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STUDY ON THERMAL ACTIVATION OF BRAZILIAN SERPENTINE APPLIED IN CO_2 SEQUESTRATION PROCESS

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Abstract. *Mineral carbonation (MC) is one of carbon capture and sequestration (CCS) technologies that could allow the continued use of fossil fuels in a sustainable way. MC is a process in which carbon dioxide (CO_2) reacts with materials containing high concentration of calcium/magnesium in order to produce carbonates, which are environmentally stable and Brazil has a large availability of materials with a potential for use on mineral carbonation processes. Actually, MC research is receiving more attention, however it faces many challenges, such as the increase of the carbonation reaction kinetics. This could be achieved using thermal activation as pre-treatment for the material. The thermal activation consists in heating the material in order to reduce the concentration of hidroxyl ions (OH^-) on its structure. This process is known as dehydroxylation which can increase the efficiency of the MC. This study evaluated the thermal behavior of dehydroxylation process of two serpentine (S) rocks named S-GO (from Goiás state) and S-MG (from Minas Gerais state). Thermal analysis (TG/DTA/DSC) results indicate that S-GO have higher amount of OH^- and that 20% dehydroxylation of it would be achieved at temperatures around 430°C, while for the S-MG it would be reached at about 600°C. This difference is related to the mineralogical structure of S-GO. Nevertheless, the energy consumption of S-GO is less than that of S-MG.*

Keywords: *thermal activation, mineral carbonation, thermal analysis, serpentinite, carbon dioxide.*

1. INTRODUCTION

The energy is substantially linked to the development of the countries, still the demand for energy has increased considerably in recent decades. Of all the sources of energy used in the world, 80% is derived from the combustion of fossil fuels. However, the high calorific value, the existing infrastucture and the low price encourage the continued use of fossil fuels, so that these will remain as the major source of energy in the coming years (Van Essendelft and Schobert, 2010).

Mineral carbonation, in addition to being exothermic, allows CO_2 to be retained for long periods, since the carbonates are thermodynamically and environmentally stable. Among several different raw materials to use in the capture of CO_2 by mineral carbonation process are the silicate minerals and industrial waste (Park et al., 2003; Demirbas, 2007; Teir et al., 2009; Daval et al., 2009; Fagerlund et al., 2009). Brazil has a land area of approximately 8.5 million square kilometers and has mineral silicates (such as serpentinite) in abundance, so it has a great potential for the implementation of this technology in its territory.

Although this technology is receiving attention, it faces many challenges, among which the increase in the carbonation reaction kinects. To overcome these challenges the thermal activation pretreatment is seen as a good option (Balucan et al., 2013). The thermal activation consists on heating the material in order to decrease the concentration of hidroxyl ions (OH^-) contained in its structure. This process is known as dexydroxylation. The dehydroxylation is a reaction where structurally linked hydroxyls are removed from solid and released as water vapor. This reaction usually occurs above 500 ^oC, so that each material polymorph (lizardite, chrysotile and antigorite) differs in thermal stability and hence has a different decomposition temperature (Dlugogorski and Balucan, 2014).

The type of heating to be used depends on parameters such as the time taken to activate, temperature and heating rate, which requires evaluation. Generally, isothermal heating requires relatively lower temperatures than progressive heating, but it requires long duration. Progressive heating involves heating the material at elevated temperatures in a constant heating ratio. The dehydroxylation degree (%OH_{res}) refers to the amount of residual hydroxyl groups after heat processing, so that the best values for partially dexydroxylated serpentinite are close to 16±8% OH_{res} (Balucan et al., 2013). The progressive heating, not only enables rapid dehydroxylation but also simplifies the process of thermal activation by associating a particular terminal temperature to the desired degree of dehydroxylation. This allows the thermal activation to proceed the raw material heating until the final specified temperature for about 16±8% OH_{res} is reached (Balucan et al., 2013).

However, the thermal activation presents its own difficulties, among which, the costs involved in implementing this technique. While energy costs for the standard pretreatment (crushing and grinding) account for 4% of global energy demand of the mineral carbonation using serpentine rock process, the thermal dehydroxylation accounts for 96% of energy demand, since the electric heating has unsustainable losses for the powerplant. Furthermore, the use of electricity is not only expensive, but also impractical due to the poor efficiency (~35%) of present technology to convert heat into electricity in addition to the production of high quantities of CO_2 to produce this amount of electricity exceeding the amount of CO_2 captured by mineral carbonation (Balucan et al., 2013).

The use of thermal heating coupled to the partial dehydroxylation and the use of a fuel that produces less CO_2 may allow the practical application of thermal activation of serpentinite. Besides implementing a practical heating method, further improvements in the thermal activation strategy include the integration of the heating, aiming at the optimal degree of dehydroxylation and the implementation of appropriate type of heating based on the duration and rate of heating. The integration of serpentinite heating can reduce the total energy needs by up to 63% (Balucan et al., 2013).

2. MATERIALS AND METHODS

Two types of serpentinite rocks were analyzed. A serpentinite from the state of Goiás (GO) provided by the mining company SAMA SA was identified as S-GO. The other serpentinite from the state of Minas Gerais (MG) provided by the mining company Pedra Congonhas, was identified as S-MG.

To achieve the thermogravimetric tests it was used analytical nitrogen 5.0 (N_2) as purge gas at a flow rate of 100mL/ min. In preliminary experiments it was observed that the stabilization temperature of the S-GO and S-MG was around 1100 °C, therefore, the heating of the samples was carried out from 30°C to 1100°C with a heating ratio of 10°C/min. The masses used for all tests were 45,53±0,33 mg and 54,88±0,12 mg for S-GO and S-MG respectively. The tests were performed three times for both samples.

The equipament used was a TA Intruments simultaneous system Q-600 - SCT- TGA- DSC. To support the samples it was used an alumina crucible, which was able to withstand high temperatures (Figure 1).

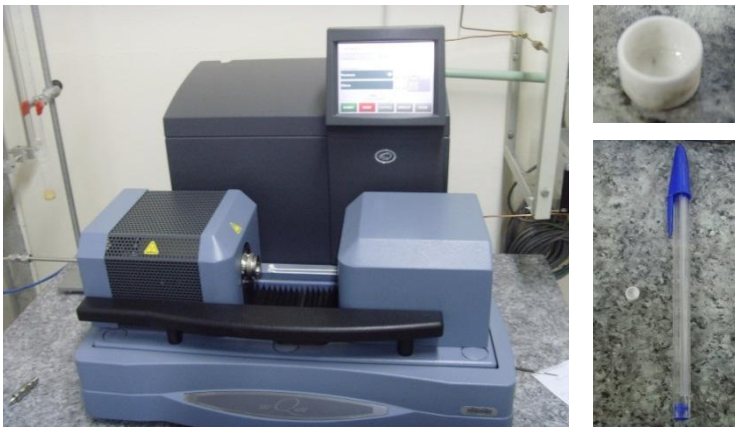

Figure 1. Simultaneous thermal analysis system installed on Combustion Laboratory and Carbon Capture LCCC/ FEG-UNESP, in Guaratinguetá/ SP.

3. RESULTS AND DISCUSSIONS

The results presented in Table 1 and Figure 2 show the weight loss in TG curves obtained for both serpentine rocks. Note that in Figure 2 the mass loss of S-GO is greater than the mass loss of S-MG. Considering that the mass loss of serpentinite is related to dexydroxilation reactions it can be inferred that the S-GO shows greater amount of ion (OH^-) than S-MG being its values: 14,8±0,1% and 9,21±0,07% respectively.

On the other hand, it can be said that for S-GO the weight losses occurred at temperatures around 750°C. But both serpentinite rocks showed the greatest weight loss in the range of temperatures around 500°C to 750°C.

Table 1. Mass loss of materials in different temperatures ranges

Material	Mass	Mass loss (%)			
		100°C – 300 °C	300°C – 500 °C	500 °C – 750°C	750°C – 1100°C
S-GO	45,53±0,33	0,92±0,08	3,52±0,13	10,40±0,15	n.a.
S-MG	54,88±0,12	n.a.	n.a.	7,03±0,03	1,48±0,05

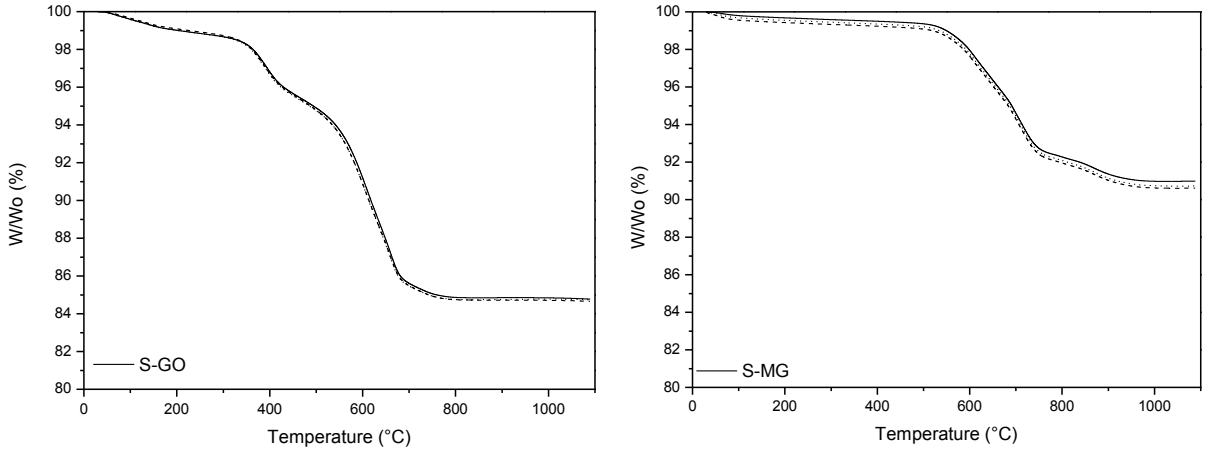

Figure 2. TG Curves.

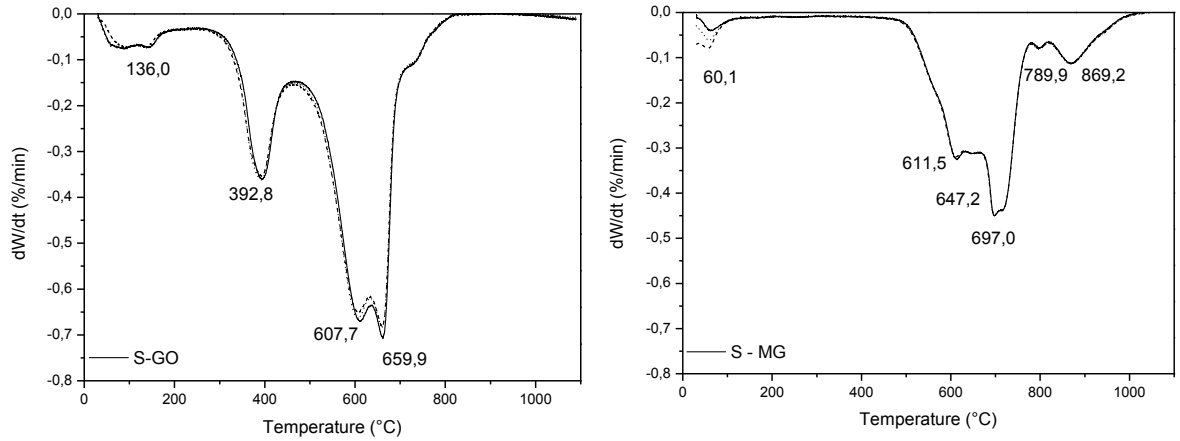

Figure 3. DTG Curves.

In Figure 3, the DTG curve peaks provide the thermal decomposition temperature of each mineral contained in the sample. In the range around 100 to 500°C, S-GO has two DTG peaks: one at 136°C and the other at 393°C. These peaks refers to the decomposition of brucite ($Mg(OH)_2$ while in the S-MG sample, this mineral was absent, therefore, there was no mass loss in this range of temperatures. In the range between 500 °C and 750 °C, both materials presented its highest weight loss. However the S-MG sample seems to have more minerals with decomposition temperatures in this range than the S-GO sample. Thus, for the S-GO two DTG peaks were observed at temperatures of around 608°C and 660°C. This refers to the thermal decomposition of chrysotile and lizardite respectively. For the S-MG three DTG peaks were observed at 611°C, 647°C and 697°C. This refers to chrysotile, lizardite and antigorite respectively. These assignments of the maximum decomposition temperature were made based on the studies of Dlugogorski and Balucan (2014), who found that the characteristic decomposition of chrysotile is between 600-620 ° C, the lizardite between 640-680 ° C and the antigorite from 700 ° C. Finally, it was noted that the weight loss between 750 °C and 1100 °C occurred only for S-MG sample. This group showed two DTG peaks at 790 °C and 869 °C, which refers to the dehydroxylation of talc and actinolite respectively.

A qualitative evaluation based on the latent heats as well as the latent heats involved in dehydroxylation reaction was determined. It can be seen in Table 2 that to achieve dehydroxylation of brucite it is necessary around 40.5 MJ / ton of material, nevertheless to dehydroxylate the serpentine it is needed between 300-450 MJ / ton of

material. Both serpentinite rocks have exothermic heats that liberates between 30 - 60 MJ / ton of material, which is a characteristic of the serpentine due to its crystalline phase transition.

Employing these heats calculated, the total heat required for 20% dehydroxylation of the material was obtained, based on the research done by Balucan et al. (2013). In this case it was found that the energy required to dehydroxylate up to 20% of the S-MG is as much as twice of that required for the S-GO.

Table 2. Amount of heat involved in each dehydroxylation reaction.

Material	100 -500 (MJ/t_{MAT})	500 – 750 (MJ/t_{MAT})	750 – 1100 (MJ/t_{MAT})	-20%$(OH)_{res}$ mg	$T_{(OH)res}$ (°C)	ΔH_L (MJ/t_{MAT})	ΔH_S (MJ/t_{MAT})	ΔH (MJ/t_{MAT})
S – GO	40,5±0,3	310,4±4,0	-58,29±7,1	1,347	378,4	30,65	517,06	547,7
S – MG	n.a.	428,1±8,7	-36,6±2,0	1,009	597,4	247,28	816,36	1.063,6

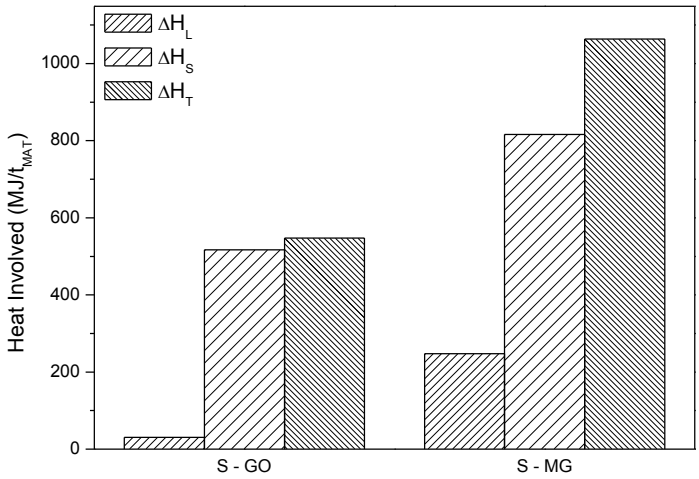

Figure 4. Total amount of heat necessary to dehydroxylate both serpentines.

4. CONCLUSION

In a general manner, it is possible to infer that not all serpentinite rocks are suitable for mineral carbonation processes through thermal activation. However, rocks with high brucite levels can be considered more appropriate for use in this process than those with high levels of serpentine and talc.

This was attributed to brucite due to its elevated reactivity at low temperatures (310 °C), while serpentine dehydroxylation temperature range is between 600-700 ° C.

Although the S-GO is presented as a promising material, the amount of energy spent to dehydroxylate up to 20% of it is still high. As pointed out by Balucan et al. (2013) it will be necessary to carry out energetical optimization studies in order to make possible the recovery of the sensible heat used to reach the dehydroxylation temperatures.

5. ACKNOWLEDGEMENTS

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