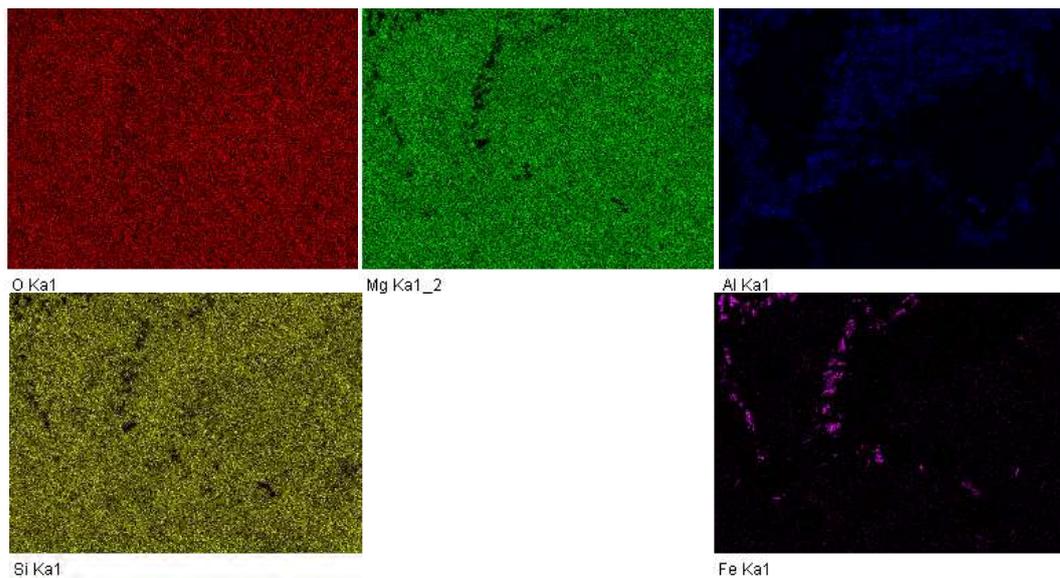
Figure 8: Compositional maps of the main elements for SB.

4. CONCLUSIONS

In this paper, it was briefly presented a literature review of the carbonation process applied to carbon capture. Furthermore, a characterization of the Brazilian serpentine was performed in order to evaluate its potential as a CO_2 sorbent.

The sample preparation was carried out to obtain particle sizes that are suitable for being used in the carbonation process. Afterwards, the sample characterization was carried out using the following techniques: porosimetry by N_2 adsorption, X-ray diffraction, scanning electron microscopy, and X-ray fluorescence.

The results found that the methodology applied in the sample preparation interfered in the final composition of the material, due to contaminations present in the used systems.

5. ACKNOWLEDGEMENTS

6. REFERENCES

Arce, G.L.A.F., 2012. "Assesment of the potential for carbon mineral sequestration applied to power plants in Brazil". 161 f *Thesis (Doctorate in Mechanical Engineering)* - Faculdade de Engenharia do Campus de Guaratinguetá, Universidade Estadual Paulista, Guaratinguetá.

Dunsmore, H.E., 1992. "A geological perspective on global warming and the possibility of carbon dioxide removal as calcium carbonate mineral", *Energy Conversion and Management*, Vol. 33, p. 565-572.

Ferreira Filho, O.B., Linares, W.B. "Crisotila". 28 January 2013 <Minashttps://sistemas.dnpm.gov.br/publicacao/mostra_imagem.asp?IDBancoArquivoArquivo=4010>

Lackner, K.S., 2002. "Carbonate chemistry for sequestering fossil carbon". *Annual Review of Energy and the Environment*, Vol. 27, p. 193-232.

Lackner, K.S., Butt, D.P., Wendt, C.H., 1997. "Progress on binding CO_2 in mineral substrates. *Energy Conversion and Management*, Supplement, Vol. 38, S259-S264.

Lackner, K.S., Wendt, C.H., Butt, D.P., Joyce, E.L., Sharp, D.H., 1995. "Carbon dioxide disposal in carbonate minerals", *Energy*, Vol. 20, p. 1153-1170.

Maroto-Valer, M.M., Fauth, D.J., Kuchta, M.E., Zhang, Y., Andrésen, J.M., 2005b. "Activation of magnesium rich minerals as carbonation feedstock materials for CO_2 sequestration. *Fuel Processing Technology*, Vol. 86, p. 1627-1645.

O'Connor, W.K., Dahlin, D.C., Nilsen, D.N., Rush, G.E., Walters, R.P., Turner, P.C., 2001. "Carbon dioxide sequestration by direct mineral carbonation results from recent studies and current status", *National energy Technology Laboratory, US Department of Energy*, DOE/ARC - 2001-029.

Park, A-H.A., Jadhav, R., Fan, L.S., 2003. "CO_2 mineral sequestration: Chemically enhanced aqueous carbonation of serpentine", *The Canadian Journal of Chemical Engineering*, Vol. 81, p. 885-890.

Park, A-H.A., 2005. "Carbon dioxide sequestration: chemical and physical activation of aqueous carbonation of Mg-bearing mineral and pH swing process", Ph.D. thesis, *The Ohio State University*, Ohio.

Penner, L., Dahlin, D.C., Gardemann, S., Saha, K.K., 2005. "Modeling flow of mineralized carbon dioxide slurry", *Department of Energy/Albany Research Center*, Report DOE/ARC-2005-056.

Seifritz, W., 1990. "CO_2 disposal by means of silicates", *Nature*, Vol. 345, p. 486.

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*, Turku, Finland, Report VT 2008-1.

Teir, S., 2008. "Fixation of carbon dioxide by producing carbonates from minerals and steelmaking slag". (*Doctoral Dissertation - TKK Dissertations 119).* Helsinki University of Technology, Faculty of Engineering and Architecture, Department of Energy Technology. Espoo, Finland.

Teir, S., Kuusik, R., Fogelholm, C-J., Zevenhoven, R., 2007a. "Production of magnesium carbonates from serpentinite for long-term storage of CO_2", *International Journal of Mineral Processing*, Vol. 85, p. 1-15.

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

Van Essendelft, D.T., Schobert, H.H. 2009a. "Kinetics of the acid digestion of serpentine with concurrent grinding - 1. Initial Investigations", *Industrial and Engineering Chemistry Research*, Vol. 48, p. 2556-2565.

Van Essendelft, D.T, Schobert, H.H. 2009b. "Kinetics of the acid digestion of serpentine with concurrent grinding. - 2. Detailed Investigation and Model Development", *Industrial and Engineering Chemistry Research*, Vol. 48, p. 9892-9901.

Wall, T., 2007. "Combustion processes for carbon capture, Proceedings of the Combustion Institute", Vol. 31, p. 31-47.

Wang, X., Maroto-Valer, M.M., 2011. "Integration of CO_2 capture and mineral carbonation by using recyclable ammonium salts. ChemSusChem, Vol. 4, p. 1291-1300.

Zevenhoven, R., Eloneva, S., Teir, S., 2006. "Chemical fixation of CO_2 in carbonates: Routes to valuable products and long-term storage". *Catalysis Today*, Vol. 115, p. 73-79.

Zhang, P-C., Anderson Jr., H.L., Kelly, J.W., Krumhansl, J.L., Papenguth, W.H., 1999. "Kinetics and mechanisms of formation of magnesite from hydromagnesite in brine", Albuquerque, N.M.: *Sandia National Laboratories*, SAND 87185-0733.

Zhao, L., Sang, L., Chen, J., Ji, J., Teng, H.H., 2010. "Aqueous carbonation of natural brucite: Relevance to CO2 sequestration". *Environmental Science & Technology*, Vol. 44, p. 406-411.

7. RESPONSIBILITY NOTICE

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