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PARTICLE SIZE ANALYSIS BY BOX-BEHNKEN MATRIX

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Abstract. Carbon dioxide (CO_2) is part of the gases classified as greenhouse gases, and the increase in the concentration of CO_2 is directly related to global warming. In order to mitigate these emissions, proposals have been disseminated with the intention of continuing the use of traditional fuels without interfering with global warming. Among these proposals, mineral carbonation or mineralization is classified as one of the carbon capture and storage technologies, in which silicate rocks are used for CO_2 sequestration, generating carbonates that are thermodynamically and environmentally stable products. This project aims to evaluate the best grain size, which influences the efficiency of acid dissolution of serpentinite. Once the best experimental parameters are determined, the experimental planning technique is applied to evaluate the acid dissolution process, statistically analyzing the results of the process, with the least amount of experimental tests, reducing analysis time and materials, considering a previous knowledge of the process verified by preliminary and exploratory analyses. The Box-Behnken response surface experimental planning is used to optimize and improve multifactorial processes.

Keywords: Mineral Carbonation, Carbon Capture, Serpentinite, Box-Behnken, Box-Behnken Design.

1. INTRODUCTION

Mitigating anthropogenic carbon dioxide (CO_2) emissions is a major challenge that must be addressed in the short term. To meet the objectives set in the Paris Agreement, aiming to keep the global average temperature increase below 2 K, preferably below 1.5 K above pre-industrial levels, it is no longer sufficient to simply reduce CO_2 emissions. Negative emissions must be generated as well (Kremer et al., 2022).

One possible approach for reducing carbon dioxide is the capture and utilization (CCU) of carbon through mineral carbonation (MC) or mineralization. The CO_2 sequestration method through MC is a permanent and secure way to store carbon (Galina; Arce; Ávila, 2019; Kremer et al., 2022). The mineral carbonation process involves the direct injection of CO_2 into rock (in situ) or indirect methods (ex situ). When considering its application in industrial processes, ex situ carbonation (CM) proves to be the most advantageous. With ex situ carbonation, CO_2 capture occurs at the location of its generation, and it can be classified as both direct and indirect. In both cases, the capture can take place through gas-solid or aqueous phase reactions (Olajire, 2013). In recent years, research on ex situ mineral carbonation has made significant advancements, with the primary focus of most studies being to enhance carbonation efficiency. Among the various routes for large-scale ex situ mineral carbonation, indirect aqueous pH adjustment has been considered one of the most viable approaches (Azdarpour et al., 2015; Han; Im; Wee, 2015; Olajire, 2013). This technology has the potential to play a crucial role in addressing climate change caused by CO_2 emissions in the atmosphere, particularly by separating CO_2 from energy generation systems (Arce et al., 2017; Metz. et al. IPCC, 2005). The products and byproducts derived from the MC process have significant potential to be used as raw materials in other industrial sectors such as construction, ceramics, agriculture, additives, polymer fillers, and other applications (Carmignano et al., 2020). Thus, mineral carbonation represents an alternative for the permanent, effective, and environmentally safe sequestration of CO_2 (Galina; Arce; Ávila, 2019). The sieving performance of soil samples through shaking is a complex procedure that presents various inconsistencies and challenges in terms of repeatability (Standish 1985, Heuer & Leschonski 1985). Standish (1985) suggests that in order to achieve a satisfactory level of reliability, strict standards must be followed during the execution of the procedures. Several parameters have been identified as influential factors contributing to measurement errors, including inadequate preparation of the base material, reintroduction of sieved samples into the base material, testing on damp days, fluctuations in motor input voltage, and sieve misalignment during testing.

The objective of this project is to evaluate the optimal particle size, which influences the efficiency of acid dissolution of serpentinite. Once the best experimental parameters have been determined, an experimental design technique is applied to assess the acid dissolution process, statistically analyzing the results with a minimal number of experimental tests. This approach reduces analysis time and material requirements, leveraging prior knowledge obtained through preliminary and

exploratory analyses. The Box-Behnken response surface experimental design is employed to optimize and enhance multifactorial processes.

2. MATERIALS AND METHODS

The research was conducted at the Carbon Capture Combustion Laboratory (LC3), situated within the Department of Chemistry and Energy at the Faculty of Engineering (FEG) of São Paulo State University (UNESP). The initial phase of the study involved a comprehensive sample preparation protocol, encompassing multiple procedural steps. Initially, the sample was subjected to segregation in order to isolate the serpentinite constituent, followed by quartering to obtain a representative sample portion. Subsequently, the segmented sample was weighed to determine its mass. The ensuing step involved particle size analysis via the process of sieving, facilitated by the use of an electromagnetic sieve shaker, specifically an apparatus from the Tyler series, as manufactured by Solotest.

In the subsequent acid dissolution phase, the laboratory employed a magnetic stirrer equipped with a heating element and digital temperature control, complemented by an encapsulated thermometer bearing the Marconi brand (model 10/1). This thermal regulation apparatus was used in conjunction with a glass reactor for the controlled dissolution of the sample. The results of the acid dissolution were analyzed utilizing the Shimadzu AA-7000 atomic absorption spectrophotometer to determine the iron (Fe) content in the sample.

Subsequently, these results underwent analysis using the Box-Behnken matrix to ascertain the factor that exerted the greatest influence on the experimental outcome. This statistical approach enabled the systematic evaluation of each factor's contribution to the acid dissolution process, allowing for the identification of the most influential factor in the experiment.

2.1 Particle size analysis

In the analyzed study, two consecutive Tyler series sieves were used to separate the material that passed through the upper sieve (with a larger opening) and was retained in the lower sieve (with a smaller opening). To determine the mean diameter, the average of the diameters of the two sieves used is calculated. There are several ways to calculate and express the mean diameter of solid particles. One of them is the Sauter mean diameter, also known as the surface-volume mean diameter (Kowalczuk & Drzymala, 2016). To calculate the mass fraction (xi), equation (1), and the mean diameter (di) between the selected sieves (upper and lower), equation (2), resulting in the mean diameter of the particle (dm) in the particle mixture, according to equation (3).

$$x_i = \frac{x_i}{\Sigma M_i} \tag{1}$$

$$d_i = \frac{1}{2}(D_{p\,i} + D_{p\,i+1}) \tag{2}$$

$$d_m = \left[\Sigma\left(\frac{x_i}{d_i}\right)\right]^{-1} \tag{3}$$

This is a simple way to determine the mean diameter of a particle mixture, but caution must be taken in selecting the sieves to avoid a discontinuous (multimodal) particle size distribution.

2.2 Figures and tables

To obtain information about the particle size distribution of the received material, evaluate the amount retained, and determine the first sieve to be used in the calculation of the Sauter diameter, a sieving process was carried out using the sieves available at LC3. The sieves were placed in the sieving system, starting from the one with the smallest mesh opening (0.025 mm - first sieve) and progressing to the one with the largest opening (1.000 mm - last sieve). As depicted in Figure 01 below, it is noticeable that the sieve with aperture sizes of 1.000 mm and 0.850 mm retained the largest amount of material, which could have a significant interference in the experiments. It was therefore decided to carry out the particle size analysis of the average Sauter diameter from the sieve with an opening of 0.710.
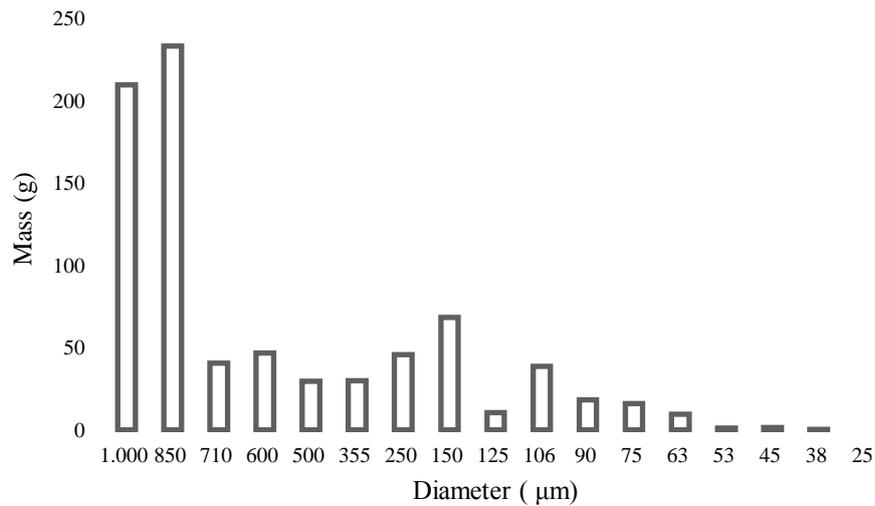
Figure 1- Mass distribution obtained in the sieving of the serpentinite sample.

The sieving bench was set up taking the selected sieves into account. Subsequently, a total mass of 370 grams of serpentinite was subjected to sieving for a duration of 20 minutes, with a sieving frequency set at 8 cycles per second (8/s). The masses of the material that were retained on each individual sieve were meticulously determined, leading to the formulation of the mass distribution graph depicted in Figure 2. This specific sample is denoted as "SMG" in the context of this study.
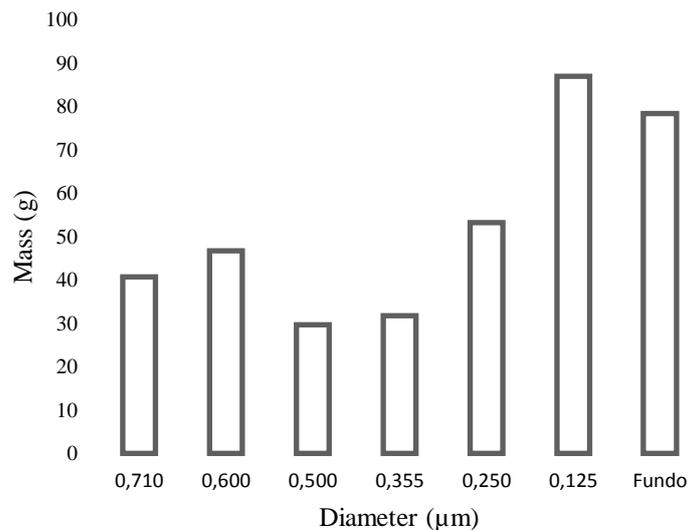

Figure 2- Mass distribution from 710 µm to 125 µm in diameter.

2.3 Equipment and glassware used in acid dissolution assays

In the development of acid dissolution research, the following equipment and glassware are used:
1.   Magnetic stirrer with heating and digital temperature control with encapsulated thermometer, from the Marconi brand (model 1085/1).
2.   Magnetic stir bar, 250 mm in length.
3.   Borosilicate glass reactor with a capacity of 250 mL, equipped with a four-necked lid, manufactured by Diogolab, with a stainless-steel clamping strap.

2.4 Acid dissolution procedure

During the acid dissolution step, a standardized procedure is followed. Initially, 100 mL of hydrochloric acid (HCl) is carefully introduced into the reactor, and the solution is then heated while subject to agitation at a constant rate of 400 rpm. Once the process temperature stabilizes, 5.4 grams of the serpentinite sample are meticulously added to the reactor.

Following the predetermined reaction time, the system is deactivated, and the resulting solution is subjected to filtration in order to separate the final liquid solution, which contains the elements of interest, from the final solid residue.

The final liquid solution is subsequently diluted to a final volume of (200±4) mL to prepare it for further analysis in the Atomic Absorption (AA) system. This dilution step ensures that the solution falls within the specified volume range for accurate analysis.

Concurrently, the filtered solid residue undergoes a distinct treatment process. It is placed in an oven and subjected to a drying process at a constant temperature of 100°C for a duration of 5 hours. This step is crucial to prepare the solid residue for subsequent characterization.

The experimental design, utilizing the Box-Behnken approach, prescribes the specific values for temperature, reaction time, and HCl concentration for each experiment, thereby enabling systematic investigation of these factors' effects on the process and its outcomes.

Finally, the determinations of iron (Fe) concentrations in the final liquid solution are conducted through atomic absorption (AA) assays. This analytical technique provides precise quantification of iron content in the solution, which is a critical aspect of assessing the effectiveness of the acid dissolution process.

3. RESULTS AND DISCUSSION

The Box-Behnken response surface experimental design is a valuable methodology employed for the efficient optimization of multifactorial processes. This approach offers the advantage of individually assessing the impact of each factor, thereby reducing the overall number of experiments needed to construct quadratic fitting models, as documented by Shengli et al. in 2018. The Box-Behnken design belongs to the category of second-order rotational designs that are rooted in incomplete factorial models, typically featuring a minimum of three factors, each with three levels. In this study, samples of serpentinite (SMG) characterized by a wide-ranging particle size distribution were utilized, and their adjusted values were derived from the findings obtained during the exploratory phase. The factors selected to define the levels and create the Box-Behnken matrix included reaction time (t), process temperature (T), and hydrochloric acid concentration (CHCl), as detailed in Tables 1 and 2.

It is important to note that, in accordance with the experimental design, the optimal conditions were established at the central point (middle level - 0). Consequently, the highest temperature utilized was 100°C, a choice informed by the fact that the process was conducted under local pressure conditions. This central point configuration serves as a reference for evaluating the impact of variations in the selected factors on the multifactorial process, thereby enabling a systematic and efficient assessment of the process parameters.

Table 1 - Box-Behnken experimental design levels and factors

Factors	Level		
	Low [-1]	Medium [0]	High [+1]
(X_1) T/°C	90	95	100
(X_2) CHCl/M	2	2,5	3
(X_3) t/min	60	120	180

Table 2 illustrates the results of iron extraction experiments, wherein Experiment 5, conducted at the conditions of 90°C, 2.5 M concentration, and a 60-minute reaction time, exhibited a notable iron extraction yield of 87.70%. Similarly, Experiment 9, with parameters set at 95°C, 2 M concentration, and a 60-minute reaction time, yielded a high extraction percentage of 87.61%. Notably, these two experiments outperformed the others in terms of iron extraction, and they both shared the commonality of a 60-minute reaction time. Conversely, the lowest iron extraction was observed in Experiment 7, which was conducted at 90°C with a 2.5 M concentration and a prolonged 180-minute reaction time. It is evident that the primary distinguishing factor between the experiments with the highest and lowest extraction percentages was the duration of the reaction. Experiments 5 and 9, with their 60-minute reaction times, significantly outperformed Experiment 7, which had a reaction time twice as long, lasting 180 minutes. Consequently, it can be inferred that the reaction time was the most influential parameter affecting iron extraction, as compared to the influence of temperature, based on the outcomes of the experiments.

Table 2 - Box-Behnken experimental matrix

Experiments	Codified Factors			Factors			Answer %
	X_1	X_2	X_3	T/°C	C_{HCl}/M	t/min	Fe
1	-1	-1	0	90	2	120	85,78
2	1	-1	0	100	2	120	84,00
3	-1	1	0	90	3	120	85,69
4	1	1	0	100	3	120	82,27
5	-1	0	-1	90	2,5	60	87,70
6	1	0	-1	100	2,5	60	84,51
7	-1	0	1	90	2,5	180	81,64
8	1	0	1	100	2,5	180	83,63
9	0	-1	-1	95	2	60	87,61
10	0	1	-1	95	3	60	84,05
11	0	-1	1	95	2	180	83,52
12	0	1	1	95	3	180	82,76
13	0	0	0	95	2,5	120	83,94
14	0	0	0	95	2,5	120	83,48
15	0	0	0	95	2,5	120	84,42

In the context of the analysis of variance (ANOVA), the significance of a statistical model is typically determined by comparing the calculated F-value to a critical F-value derived from a specified distribution table, such as the Fisher-Snedecor 5% distribution table, as described by Mbuya et al. in 2019. Additionally, a model is considered significant when the p-value associated with the F-test is less than 5% (usually corresponding to a significance level of 0.05).

Table 3 – ANOVA - Analysis of Variance

Source of Variation	Df (Degrees of Freedom)	Sum Sq (Sum of Squares)	Mean Sq (Mean Squares)	F value (F-statistics)	Pr (>F) (p-value)
X_1	1	5.120000	5.120000	9.954835	0.0134937066
X_2	1	4.712450	4.712450	9.162434	0.0163852325
X_3	1	18.972800	18.972800	36.888887	0.0002980211
X_1:X_2	1	0.672400	0.672400	1.307350	0.2859343792
X_1:X_3	1	6.708100	6.708100	13.042584	0.0068671958
X_2:X_3	1	1.960000	1.960000	3.810835	0.0867055269
Residuals	8	4.114583	0.5143229		

In Table 3, the significance of various factors and interactions in the experiment is assessed. The factors X_1 (temperature) and X_2 (HCl concentration) both exhibit p-values below 0.05, indicating that they can exert a significant effect on the response variable, depending on the chosen significance level (typically 0.05). The factor X_3 (time/minute) displays an extremely low p-value (0.0002980211), suggesting a high level of significance in the experiment. This indicates that factor X_3 has a substantial and influential impact on the response variable.

Moreover, the interactions between the factors, specifically the interactions of temperature by time and acid concentration by time, also exhibit p-values below 0.05. This implies that these interactions may possess statistical significance at a significance level of 0.05.

Conversely, the interaction $X_1:X_2$, which represents the interaction between temperature and acid concentration, has a p-value greater than 0.05. This suggests that this specific interaction may not be statistically significant at the 0.05 significance level, indicating that it may not substantially influence the response variable.

4. CONCLUSIONS

Based on the analysis of variance conducted in this study, which considered X_1 as the temperature in degrees Celsius (°C), X_2 as HCl concentration in molarity (M), and X_3 as time in minutes, it becomes evident that the interactions $X_1:X_3$ and $X_2:X_3$, with X_3 being a common factor in both interactions, hold significance in influencing the response variable. This suggests that the combined effects of temperature and time, as well as HCl concentration and time, are statistically significant and influential in shaping the response variable. Notably, X_3, which represents time in minutes, emerges as a pivotal factor that can exert a substantial and highly significant influence on the response variable.

Conversely, the interaction between X_1 and X_2 (temperature and HCl concentration) does not demonstrate statistical significance at the 0.05 significance level. This implies that, within the scope of this experiment, the combined effect of temperature and HCl concentration may not be as influential in determining the response variable.

To gain a more comprehensive understanding of the relationships and effects of these factors on the response variable, further investigations are warranted. These findings underscore the importance of considering both individual factors and their interactions to optimize the multifactorial process efficiently.

5. ACKNOWLEDGEMENTS

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