RESEARCH PROJECT

ENHANCED WEATHERING AND CARBONATATION: USE OF WOLLASTONITE MINERAL TO REDUCE THE ATMOSPHERIC CO2

FEDERAL UNIVERSITY OF CATALÃO ENGINEERING COLLEGE MINING ENGINEERING COURSE



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Catalão/GO November, 2020

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1. INTRODUCTION

Healthy soils provide the largest reserve of terrestrial carbon. When managed irresponsibly or cultivated through unsustainable agricultural practices, the carbon present in the soil can be released into the atmosphere in the form of carbon dioxide (CO₂), which can contribute to climate change. The constant conversion of forests to agricultural land and pastures has resulted in historical losses of soil carbon worldwide, however, with the restoration of degraded soils and the adoption of soil conservation practices, there is great potential to reduce the emission of greenhouse gases from agriculture, increase carbon sequestration and build resilience to climate change (Food and Agriculture Organization of the United States, 2015).

There is no doubt that atmospheric concentrations of CO_2 and other gases have increased as a result of human action, possibly dating back to the beginning of agriculture (KUTZBACH et al., 2010), as well as through the comparatively recent combustion of fossil fuels since the industrial revolution (DENMAN et al., 2007). Increased gas concentrations are known to be responsible for a change in climate and global temperatures in general are increasing with implications for sea level and the frequency of extreme weather events (DENMAN et al., 2007).

Thus, knowing the safe and sustainable management of soils used in food production combined with the improvement of time with the sequestration of carbon dioxide from the atmosphere, several studies have been used with the application of remineralizers capable of interacting with CO_2 in order to mitigate anthropic actions. Even if gas emissions were drastically reduced to zero, it would take hundreds of years today for atmospheric CO_2 to stabilize back to pre-industrial concentrations (LOWE et al., 2009).

The application of rock waste as agricultural fertilizers is incredibly old. Leonardos (1976) reports centenary cases of application of rock fragments to soil in Brazil. Meert et al. (2009) affirm that the use of ground rocks for soil fertilization purposes, known as rock formation or remineralization, has been practiced for a long time via liming and phosphating.

Law No. 12,890, of December 10, 2013 (BRASIL, 2013), defines remineralizer as material of mineral origin that has undergone only reduction and size classification by mechanical processes and that changes the soil fertility indexes through the addition of macro and micronutrients for plants, as well as promoting the improvement of physical or physic-chemical properties or biological activity of the soil.

The first works with remineralizers were developed by the French M. Missoux (1853) and by the German J. Hensel (1880) (LAPIDO-LOUREIRO; NASCIMENTO, 2009;

STRAATEN, 2006). Since then, several researchers are advancing on this topic.

According to Pádua (2012), remineralization can become an important plant nutrition technique complementary to traditional practices with high concentration and high solubility fertilizers, mainly due to the diversity of raw materials and wide geographical distribution.

Remineralization is characterized by the beneficial effects provided to the soil and crops. Minerals from igneous and metamorphic rocks contain most of the nutrients needed for plant growth. In general, among the elements provided are K, P, Ca, Mg and S, in addition to micronutrients, beneficial elements such as Si and Na (MELO; CASTILHOS; PINTO, 2009; STRAATEN, 2006).

It is widely accepted that the chemical weathering of calcium silicate rocks can control climate change in the long term, impacting the reduction of atmospheric CO_2 through carbon precipitation. Research by Liu; Dreybrodt; and Liu (2011), demonstrate that the CO_2 consumed in areas with the presence of silicates does not necessarily result from the weathering of the silicates, and must take into account the contribution of the rapid dissolution of calcite in the silicate rocks, that is, by carbonate weathering. This indicates that the contribution of weathering of silicates to the sequestration of atmospheric CO_2 may be only 6%, while the other 94% is due to carbonate weathering. All water in contact with air has dissolved carbon dioxide, giving rise to an acidic solution referred to as carbonic acid (H₂CO₃). The reaction between this solution and the minerals is called carbonation, which is described in eq.1, 2 and 3, below:

CO₂ dissolution:

$$CO_{2(g)} + H_2O_{(l)} \leftrightarrow H_2CO_{3(aq)} \leftrightarrow HCO_3^- + H^+$$
 (1)

Release of calcium from a silicate mineral, which in this case is Wollastonite:

$$CaSiO_{3(s)} + 2H^+ \rightarrow Ca^{2+} + H_2O_{(1)} + SiO_{2(s)}$$
 (2)

Precipitation of calcium carbonate:

$$Ca2+ + HCO3 \rightarrow CaCO3(s) + H2O(l) + CO2(g)$$
(3)

Many studies explore the application of organic matter in soils, such as poultry and livestock manure, green manure, sludge, ash, and geological resources such as marl and phosphate rock (DIACONO and MONTEMURRO, 2010). This habit is slow to build carbon stocks in the soil, for example, Triberti et al. (2008) report the annual increase in organic carbon from 0.16 to 0.26 t C/ha over a period of 30 years in a cultivated soil system. Other research

reveals that, in general, about 90% of the carbon input as a compound is lost in the soil in 10 years (LIN et al., 1997).

In many parts of the world, food security is at risk. One of the biophysical causes of the per capita drop in food production is the decline in the quality and quantity of arable land. To reverse this trend and increase soil fertility, soil and plant nutrients must be replenished.

Emergencies of artificial calcium silicates with potential for carbonation are estimated by Renforth et al. (2011) to have a potential to mitigate 4 to 7% of emissions in the next 100 years. The use of silicate fertilizers is attractive, as they have the characteristic of raising the pH of soils, providing a wide variety of macro and micronutrients compared to commercially available soluble fertilizers, which commonly provide nitrogen, phosphorus and potassium, but do not supply of nutrients like calcium, magnesium and micronutrients (FYFE et al. 1983; LEONARDOS et al. 1987).

The combination of waste composted with calcium and rocks rich in silicates derived from quarries allows the formation of a mixed artificial soil that has the capacity to produce pedogenesis, causing the reduction of carbon dioxide. Even though silicates may not be as reactive as hydroxides, they dominate the earth's crust, making them ideal candidates for studies of improved weathering of rocks.

Carbon sequestration occurs when carbon from the atmosphere is absorbed and stored in the soil. This is an important function because the more carbon is stored in the soil, the less carbon dioxide there will be in the atmosphere, thus contributing to climate change. This CO2 reduction is important, as it increases the production of fertile soils that are rich in organic matter (carbon), keeps soil surfaces vegetated, requires fewer chemical inputs and promotes crop rotation and biodiversity. These soils are less susceptible to erosion and desertification, in addition to maintaining vital ecosystem services such as hydrological and nutrient cycles, which are essential for maintaining and increasing food production (Food and Agriculture Organization of the United States, 2015).

Lal (2020) describes that the carbon stock in the soil is divided into two components: organic and inorganic. Organic carbon is linked to activities related to photosynthesis ($6CO_2 + 6H_2O + energia \rightarrow C_6H_{12}O_6 + O_2$), where much of the carbon enters the soil. The inorganic can be absorbed, for example, from the sequestration of atmospheric CO₂.

As previously mentioned, the use of silicates is possible since they are the most abundant rocks in the earth's crust. Also, the application of carbonated rocks, because the interest is that there is precipitation from the reaction with the CO_2 present in the atmosphere. Therefore, the carbonation reaction will form a precipitate, calcium carbonate, which is beneficial for

correcting soil pH and plant nutrition. Silicon is recognized due to its influence on plant resistance in response to insect attacks, diseases, nutritional status, transpiration and possibly some aspects of photosynthetic efficiency (DEREN et al., 1994).

The characteristics considered ideal for a silicon source to be suitable for use in agriculture are: high Si content available to plants, good physical properties, ease in mechanized application, balanced Ca and Mg ratio and ratio, no potential for soil contamination heavy metals, low cost and good availability in the market (PEREIRA and CABRAL, 2005). Thus, according to Martins (2018), the main Brazilian rocks that can be applied in these conditions are: Basalt, Shale carbonate, Diabase, Dunite, Kamafugite, Peridotite and Serpentinite.

2. OBJECTIVES

To facilitate the development of activities, the objectives will be divided into general and specific.

2.1 General objective

Evaluate the potential of Wollastonite mineral from the Anicuns / GO region, as a source of atmospheric CO_2 sequestration, aiming to increase the inorganic carbon in the soil.

2.2 Specifics objectives

- Assess the chemical and mineralogical composition of the material;
- Assess the carbonation reaction; and
- Assess the sequestration of atmospheric CO₂.

3. MATERIALS AND METHOD

To achieve the proposed objectives, the method is divided into a few steps, which are presented below:

3.1 Chemical and mineralogical characterization

The content of the elements will be determined by emission spectrometry techniques (ICP-OES and ICP-MS), considering the method of digestion with aqua regia. The global chemical composition will be obtained by X-ray fluorescence (FRX) (Wu et al., 2010)., In fused tablets, with quantitative determinations of the SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, TiO₂, P₂O₅, Na₂O, K₂O oxides , MnO, ThO₂ and U₃O₈. The determination of mercury (Hg) will be done by atomic flame absorption spectrometry (AAS), via cold vapor generation.

The description of the rock will be carried out through a petrographic microscope, using transmitted light plane-polarized, with image capture. The modal composition will be performed by visual percentage estimate of mineralogical constituents. The mineralogical analysis by X-ray diffraction (XRD) will be carried out in a diffractometer operating with CuK α radiation and a position sensitive detector. The identification of the crystalline phases will be carried out by comparing the diffractogram with a database.

3.2 Analysis of the variation of CO₂ retained in the soil

The measurement of soil carbon is the focus of attention in current and future international conventions and agreements, related to global climate change. However, more efficient methods of quantifying soil carbon are needed to provide better estimates of terrestrial carbon inventories (Watson et al., 2000). Thus, the total carbon (TC) covers the sum of the total inorganic carbon (TIC) and total organic carbon (TOC) present in the soil.

To determine TOC, TIC must be removed first. For its removal, 30g of soil must be added to 50 mL of deionized water with 1 M HCl, which is sufficient to remove the TIC present in the sample. This suspension must be filtered using Whatman paper (45μ m) for 10 minutes, followed by drying. The elementary analysis of the sample treated with acid results in TOC, whereas TIC is calculated by the difference between TC and TOC.

The determination of the organic matter content can be done by the muffle method, being the previous drying of the samples in an oven at 105°C, for a period of 24 hours, aiming

to eliminate all the water present in the residues, such as hygroscopic, capillary or from crystallization (Rodella & Alcarde, 1994). After this period, add the ceramic crucibles with the samples in a muffle oven and incinerate at a temperature of 550°C, for 3 hours. Subsequently, the set (crucible + waste) must be stored in a desiccator and then weighed. The organic matter content is determined due to the mass loss of the incinerated waste, considering the material lost by burning in the temperature range of 105°C to 550°C (CARMO; SILVA, 2011).

The analysis of the total carbon of the residues can be carried out by dry combustion in an analyzer, with the weighing of the samples (2 to 5 mg) carried out on an analytical balance. The samples must be macerated in a mortar and sieved (0.250 mm mesh). Then, it is ideal that the samples pass through the oven at 65°C, for 48 hours, to remove the moisture before weighing and analysis. The samples must be packed and sealed in tin capsules, and then incinerated at a temperature of approximately 950°C, for 5 minutes, in a combustion quartz tube, with 99.998% purity O₂ gas being used as a carrier. After combustion, all organic matter will be converted into CO₂ and an infrared sensor will detect the amount of carbon dioxide (CO₂) generated by combustion, automatically relating it to the amount of total carbon and total organic carbon, it is possible to reach the total inorganic carbon content in the soil, that is, the CO₂ contained in the soil samples.

4. EXPECTED RESULTS

From the results, it is expected to enable the use of Wollastonite mineral to remove atmospheric CO₂.

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