UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY TECH

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CO_2 adsorption at variable temperatures using clays from Ecuador

Potential uses in the cement industry

Trabajo de titulación presentado como requisito para la obtención del
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Dedication

“To you, Cinthia Salomé, who fills my days with love and joy, thank you for being my unconditional companion. Your support and sweetness make each day better. You are my greatest inspiration and my reason to move forward with strength”

"To my colleagues and friends Néstor, Josué and Lily, thank you for the collaboration and camaraderie that make work a more pleasant place. Each challenge is overcome more easily thanks to the good vibes and effort we share together. They are the better!"

"To my dear parents, thank you for being my greatest pillar and source of inspiration. Your love, sacrifice and teachings are the engine that drives me to overcome any obstacle. Everything I am and what I aspire to be is thanks to you"

.

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Resumen

El presente estudio propone el uso de arcillas ecuatorianas que sean beneficiosas para encapsular o adsorber (líquido o gaseoso) partículas de CO_2 u otras sustancias de bajo peso molecular, con el objetivo de desarrollar de nuevas técnicas para el cuidado del medio ambiente.

Por tal motivo en este trabajo, se ha realizado la síntesis y caracterización de arcillas ecuatorianas extraídas de diferentes provincias y que están disponibles en el laboratorio de Química de la Universidad Yachay, aprovechando la infraestructura y equipos existentes (reactores de alta presión, difractómetro de rayos X, centrífugas, estufas y hornos), que son los adecuados para este tipo de aplicaciones. Además, estos tratamientos deberán garantizar una adsorción eficiente a diferentes temperaturas y presiones, acompañada de una comparación exhaustiva con procesos similares descritos en la literatura científica.

Dado que la captura de dióxido de carbono CO_2 es una prioridad para el cuidado del medio ambiente, la justificación de este proyecto es el desarrollo de un material que sea un buen adsorbente que sea de fácil instalación y sea aplicable en el sector industrial como puede ser la industria del cemento, este material podría ser una solución innovadora y efectiva para reducir las emisiones y mejorar las técnicas de captura de CO_2.

Palabras Claves: Captura de CO_2, pilarización, arcillas, aminas, temperaturas variables, reactores de alta presión.

Abstract

The present study proposes using Ecuadorian clays that are beneficial for encapsulating or adsorbing (liquid or gaseous) CO_2 particles or other low molecular weight substances, aiming to develop new techniques for caring for the environment.

For this reason, the synthesis and characterization of Ecuadorian clays extracted from different provinces and available in the Chemistry laboratory of Yachay University has been carried out, taking advantage of the existing infrastructure and equipment (high pressure reactors, X-ray diffractometer, centrifuges, ovens and furnaces), which are suitable for this type of applications. In addition, these treatments must guarantee efficient adsorption at different temperatures and pressures, accompanied by an exhaustive comparison with similar processes described in the scientific literature.

Given that the capture of carbon dioxide CO_2 is a priority for the care of the environment, the justification of this project would be the development of a material that is a good adsorbent that is easy to install and is applicable in the industrial sector such as the cement industry, this material could be an innovative and effective solution to reduce emissions and improve CO_2 capture techniques.

Key Words: CO_2 capture, pillarization, clays, amines, variable temperatures, high pressure reactor

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Abbreviations

CO_2	Carbon dioxide
BEP	Barrels of oil equivalent
CCS	CO_2 capture and storage
PPC	post-combustion carbon capture
WGS	Water gas shif
Z	Compressibility factor
P	Pressure
V	Volume
n	Gas mole
R	Universal ideal gas constant
T	Temperature
t	Time
n_{to}	Initial moles of gas
n_{tf}	Moles of gas in time (t)
m_i	Initial mass
m_f	Mass at time (t)

CHAPTER 1

Introduction

Today, carbon dioxide (CO_2) emissions have gone from minor concerns to one of the most significant environmental challenges worldwide [1]. Since the industrial revolution, the use of fossil fuels has transformed energy production, transportation, and development in the global economy[2]. However, this progress has been accompanied by a high environmental cost. Although CO_2 is a greenhouse gas necessary to maintain the planet's temperature, it traps more heat in the atmosphere and causes global warming in excessive concentrations. Since the beginning of the industrial era, thousands of tons of CO_2 have been emitted into the atmosphere, which has led to a significant increase in the earth's global temperature[3].

This warming has far-reaching consequences. For example, the increase in global temperature is melting glaciers and polar ice caps, which raises sea levels and threatens coastal communities worldwide. Another example would be the variation in climate patterns, which have generated extreme weather events, such as hurricanes, droughts, and floods, becoming more frequent and intense. Ecosystems are under pressure, and many species face extinction due to the alteration of their habitat [4].

Carbon dioxide emissions are no exception in Ecuador, reflecting its economic development and dependence on some energy sources. Although Ecuador is not one of the largest emitters of CO_2 globally, its emissions have significant environmental implications. Currently, the population of Ecuador is around 18 million inhabitants, and the primary energy consumption per capita in Ecuador is around 1.0 to 1.2 tons of oil equivalent (TEP) per inhabitant per year. This equals 7.33 and 8.80 barrels of oil per inhabitant per year (7.33 – 8.80 BEP). Ecuador's largest energy source is fossil fuels, which are closely related to transportation activities, energy generation, and the industrial sector, directly related to high CO_2 emissions[5].

Implementing strategies and multilateral treaties (like the Kyoto Protocol and the Paris Agreement) is essential to reduce CO_2 emissions into the atmosphere. The implementation of these strategies for capturing and storing CO_2 which are detailed below: [6]

- *Transition to renewable energy*. One of the most effective alternatives to reduce CO_2 emissions is to switch from fossil fuels (such as coal, oil, and natural gas) to renewable energy sources such as solar, wind, hydroelectric, and geothermal. These sources produce energy without emitting CO_2, making them a viable option to decarbonize the global economy [7].

- *Improving energy efficiency:* In sectors such as industry, transport, and construction, developing more efficient technologies, adopting sustainable practices, and modernizing infrastructure can be implemented to reduce energy consumption [8].

- *Electrification of transport:* The electrification of transport through the adoption of electric vehicles (EV) and the development of charging infrastructure is essential to reduce CO_2 emissions in this sector, and public transport and sustainable mobility should be promoted more [3].

- *Reforestation and forest protection:* Forests act as carbon filters or sinks, absorbing CO_2 from the atmosphere and storing it in biomass. Reforestation, conservation of existing forests, and restoration of degraded ecosystems are key strategies to reduce CO_2 concentrations in the atmosphere [6].

- *Circular economy and waste reduction:* This should focus on waste and maximize the reuse and recycling of materials. By reducing the need to extract and process new resources, the energy required is reduced, and therefore CO_2 emissions are reduced [9].

- *Policies and regulations:* Governments have a fundamental role in reducing CO_2 emissions by implementing policies and regulations [9].

- *Carbon capture and storage (CCS):* Carbon capture and storage technologies capture CO_2 emitted by power plants and industries, then store it underground in safe geological formations. This technology can be beneficial in sectors where decarburization is more complex, such as cement and steel production[10][11].

Based on the above, this study will investigate a method for capturing and storing CO_2 emissions, which will be the adsorption of CO_2 through clays that exist in Ecuador [12]. These studies will be carried out under variable conditions of variable temperatures (25° C - 30° C) [13] and under high pressure (500 psig) in an experimental setup for CO_2 capture tests [14], as well as the study of the clays, their treatment (purification) and their adsorption of CO_2 and their analysis of chemical interactions between the CO_2 gas and the adsorbent material [15].

1.1 Justification

With the development of this research topic, one aims to summarize the development of the installation of the high-pressure setup for CO_2 adsorption processes [14]. It will deal with the processes carried out by the reactors in the Chemistry laboratory located in the E2-E3 laboratory building at Yachay Tech University. A high-pressure system comprises a pressure vessel built rigidly and made of materials resistant to high temperatures and high pressures containing a fluid such as steam, gas, etc. Whether pressurized with steam, hot water, gas or vapor, pressure systems can be divided into low-pressure and high-pressure systems. According to the information collected, high-pressure processes will be carried out in various fields, and work will be done directly with the UITEY research teachers. There is very little literature on examples of high-pressure applications [16].

In recent years, the objective of eliminating carbon dioxide produced by industries has been a great topic of debate worldwide due to its high pollution [10]. One alternative is the use of different technologies such as solid adsorption. The problem with these technologies would be the low adsorption capacity at low pressure and the influence of water vapor or other vapors that can be adsorbed on the solid. CO_2 adsorption test have been tested on activated carbon, zeolites, mesoporous solids, and clays.

1.2 Problem Statement

The steady increase in atmospheric carbon dioxide (CO_2) concentrations is one of the main drivers of climate change, causing severe environmental, social, and economic consequences globally. Human activities, mainly burning fossil fuels in power generation, transport, and industry, have significantly increased CO_2 emissions, bringing atmospheric concentrations to unprecedented levels [17]. Faced with this problem, the scientific community and international policies have sought various solutions to mitigate CO_2 emissions. One of the emerging technologies is CO_2 adsorption, a process that allows CO_2 to be captured and retained in solid materials, preventing this gas from reaching the atmosphere [18]. However, implementing this technology faces multiple challenges that prevent its adoption on a large scale.

The central problem lies in developing and optimizing CO_2 adsorption technologies that are economically viable, highly efficient, and sustainable for large-scale application in various industries [19]. Currently, available adsorption solutions have limitations in cost, capture capacity, selectivity towards CO_2 in the presence of other gases, long-term stability, and efficiency under different operating conditions. Other aspects were that current adsorbent materials, such as activated carbons, zeolites, and metal-organic frameworks (MOFs), have different CO_2 adsorption capacities [20]. However, these materials may not be efficient enough in industrial conditions, where other gases, humidity, and temperature fluctuations affect the capture capacity. Many of the most effective materials for CO_2 adsorption, such as MOFs, are expensive to produce and process. This limits their practical application, especially in developing countries or industries with tight economic margins.

A significant challenge is the regeneration of adsorbents for reuse. The CO_2 desorption process (release of captured CO_2) must be efficient and require as little energy as possible for the adsorption-desorption cycle to be economically sustainable. The total environmental impact of adsorbent materials must be assessed, including their production, use, and disposal. In addition, the technology must be scalable to be implemented in extensive industrial facilities or to capture CO_2 from the air directly at global levels [21]. As a severe research question, how can CO_2 adsorbent materials be developed and optimized to be economical, highly efficient, sustainable, and capable of operating on a large scale under various industrial conditions?

1.3 Objectives

1.3.1 General Objective

To investigate and optimize the use of clay-based materials for efficient carbon dioxide capture, focusing on their adsorption capacity to provide a sustainable and cost-effective solution for reducing atmospheric CO_2 levels.

1.3.2 Specific Objectives

- To carry out the installation and commissioning of the testing system for CO_2 capture in the Chemistry laboratory.
- Evaluate the CO_2 adsorption capacity of Ecuadorian clays under different temperature and pressure conditions
- Analyze the thermal stability and regeneration of clays after several adsorption cycles.
- Determine the influence of factors such as temperature, pressure and humidity on the performance of clays for CO_2 capture.
- Propose recommendations on the most suitable type of clay for capture processes on an industrial scale

CHAPTER 2

Theoretical Background

2.1 High-temperature industrial processes in Ecuador

Ecuador has developed various industrial processes that have been key to improving the economy. High-temperature industrial processes are essential in many industries because they facilitate chemical reactions such as melting materials and synthesizing more complex compounds that improve their physical and chemical properties [22]. The main material synthesis processes and their applications and benefits are described below: [23][24]

- *Metal casting:* This process involves heating the material to its melting point to mold it into a specific shape or modify it to make it more resistant. The main applications include manufacturing metal parts (industry) and producing new alloys. The main benefit related to metal casting is it allows the production of complex, high-strength, and high-precision parts [25].

- *Heat treatment of materials:* The heat treatment process is used to harden or improve the characteristics of metallic materials, including tempering, annealing, and quenching, which are subjected to high temperatures in which the properties of the materials are modified. The main applications are automotive industry transmission components, tool manufacturing, and structural components. The benefits of heat treatment of materials have improved the hardness, toughness, and resistance of metals and extended their useful life [26].

- *Glass production:* For glass production, a mixture of silica sand, soda, and limestone is used at very high temperatures to form a liquid and give it different shapes. The main applications include manufacturing containers, flat glass, and elements for electronic and optical applications [27].

- *Ceramic production:* In the process of firing non-metallic inorganic materials at high temperatures to form more resistant materials. The main applications are construction materials, consumer products, and insulating technical components. Some benefits are high resistance to high temperatures and thermal and electrical insulating properties [28].

- *Oil Refining:* The processes for oil refining are very varied, such as thermal cracking, in which large hydrocarbon molecules are broken down into smaller fractions at high temperatures. The main applications include fuel production, the manufacture of petrochemical products, and the provision of essential raw materials for the chemical industry. Some benefits related to oil refining are improving the efficiency of extracting valuable products from crude oil and producing cleaner and more efficient fuels [29].

- *Cement production:* It is a complex industrial process that transforms raw materials such as limestone and clay into essential construction materials. The stages of the process are detailed below: [30]

***Table 1**. Procedure for the production of cement in the industrial sector.*

Processes	**Process description**
Extraction and preparation of raw materials	· Extraction: All the material is extracted from quarries. · Preparation: The raw material is transported to the cement plant and undergoes crushing to reduce its size.
Homogenization and storage.	· Homogenization: The crushed raw material is mixed and ground again to form a homogeneous mixture · Storage: The homogeneous mixture is stored in silos, where it continues to homogenize by aeration and mixing to ensure a uniform composition.
Calcination and clinkerization	· Preheater: The homogeneous mixture is preheated in rotating silos reaching temperatures of up to 900 °C. · Calcination: During preheating, part of the carbonate decomposition occurs, releasing CO_2 in large quantities.

	· Rotary kiln: The preheated mixture enters a rotary kiln where the temperature is raised to 1450 °C, where sintering occurs, forming the clinker, a small grey sphere.
Clinker Cooling	· Cooler - Hot Clinker is cooled rapidly in a grate cooler using forced air.
Cement Grinding	· Additives: Cooled Clinker is mixed with additions such as gypsum or pozzolan. · Grinding: All mixed material goes through a grinding process in a ball mill to produce an excellent powder. The cement is used as a finished product.
Storage and Shipping	· Storage - Cement is stored in silos where it can be shipped. · Shipping - Cement is packed in sacks or transported in bulk to construction sites.

Environmental considerations of the cement manufacturing process: Cement production is one of the most significant sources of CO_2 emissions, contributing significantly to climate change. These emissions come mainly from the decarbonization of limestone during the clinkerization process and the combustion of fossil fuels used to generate the heat needed in the kilns [31] [32].

2.2 CO_2 capture

CO_2 capture is an essential technology in mitigating and combating climate change, which aims to reduce CO_2 emissions from industrial sources and burning fossil fuels. This technology has processes based on well-established theoretical backgrounds covering several scientific and technological disciplines described below [33].

Properties of CO_2 – being a greenhouse gas that is released in large quantities as a result of human activities, such as the burning of fossil fuels and industrial processes, this gas is colorless, odorless, and slightly acidic when dissolved in water, leading to the formation of carbonic acid (H_2CO_3) [34].

Absorption reactions – The theoretical background is based on the ability of CO_2 to react with chemical compounds, such as amines, forming stable compounds that can then be decomposed to release pure CO2. This process is crucial for post-combustion capture [35].

2.3 CO_2 capture methods and techniques

Chemical absorption: It involves the reaction of CO_2 with a chemical solvent, which could be amines, in absorption towers. This process is well understood from a thermodynamic and kinetic point of view, which allows for the efficient capture of CO_2 [36].

Physical adsorption: It uses porous solid materials, such as zeolites or activated carbons, which adsorb CO_2 on their surface "physical adsorption" (Van der Vaals forces) as well as the ability of the materials to retain and release CO_2 under certain conditions [37].

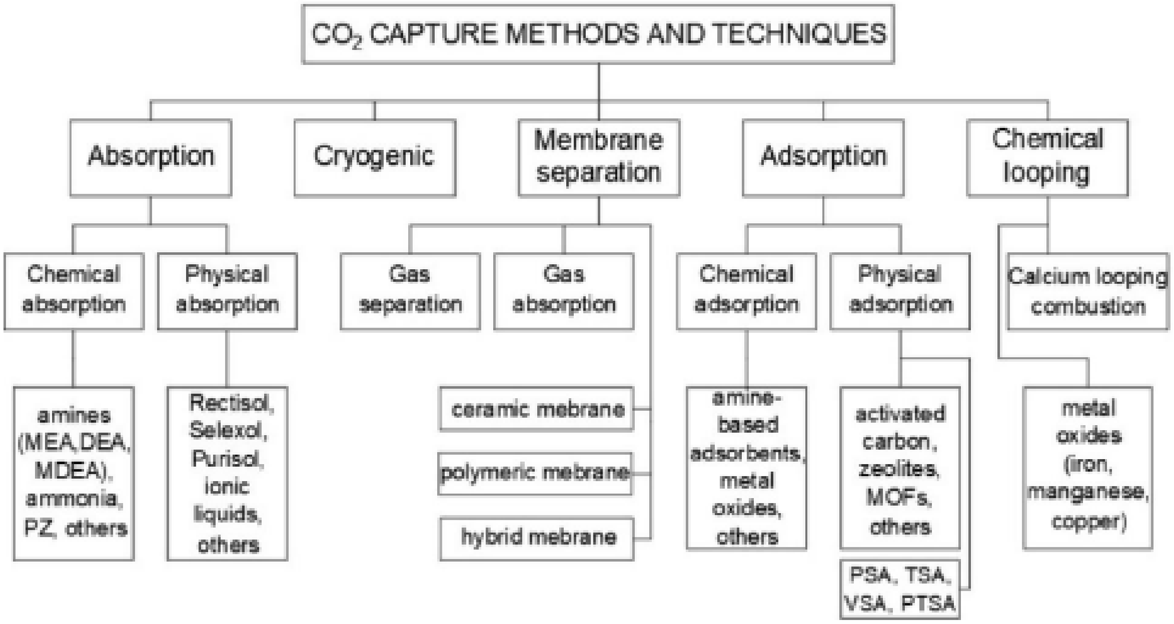


Figure 1. Techniques and methodologies for capturing CO_2. [38]

Membrane capture: It uses membranes that have been specifically selected as permeable to separate CO_2 from other gases. This theory is based on differential diffusion through the membrane, where CO_2 moves faster than other gases [39].

CO_2 capture methods and techniques will need to address two key aspects: thermodynamic and kinetic factors, which will be explained below.

Solubility equilibrium: The solubility of CO_2 in different solvents, such as aqueous solutions of amines, follows thermodynamic principles such as Henry's law [40], which describes the solubility of a gas in a liquid as a function of its partial pressure.

Reaction kinetics: It applies the principle of the rate at which CO_2 reacts with adsorbents and absorbents, which is determined by chemical kinetics [37].

2.4 CO_2 adsorption process

CO_2 adsorption is a process by which carbon dioxide is captured and retained on the surface of a solid material. This method is considered an efficient and promising technique to reduce CO_2 emissions in various industrial processes and is an essential component in the fight against climate change. This process's fundamental principles, materials, adsorption mechanisms, and applications are described below [4].

Physical adsorption (physisorption) – is based on Van der Waals forces between CO_2 molecules and the adsorbent surface. It is a reversible process and depends mainly on temperature and pressure. This principle is generally effective at low temperatures [4] [38].

In this process, CO_2 adheres to the surface of the adsorbent through weak interactions. This process does not involve a chemical reaction; the CO_2 molecules are simply trapped in the pores of the adsorbent.

Typical adsorbents include:

- Zeolites
- Activated carbon
- Silica gel
- MOFs (Metal Organic Frameworks)

And the formula to determine the amount of absorbed CO_2 is the following:

$$CO_2(g) + \text{Surface of the adsorbent} \rightarrow CO_2 \text{ adsorbed}$$

Where:

$CO_2(g)$: It represents carbon dioxide in a gaseous state, which is the adsorbate (the substance that will be absorbed).

Surface of the adsorbent: It is the solid material (such as zeolites, activated carbon, metal oxides) that provides active sites where the adsorbent molecules CO_2 can join.

CO_2 adsorbed: It is carbon dioxide that has adhered to the surface of the adsorbent by physical forces (such as van der Waals) or chemical forces (chemical bonds)

Chemical adsorption (chemisorption) – involves the formation of chemical bonds between CO_2 molecules and active sites on the surface of the adsorbent material [41].

A chemical reaction occurs between the CO_2 and the adsorbent in this process. These sorbents react with the CO_2, forming a stable chemical compound. For example, alkaline metals or amines react very well with CO_2.

Example of functionalized amine in a CO_2 capture process in reactors.

Reaction:

$$RNH_2 + CO_2 \rightarrow RNHCOOH \quad (1)$$

where ***RNH_2*** is an amine that reacts with ***CO_2*** to form a carbamate.

2.5 Types of materials for CO_2 adsorption

In the adsorption process, there are highly effective and favorable materials for the capture of carbon dioxide (CO_2). These materials, due to their physical and chemical properties, are particularly efficient and environmentally friendly for this purpose. Below are some of the most used materials in the CO_2 adsorption process

*Zeolite*s – are aluminosilicates with a porous structure that allows the adsorption of CO_2 in their cavities. They are very selective and effective in the adsorption of CO_2 in the presence of other gases [42].

Activated carbons – these materials have a high specific surface area and are effective in adsorbing CO_2 at low pressure, and their performance can be improved with chemical modifications [43].

Metal – Organic Frameworks (MOFs) – are crystalline materials with metal nodes connected by organic ligands. Their highly porous and customizable structure makes them very effective for the adsorption of CO_2 [44].

Modified clays – natural clays can be treated to improve their adsorption capacity. They are cheaper and abundant in the earth's crust [40].

2.6 Types of clays for CO_2 adsorption

From the composition of the materials, the types of clay can be determined, which are described below:

Kaolinite ($Al_2Si_2O_5(OH)_4$). – is one of the purest clays, formed mainly by hydrated aluminum silicate, has a low cation exchange capacity, its structure is stable and is generally used for the manufacture of ceramics, paper and cosmetics [45].

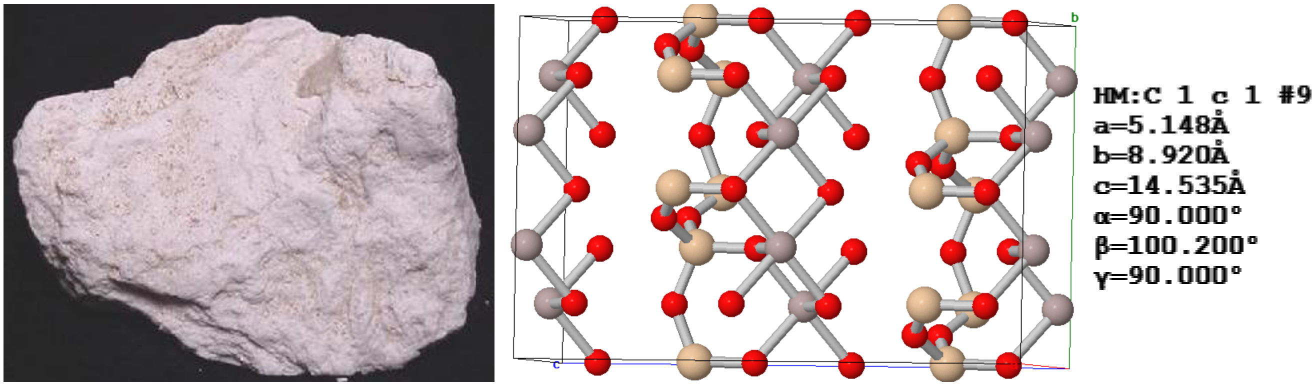


Figure 2. Molecular structure of kaolinite (source: mindat.org)

Montmorillonite ($Al_2Si_4O_{10}(OH))_2$*nH_2O). – belongs to the smectic, its chemical composition allows the layers to expand to absorb water easily, it is found in bentonite and has a high ion exchange capacity, it is usually used in waterproof seals and in the well drilling industry[12].

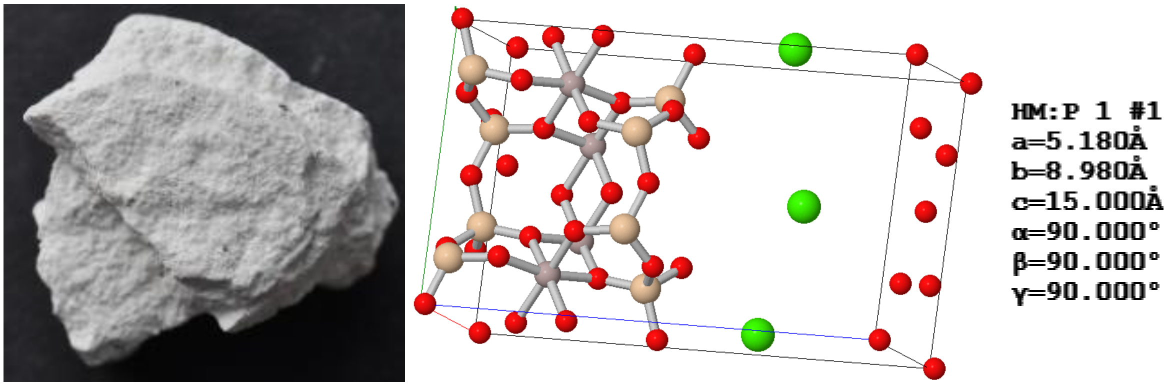


Figure 3. Molecular structure of montmorillonite (source: mindat.org)

Illite ($K_{0.6}Al_4(Si_7Al)O_{20}(OH)_4$). – is similar to mica, but is rich in potassium, is usually found in clay soils, it is found in sediments and metaphoric rocks. It does not expand with water, so it has less plasticity than montmorillonite.

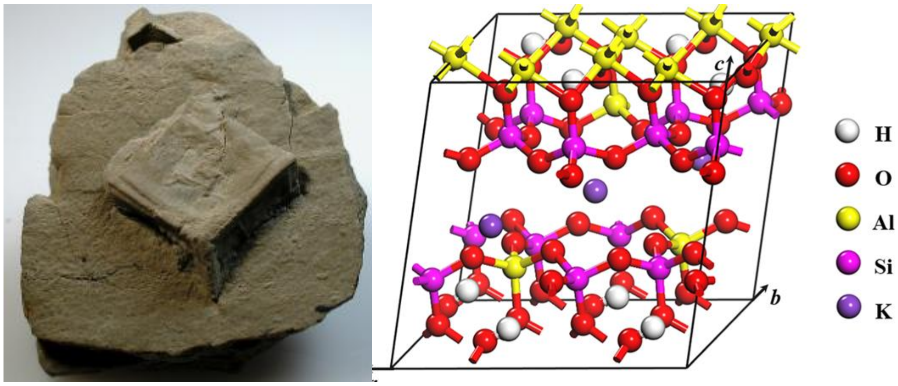


Figure 4. Molecular structure of illite (source: mindat.org)

Vermiculite $(Mg,Fe,Al)_3(Si,Al)_4O_{10}(OH)_2$ * $4H_2O$. – contains magnesium, iron, silica, and alumina. It is expensive and has a structure similar to montmorillonite, but with larger interlayer spaces. It is mainly used in the agricultural industry as soil for thermal insulation.

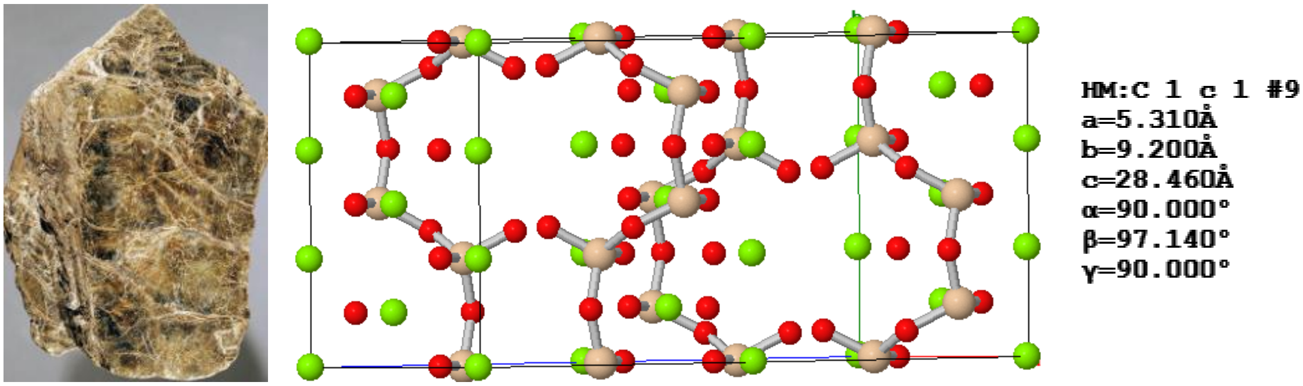


Figure 5. Molecular structure of vermiculite (source: mindat.org)

2.7 General characteristic of clays

The main characteristics of the clays that will be studied in this work are detailed, which are referenced from the INEDITA[12] project and are detailed below:

Chemical composition

Clays are characterized by their laminar structure, their ability to adsorb water and ease of molding when wet. The composition of clays varies according to the type, but they are generally made up of hydrated aluminum silicates, the most common of which are described.

General composition of a typical clay with its main components:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$$

Silica (SiO_2): This is one of the main components of clays and is part of the crystalline structure of the minerals that make up the clays. It is found in the form of silica tetrahedrons (SiO_4)[46].

Alumina (Al_2O_3): Another essential component of clays is aluminum oxide. Alumina octahedrons are present in the structure of many clays, combining with silica [47].

Water (H_2O): Clays usually contain water molecules in their structure, both in the form of water of crystallization (water that is part of the structure of the mineral) and in the form of adsorbed water (water that adheres to the surface of the clay particles).

Oxides and hydroxides of other elements: To a lesser extent, clays may contain traces of other elements such as iron (Fe_2O_3), magnesium (MgO), potassium (K_2O), calcium (CaO), sodium (Na_2O), and other elements, depending on the origin of the clay [48].

Physical properties

A clay is greatly influenced by its ability to adsorb CO_2, which determines its efficiency in gas capture processes. The properties are directly related to the structure and composition of the clay, which gives it a high capacity to retain gases in its pores and surfaces. The main physical properties of a clay that are important for CO_2 adsorption are described below.

Surface area (particle size) – is crucial for its adsorption capacity. The larger the area, the more space there is for CO_2 molecules to adsorb on the surface. Montmorillonite can adsorb large amounts of CO_2 due to the high number of sites available for adsorption. The area is usually expressed in m2/g [49].

Porosity – refers to the proportion of empty spaces (pores) within the structure, these pores provide additional space for CO_2 to adsorb. Pore sizes range from (2-50 nm). Montmorillonite and smectites typically have high porosity, making them suitable for CO_2 capture [50].

Cation exchange capacity (CEC) – is a measure of the clay's ability to exchange positively charged ions (cations) between the clay layers and their surroundings. Montmorillonite has a high CEC, allowing it to adsorb cations and improve CO_2 capture capacity [51].

Swelling – some clays, such as montmorillonite, can expand when they absorb water or gases. As the clay layers swell, they separate and increase the space available for CO_2 to adsorb between them[52].

2.8 Captured CO_2 storage

Once the CO_2 has been captured, it must be transported to a storage site, which can be by pipeline, truck or ship depending on the scale and location of the storage facility and finally; after having carried out all the necessary procedures, it is necessary to store all the CO_2 that has been captured. The main methods of storing CO_2 are detailed below:

Injection into geological formations – once the CO_2 has been captured, it can be compressed and stored in deep geological formations such as: saline aquifers, depleted oil fields or coal formations [53].

Storage on the seabed – storage of CO_2 on the ocean floor should be studied, where it can remain trapped due to high pressures and low temperatures [53].

Mineralization – CO_2 reacts with some minerals and becomes solid compounds, such as carbonates, which provides a permanent form of storage [54].

Bio-storage – Capturing CO_2 through photosynthesis and storing it in biomass or soils. This method is more natural but limited in capacity [55].

CHAPTER 3

Methodology

This chapter will outline the methodology to carry out the proposed study. The fundamental stages are detailed below:

- *Reactor selection*
- *Clay sample selection*
- *Preparation of material of adsorption test*
- *Commissioning of the test system*
- *Thermodynamic study*
- *Experimental setup*

For developing of this thesis project, Ecuadorian clays collected by GIAMP from the School of Chemistry will be used under the INÉDITA project. These materials have been purified, synthesized and previously characterized to determine their chemical composition, in which their specific surface area, pore structure and chemical properties will be verified, and the most suitable material will be selected as an effective CO_2 adsorbents.

3.1 Reactor selection

In the first stage, the evaluation of the different types of reactors available at the School of Chemical Sciences will be carried out, considering factors such as:

Characteristics

Currently, the School of Chemical Sciences and Engineering has 4 reactors (2 with agitation and 2 without agitation) which come from the INÉDITA Project "Ferruginous and titaniferous sands of Ecuador as adsorbents of acid gases in the hydrocarbon industry" [56] which are described below.

Table 2. CO_2 capture systems available

Quantity	Description	Technical characteristics	Ref
2	Parr 5100 Series Medium Pressure Reactor	Maximum pressure 1000 PSI (69 bar) Volume 660 ml Temperature: max 225 °C	[57]
2	Parr 4973 Series Corrosion Resistant High Pressure Reactor	Maximum pressure 3000 PSI (206 bar) Volume 100 ml Temperature: max 225 °C	[58]

Operating conditions

For CO_2 capture, the conditions vary depending on the type of technology used, the capture method and the material used. These conditions, such as temperature, pressure, gas flow and CO_2 concentration, are crucial to optimize the efficiency of the process as indicated below:

Table *3. Operating conditions for adsorption systems*

Method	Temperature (°C)	Pressure (psi)	Observations	Ref
Adsorption with amines	adsorption: 40 – 60 desorption: 80 – 150	29 – 101 (2 – 7 bar)	It is common in post combustion capture	[59]
Adsorption on solids (PSA/TSA)	20 – 50	72.5 – 145 (5 – 10 bar)	Used in adsorption with solids such as zeolites and MOFs	[60]
Carbonation/ calcination	carbonation: 600 – 700 calcination: 850 – 950	14.5 – 29 (1-2 bar)	Based on reaction with calcium oxides (CaO)	[61]
Membranes	20 – 300	72.5 – 290 (5 – 20 bar)	Pressure differences improve separation efficiency	[62]

Installation, operation, and maintenance costs

Installation costs are generally the highest expenses because they include the purchase of equipment for CO_2 capture testing. These costs vary depending on the type of technology to be applied and the efficiency of the equipment. You must add the cost of maintenance which is essential to ensure that the equipment works efficiently

3.2 Clay sample selection

The selection of the appropriate material is crucial to guarantee the efficiency and effectiveness in the capture of gases such as CO_2 [63]. These materials must meet certain requirements that optimize adsorption processes under controlled experimental conditions [64].

In the present study, a review of solid materials will be carried out, specifically aluminosilicate minerals with porous structures derived from clays and zeolites [20], These materials are available at the Faculty of Chemical Sciences, and the properties they possess make them ideal for application in the adsorption of CO_2.

Three types of clay: **CZY-305, CZY-306 and bentonite**, from natural sources will be selected and prepared for adsorption tests. The samples will be purified to remove impurities and improve the adsorption capacity.

The clay selected will be the one that has the best properties for use in the reactor and meets the objectives of this study. Based on studies carried out by the School of Chemical Sciences and Engineering, the following list of clayey materials that exist in the E3 laboratory and have been extracted from betas from different parts of Ecuador has been prepared, detailed below.

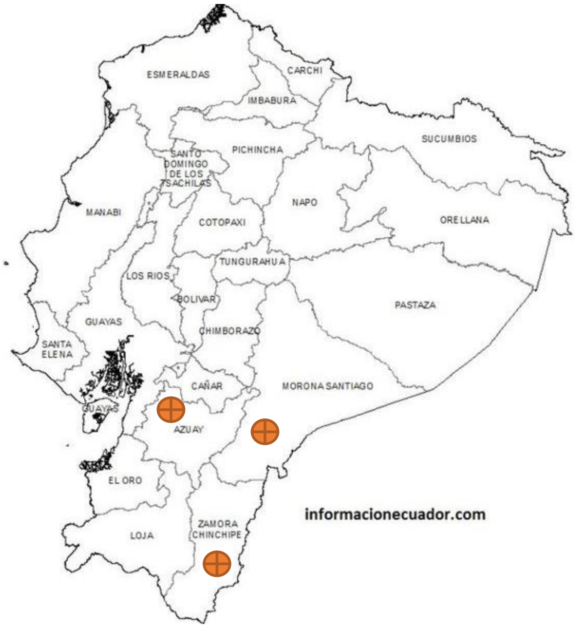


Figure 6. *Map of the Ecuadorian provinces and sites where clays [12] This sampling was performed by GIAMP (Research Group applied in Material and Processes)*

***Table 4**. Data corresponding to know mineral phases of each sample analyzed by XRD and treated via QUALX2.0, the values in parenthesis correspond to relative abundance (%)*

Sample	Location	Mineral Phases
CAN-301	Azuay	Quartz (31,7%), kaolinite (68,3%)
CZN-302	Zamora Chinchipe	Quartz (27,2%), kaolinite (70,6%), Alunite (2,2%)
CZP-303	Zamora Chinchipe	Quartz (33,5%), kaolinite (48,5%), Bimessite (2,0%), Titanite (14,0%)
CZY-305	Zamora Chinchipe	Quartz (20,0%), kaolinite (22,0%), Antigorite (19,0%), Microcline (29,6%)
CZQ-306	Zamora Chinchipe	Quartz (9,0%), kaolinite (63,4%), Muscovite (10,3%), Nacrite (17,3%)
COL-307	Morona Santiago	Quartz (13,8%), kaolinite (86,2%)
COL-308	Morona Santiago	Quartz (39,1%), kaolinite (57,6%), Dickite (3,4%)

After analyzing the chemical composition of the different clays presented in Table 4, samples CZY-305, CZY-306 and COL-308 were selected due to their low quartz concentration and high percentage of kaolinite [12]. These characteristics are favorable, since a higher quantity of kaolinite is essential to perform adsorption tests with greater efficiency and precision. Various CO_2 adsorption tests will be carried out. These tests will be carried out under controlled conditions, evaluating the behavior of the selected clays at different temperatures and pressures. This approach will allow determining their adsorption capacity under different operating conditions, providing key data for their possible application in carbon dioxide capture and storage processes.

3.3 Preparation of material for adsorption test

Once the material has been selected, the next step is to prepare all the necessary inputs to carry out the experimental CO_2 capture trials. This process requires a meticulous approach, following a series of phases designed to ensure that the clay is in optimal condition for the experiments. The key preparation phases are described below:

- *Selection of the appropriate clay:* Selection of the appropriate clay: CZY-305, CZY-306, COL-308 and bentonite clays have been considered, which come from a natural deposit in south-central Ecuador, has been considered. The clay that offers the best properties for the adsorption or capture process of CO_2 must be selected. Among these are bentonite, montmorillonite or kaolinite.

- *Clay size classification:* As the clay comes from a natural deposit, it is necessary to perform a classification to separate impurities or unwanted minerals. In this process, the following will be done:

    - Grinding of the material.
    - Sieving to separate fine particles of (60-120-230) mesh.
    - Washing to remove organic matter or surface impurities.
    - Drying is done to remove natural moisture and create a homogeneous material.

- *Characterization of the clay:* Characterizing the selected clay is a set of techniques and studies that allows for determining the clay's physical, chemical, mineralogical, and structural properties. This characterization is essential to identify the quality and evaluate its suitability for some applications. For the present study, the equipment available at the School of Chemical Sciences will be used, which is the X-ray diffractometer, in which the minerals present in the clay will be identified, which will mainly be phyllosilicates (kaolinite, montmorillonite, illite, chlorite).

Figure 7*. XRD equipment.*

After the clay's characterization, the present minerals can be determined. Additionally, if there is the presence of quartz, it must be evaluated whether purification is required and verify whether the material is suitable for carrying out CO_2 capture tests.

- *Solution and purification of clay:* Considering the type of clay and the minerals it contains, including impurities (quartz), it must be purified using sodium hexametaphosphate ($Na_6P_6O_{18}$) (SHMP). This is an inorganic compound belonging to the polyphosphate family, which is a sodium salt that appears as a white or slightly crystalline powder and has a cyclic structure composed of linked phosphate units. This dispersant and deflocculant agent is crucial to optimizing the quality of the material and is frequently used in industrial processes that require highly pure and uniform clays.

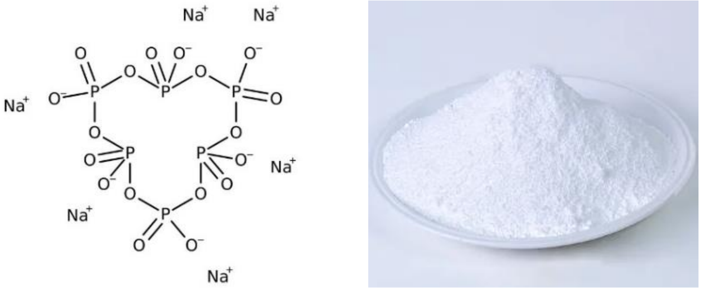


Figure 8. *Powder and structure of sodium hexametaphosphate [$Na_6(PO_3)_6$] (SHMP).*

Clay purification with SHMP is a process used to improve the properties of clays by removing impurities and dispersing fine clay particles. This process is used where pure and high-quality clay is required. This process usually has stages with determined times which are described below:

  - Preparation of HSMP solution. – 152.94 g of HSMP is mixed in 250 ml of distilled water and left to stir for 24 hours.

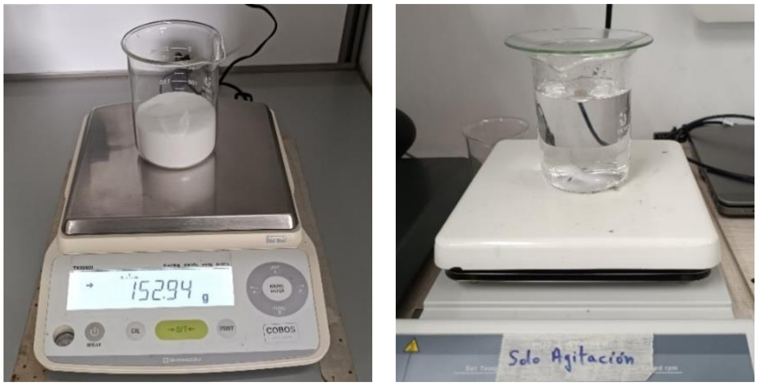


Figure 9. Preparation of HSMP.

- Preparation of clay. – After the washing and drying process, 400 gr of clay is mixed with 1.8 lt of distilled water in a 2 lt biker, in which it is mixed with a homogenizer or, in this case, a mixer that will perform the same function for 5 minutes to form a suspension or pulp.

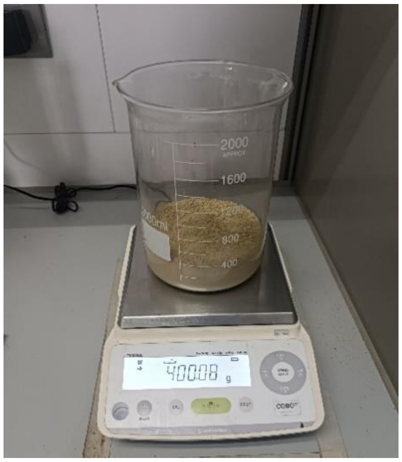


Figure 10. *Preparation of clay.*

It is then mixed with 23.5 ml of SHMP with stirring for 1 hour (60 minutes) and 12,700 RPM until a homogeneous solution is obtained and left to rest for 2 days in decanting vessels or graduated cylinders.

Figure 11. *Decantation of CZY-305 clay.*

After time has passed (2 days) it can be observed that the clay has separated into large particles and impurities such as (sand, unwanted minerals, and organic matter), the organic material and sediments are removed to leave only the purified material, which will be filtered, and after this the material will be placed in conical tubes (Falcón) to carry out the separation treatment by the centrifugation method at 10,000 RPM for a time of 30 minutes.

Figure 12. *Centrifugation of preprocessed clays.*

It goes through a drying process at room temperature for 3 days (72 hours) and will go on to perform new X-ray diffraction (XRD) tests and verify if the inert or filler material such as quartz has been removed.

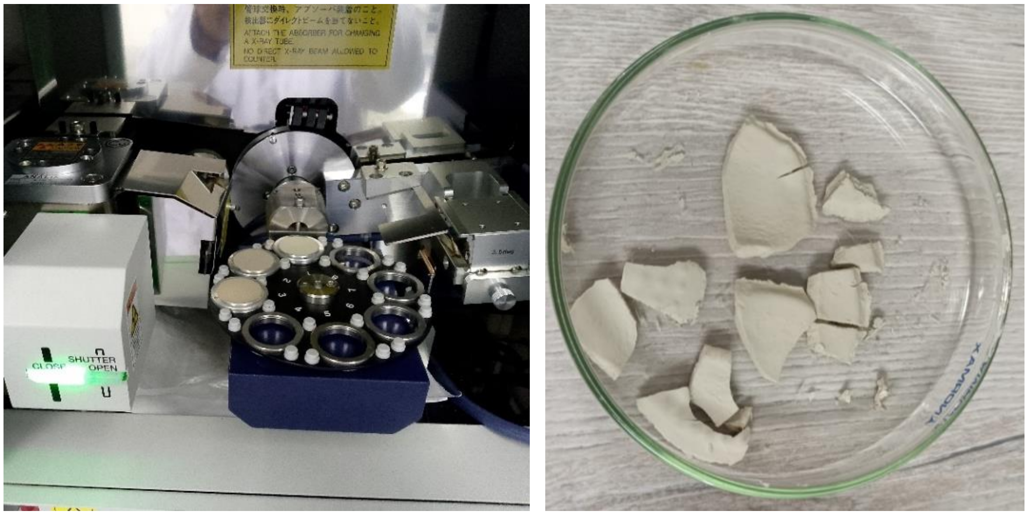


Figure 13*. Preparation of powder samples for XRD analysis*

- *Clay activation:* Clay activation for CO_2 adsorption is a process of physical, chemical or thermal modification of minerals (clays), intending to improve the adsorbent properties, increasing their capacity to capture CO_2 more efficiently. Due to their structure, natural clays do not have a very high adsorption capacity[65]. However, when activated or modified, these improved clays increase their performance. There are different methods to activate clays, each with a specific impact on their structural and chemical characteristics. Before carrying out any activation process, it is necessary to grind or crush the clay to reduce its particle size and increase its specific surface area to facilitate the entry of CO_2 molecules to the active sites[66].

    - Thermal activation (calcination). – involves the controlled heating process of the clay at high temperatures of 300 °C – 800 °C. The objective is to eliminate the interlayer water and modify its crystalline structure, which increases the specific surface and generates more active sites for adsorption, as well as improves the thermal stability of the clay, which is useful for high-temperature work.

    - Chemical activation – acids (acid activation) or bases (alkaline activation) are used to chemically modify the surface of the clay.

    - In acid activation, it is treated with strong solutions such as sulfuric acid or hydrochloric acid, removing impurities and increasing porosity.

    - While alkaline activation, treatment with bases can introduce new functional groups on the surface of the clay, which improves the chemical interaction with CO_2.

    - Ion exchange – the cations exchange between the clay's layers with other metal ions can modify its chemical affinity and adsorption capacity.

    - Modification with metal compounds – is a method of functionalizing the clay with organic molecules, such as amines or functional groups that interact strongly with CO_2. Amines have a high affinity for CO_2 because they can react with the gas to form stable compounds such as carbonates.

- Pillarization – This is a technique by which metallic species are introduced between the layers of clay with the aim of increasing both the porosity and the thermal stability of the material. These pillars, formed mainly by metallic oxides such as aluminium, zirconium or titanium, are inserted between the layers of clay, increasing the interlaminar space. This process results in a more stable structure, with rigid columns that generate an accessible and highly effective surface for adsorption processes. The procedure for carrying out the pillaring of the CZY-305 clay sample is described in detail below.

After purification, a clay pillaring process is carried out to improve its adsorption properties and increase its thermal and mechanical stability[65]. To carry out this procedure, the following steps were taken:

✓ Preparation of the pillaring solution – a 0.2 M $AlCl_3$ solution is prepared. The Al^{3+} ion is the pillaring agent that will be inserted between the clay layers. To stabilize this solution and control the hydrolysis of the aluminum, a NaOH solution is added drop by drop until reaching an appropriate molar ratio (generally Al^{-} between 1:1 and 1:2). This produces oligomeric aluminum species, which are the ones that will be inserted between the clay layers.

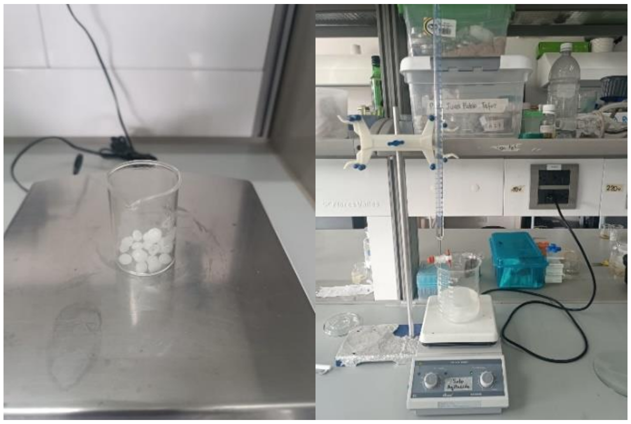


***Figure 14**. Pillaring solution preparation*

✓ Intercalation of the pillarized in the clay. - The clay is dispersed in distilled water to create an aqueous suspension. Then, the aluminum solution prepared in the previous step is added to the clay suspension slowly and under constant stirring. This step allows the aluminum species' intercalation between the clay layers. During this stage, the exchange cations in the clay (such as Na^+ or Ca^{2+}) are replaced by the aluminum complexes, expanding the interlayer distance.

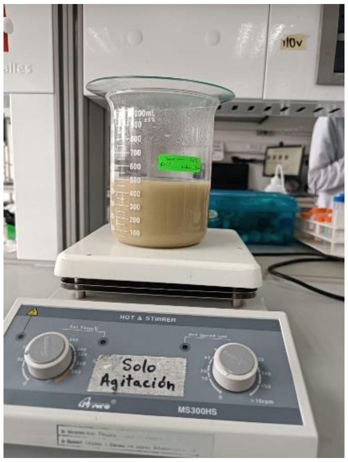


***Figure 15**. Pillarization of CZY-305 clay*

✓ Maturation and ageing. - After intercalation, the mixture is left to rest (usually between 12 and 24 hours) to allow the aluminium complexes to accommodate themselves between the clay layers fully. During this period, the aluminium pillars become organised and more firmly fixed in the laminar structure

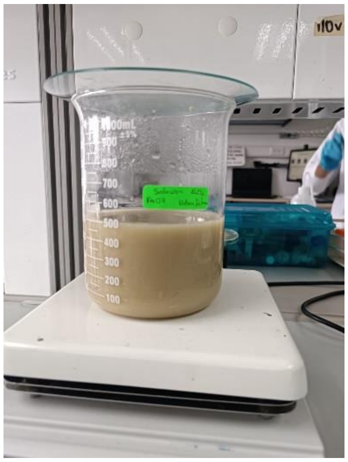


***Figure 16**. Maturation of CZY-305 clay*

- ✓ Washing and filtering. - The pillared clay is filtered to remove non-intercalated ions and any unwanted reagent residue. It is then washed several times with distilled water until the chloride residues are minimal, verifying the chloride content using the $AgNO_3$ test.

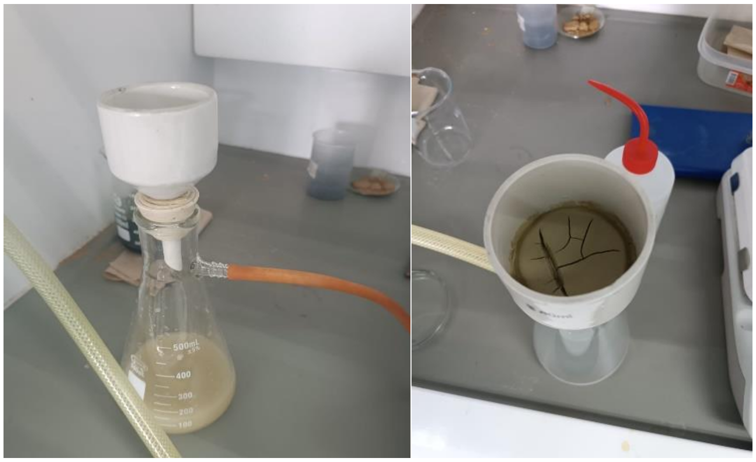


***Figure 17**. Washing and filtering of pillared CZY-305 clay*

- ✓ Drying and calcining - After filtering, the clay is dried in a low-temperature oven (approximately 100°C) to remove water. It is then calcined at temperatures between 300° C and 500°C. The purpose of calcining is to transform the aluminium complexes into aluminium oxides (Al_2O_3), which will act as rigid pillars between the clay layers, stabilising the structure.

***Figure 18**. Drying and calcining*

- ✓ After the pillarization process, a clay with a greater specific surface area, greater porosity and better thermal and mechanical resistance is obtained. This will make it more useful in the CO_2 adsorption process.
- ✓ With the pillarization treatment, a mineral from the mica group was obtained, which is widely used in CO_2 adsorption applications, due to its laminar structure, thermal stability and surface properties, which will serve to improve the CO_2 adsorption capacity.

Activation of clays is a key process to improve their CO_2 adsorption capacity, as it allows the structure to be modified, the specific surface area, porosity and chemical affinity with CO_2 to be increased. The choice of the activation method depends on the desired properties and the specific application, such as CO_2 capture in industrial processes or in climate change mitigation. In the present study, clay activation was carried out by calcination, pillarization, and modification using amines.

3.4 Commissioning of the test system

Before selecting the reactor for CO_2 capture, a process of installation and commissioning of the equipment, in this case, the reactors (stirred/non-stirred), is expected. This step is crucial to evaluate the adsorption process's performance, feasibility, and efficiency under different operating conditions.

These reactors are critical equipment for CO_2 capture processes, playing a fundamental role in the development and optimization of technologies that allow reducing carbon dioxide emissions. These systems, specifically designed to carry out CO_2 capture studies, are essential to address environmental challenges related to climate change.

The reactors for CO_2 capture will be installed in an area of the Chemistry laboratories, located in the E2-E3 Laboratory Building, upper floor (figure 20), Chemistry Laboratory 3, which will allow experimental tests and simulations of the capture processes at the laboratory level, to study and improve different techniques, such as chemical adsorption and solid adsorption.

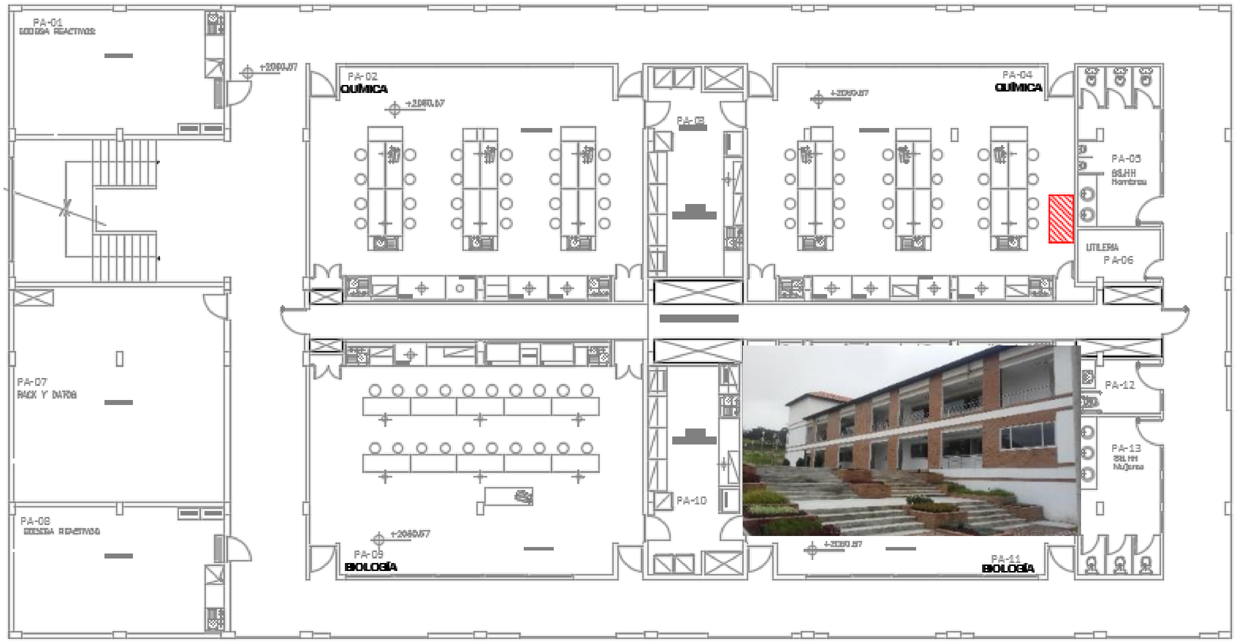


Figure 19. *E2-E3 laboratory*

A schematic diagram showed the components, accessories, and devices used, represented by letters to facilitate understanding of the system.

As can be seen in the figure; initially, there were pipes for only one piece of equipment, which was fed by a CO_2 cylinder that could be supplied with the feed gas for only one reactor.

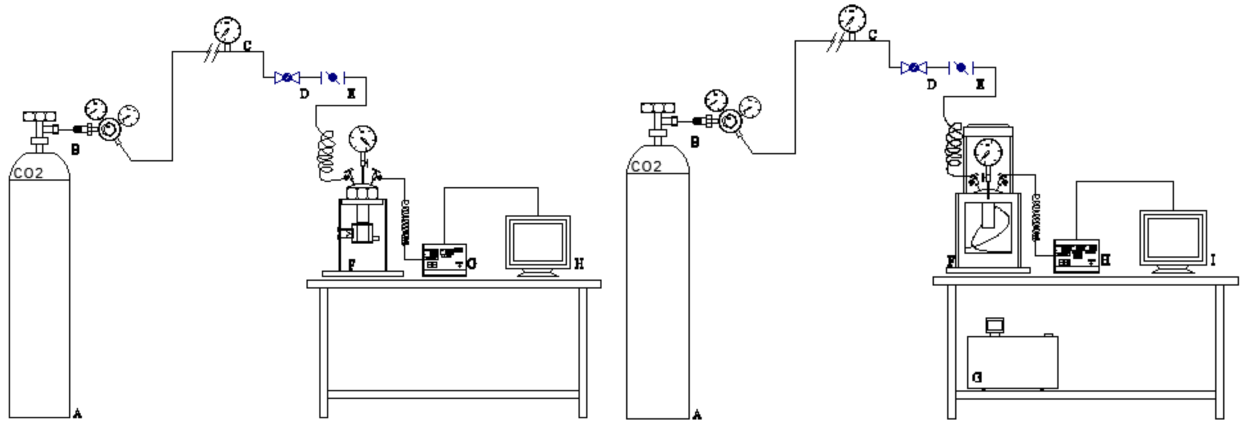


***Figure 20.**. Diagram test systems (A) Non-stirred reactor (B) Stirred reactor*

The assembly of the system for experimental CO_2 capture tests is composed of 4 reactors, 4 controllers, 4 valves, 1 pipe feeding system, 1 pressure regulator, two gas extraction hoods, 2 heat exchangers, 2 pressure relief and purge valves, 1 CO_2 cylinder and other accessories for its correct operation.

Figure 21.*. Test systems*

After having carried out pressure tests with the different reactors, the next thing to do is make a general diagram for the installation and start-up of the four reactors which will work simultaneously with valves and pipes for each equipment, as shown in the following diagram.

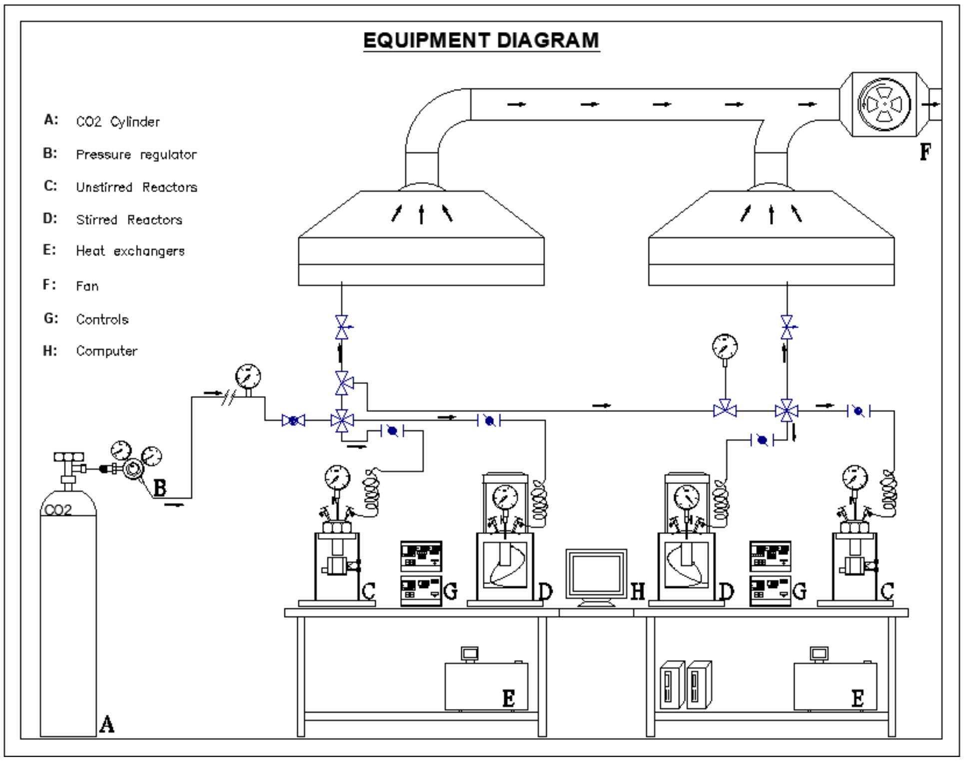


Figure 22.*. Test systems*

For the implementation, a design was made using AutoCAD software, which has an isometric model to detail how the facilities and equipment would be set up.

Figure 23. *Test systems modelated with AutoCad*

Once the assigned location (Chemistry laboratory in space E3) has been assigned, the materials and supplies acquired for the installation, assembly and start-up of the systems for experimental CO_2 capture tests, a detailed installation plan will be carried out. This plan includes the steps necessary to ensure an efficient and safe equipment installation, facilitating the subsequent development of the experimental tests. As described below.

Installation of anchors and supports. – its objective will be to provide a solid and safe structure for installing pipes and equipment for the CO_2 capture system. The actions will include placing and fixing anchors designed for 1/8" pipes in walls and ceilings, ensuring that they are correctly aligned and can support the system's weight, and complying with technical installation specifications.

Installation of a gas extraction system. – the objective of installing this system is to guarantee adequate ventilation and extraction of residual gases, especially CO_2 and H_2S, to maintain the safety of the laboratory. Among the necessary actions is manufacturing two galvanized gas extraction hoods measuring 1.20 m x 0.60 m. This system is connected to an extraction fan that will safely evacuate the gases to the outside of the building.

Manufacturing of a specialized piece of furniture for equipment support. – its objective is to manufacture a specialized piece of furniture that allows the placement and securing of the equipment involved in the CO_2 capture process. The actions will include designing and manufacturing a robust cabinet with chemical-resistant materials and laboratory conditions.

Assembly of the equipment for the CO_2 capture system. – The objective is to assemble the experimental test system using each piece of equipment, ensuring correct connection and operation. The actions will include: installing the reactors, controllers, and heat exchanger in the manufactured cabinet. Connecting the gas supply pipes from the power supply through the pressure regulator to the test system. Connecting the gas extraction. Performing tests to check for leaks. Performing the electrical installations from the laboratory power supply to the equipment. Connecting the measuring instruments and control systems for the equipment. Performing calibration tests ensures that equipment, sensors, and other system components operate accurately and efficiently.

After all the installations have been completed, the system will be put into operation, in which the first tests will be carried out to ensure that all the equipment works in the best operating conditions. The installation can be seen in the following image.

Figure 24. *Installed CO_2 adsorption Test systems*

After carrying out the first tests without load (without reagents), it was possible to verify that there were no problems with leaks, gas flow, pressure and ventilation problems. Then, tests were carried out with filler material (water) to evaluate the system's efficiency under different operating conditions, and the parameters were adjusted according to the results obtained to optimize the system.

After the installation and start-up of the system for capturing gases such as CO_2 and H_2S, which is fully integrated and ready to carry out experimental tests in the laboratory, we continue with the next phase, which is the selection of the material to be used.

3.5 Thermodynamic study

After defining the type of clay and completing its purification and chemical activation process, we are in the phase of carrying out the adsorption tests using the equipment available at Yachay University.

An adsorption reactor is a device used in chemical processes for the capture and elimination of gases or vapors such as CO_2, using adsorbent materials (clay material) which will be equipped with: gas feed pipes, heat exchangers to maintain temperatures, measurement devices for constant or variable experimental conditions.

Feeding system

The feeding system comprises pipes, valves, CO_2 bottles with pressure regulators and mass flow controllers to adjust the amount of CO_2 in the reactor.

Figure 25*. CO$_2$ Feeding system*

Jacketed stirred reactor

A Parr Series 5100 reactor (figure 18) will be used, with a capacity of 660 ml. This equipment is mainly used in the chemical, pharmaceutical, and biotechnology industries to carry out chemical reactions or processes that are crucial to controlling the temperature and the mixture of components.

Among its main features are the agitation, which contains a stirring system that will guarantee that the reagents are mixed uniformly, avoiding the formation of hot or cold spots, thus optimizing the efficiency of the reaction.

The reactor is surrounded by a jacket or external casing through which a fluid (water, coolant, steam or thermal oil) circulates. This allows the temperature inside the reactor to be controlled by cooling or heating the mixture as necessary for some processes.

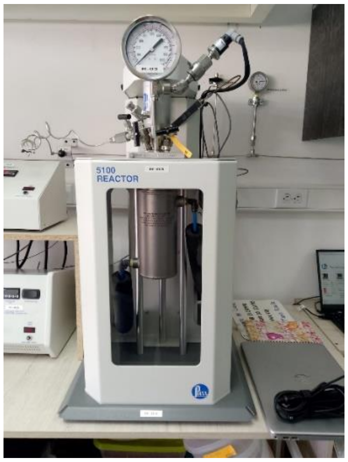


Figure 26*. Jacket stirred reactor*

Non-Stirred reactor

A Parr Series 4790 reactor (figure 12) pressure vessel system, made from a C-276 alloy, will be used. This equipment is used in the chemical industry and other sectors where mixing components during the reaction is unnecessary. Generally, this type of reactor is used in processes where the reagents can interact adequately without mechanical agitation, which may be more suitable for certain reactions such as experimental CO_2 capture tests.

Its features include temperature control, the simplicity of the design allows for improved processes since it does not have many moving parts, lower energy consumption.

Figure 27*. Non-stirred reactor*

Heating system (heat exchanger)

It is a system used to control the temperature during a chemical or mixing process, ensuring that the reaction occurs under optimal thermal conditions. It is integrated with the reactor and has the function of transferring heat between the reactor contents and a service fluid (water, steam, coolant, thermal oil), which circulates through pipes or a specific system that allows cooling (exothermic reaction) and heating (endothermic reaction) the reactor contents.

Figure 28*. Heat exchanger*

Measuring devices

These are all devices that allow pressure and temperature to be read. It is a key system that ensures the process conditions are optimal, stable and safe.

The temperature controller regulates the control within the reactor to ensure that the chemical reaction occurs under the right conditions. Precise temperature control is crucial since a deviation can affect the reaction rate or even cause product degradation.

The pressure controller regulates the internal pressure of the reactor, which is vital to avoid dangerous conditions and ensure the correct development of the reaction. Pressure control is significant in processes that involve gases or reactions that generate large volumes of steam or gases.

Figure 29*. Drivers*

All of this data will be collected using SpecView software, which is specialized software used to monitor, control, and record data in real-time in industrial processes, including those involving chemical reactors. Its main function is to provide a graphical interface and tools to manage the operation of different reactor equipment and systems.

Among the main uses:

Real-time monitoring. - SpecView allows you to view and monitor critical parameters of a reactor, such as temperature, pressure, level, pH, stirring speed, among others, in real time. This is crucial in industrial processes where precise control of these variables is critical to product safety and quality.

*Process contro*l. - Besides monitoring, SpecView can automatically control reactor parameters by adjusting equipment such as heating, cooling, pressure control valves, and pumps. Operators can set setpoints (desired values) for each parameter, and the software adjusts reactor systems based on sensor data.

Data logging and historical analysis. - The software stores historical records of reactor parameters, allowing performance to be analyzed over time, trends to be identified and improvements to be made to the process. This is also useful for audits, quality reporting, and investigating problems that have arisen during the process.

Alarms and notifications - SpecView can set up automatic alarms if any of the reactor parameters exceed predefined limits. This is especially important to prevent dangerous situations, such as excessive pressure or temperature increases that could damage equipment or compromise personnel safety.

User-friendly and customisable interface - One of the advantages of SpecView is its customisable graphical interface, which makes it easy for operators to see the status of a reactor at a glance. Specific graphs, tables or diagrams can be created for each reactor type, simplifying monitoring of the entire system.

Integration with other systems - SpecView can be integrated with other industrial automation and control systems (such as PLCs and SCADA), allowing the software to manage the reactor and the entire production process. This is essential in plants where reactors are interconnected with other equipment and processes.

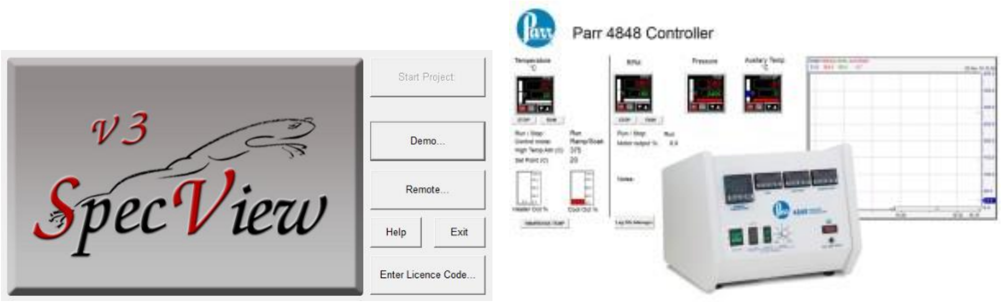


Figure 30. *SpecView System*

3.6 Experimental setups

Experimental setups for CO_2 capture in high-pressure reactors are fundamental in developing carbon capture and storage (CCS) technologies. There are various configurations, depending on the capture technique, the type of reactors, the absorbent or adsorbent materials, and the specific experimental conditions.

Additionally, there are several factors that significantly influence the CO_2 adsorption process. These factors determine both the efficiency and the ability of the adsorbent materials to capture carbon dioxide under different operating conditions. Some of the main factors that affect this process are described below [13].

Temperature. - It is one of the most critical factors affecting CO_2 adsorption. In general, physical adsorption or physisorption is more effective at low temperatures, as the Van der Waals forces, which hold CO_2 molecules on the surface of the adsorbent, decrease when the temperature increases. This means that at higher temperatures, CO_2 tends to desorb from the surface of the material [67]. On the other hand, in the case of chemical adsorption or chemisorption, increasing the temperature can favor the formation of stronger chemical bonds between CO_2 and the active sites of the adsorbent. However, temperatures that are too high could degrade or deactivate some adsorbents, which would decrease their capture capacity. Therefore, it is essential to find an optimal temperature balance depending on the type of adsorbent used.

Pressure. - The adsorption process is a determining factor. At higher pressures, the amount of CO_2 available in the gas phase to be adsorbed by the material increases. In general, an increase in pressure favors physical adsorption, since more CO_2 molecules interact with the surface of the adsorbent. However, the effect of pressure varies depending on the type of isotherm that describes the behavior of the system (Langmuir, Freundlich, among others). Some adsorbents can quickly saturate at low pressures, while others continue to increase their adsorption capacity as the pressure increases. It is essential, then, to adjust the pressure conditions based on the type of material and the needs of the industrial process [68].

Nature of the adsorbent. - The physical and chemical characteristics of the adsorbent play a key role in the efficiency of CO_2 adsorption. Factors such as porosity, specific surface area and the presence of active sites on the surface determine how much CO_2 can be captured [69].

Humidity. - The presence of water vapor in the gas to be processed is a factor that can complicate the adsorption of CO_2. Many adsorbents, such as zeolites, are highly sensitive to water and can adsorb H_2O instead of CO_2, which reduces their ability to capture carbon dioxide. On the other hand, some materials such as activated carbons can tolerate humidity better, although their adsorption capacity can also be affected [70]. This is why in industrial applications it is common to dehumidify gases before subjecting them to adsorption processes to avoid competition between water and CO_2 molecules at the active sites of the adsorbent [71].

Contact time and flow rate. - The contact time between the CO_2-containing gas and the adsorbent is also an important factor. Longer contact time allows more CO_2 molecules to interact with the active sites on the adsorbent, improving process efficiency. If the gas flow is too fast, there may not be enough time for the CO_2 molecules to be effectively adsorbed. Therefore, controlling the gas flow rate to maximize CO_2 adsorption is essential, maintaining a proper balance between contact time and system operating efficiency.

The tests were carried out in the experimental systems with and without agitation between 25 °C and 30 °C at 500 psi. For the experimental setup, clays that were in stock at the School of Chemical Science and Engineering were used, such as CZY-305 clay, and commercial bentonite in which 5 gr - 30 gr were loaded depending on the quantities in the different states (raw, purified and activated clays) that have been deposited in the reactor vessels. After having sealed everything hermetically, the gas inlet connections and controller signals are made. The temperature is stabilized at 25 °C – 30 °C, and once this temperature is reached, the system is pressurized to 500 PSI. These tests will last approximately 12 hours to record the data and for the reaction to reach equilibrium.

Initially, tests were carried out with water to validate the experimental configuration of the CO_2 capture systems. After making the correct configurations, tests were started with the different clays.

Data processing

In this phase, all the data recorded from each CO_2 capture test is processed using the Specview software. This provides us with pressure, temperature, agitation and time. With all these results, the Peng-Robinson state equation will be used, where the compression factor (Z) is determined and allows the gas to be calculated in moles (mol) within the system, using the ideal gas equation adjusted for real gases

$$PV = nZRT$$

The determination of CO_2 in clays is carried out using experimental and analytical methods that allow quantifying the amount of CO_2 retained on the material's surface (clay) under pressure and temperature conditions. Among the most common methods are gravimetric, volumetric, and calorimetric, the volumetric method has been selected.

The volumetric method is based on measuring the changes in gas volume before and after the adsorption process using the ideal gas equation.

$$n\ adsorbed = \frac{(P1 - P2) * V}{R * T}$$

where:

P1: initial pressure of the system

P2: final pressure of the system (after the process)

V: volume of the system

R: ideal gas constant

T: temperature in Kelvin

Consequently, with these values, the adsorption isotherms will be made, which are the quantity of CO_2 adsorbed under different pressure and temperature conditions, these show the relationship between the adsorbed quantity and the pressure at constant temperature.

CHAPTER 4

Results and Discussion

In this chapter, the results obtained at each stage of the clay preparation process, including cleaning, purification, calcination and pillarization, will be evaluated in detail. Subsequently, the data generated from CO_2 adsorption tests performed in high-pressure reactors will be analyzed. These analyses will provide crucial information on the efficiency and CO_2 capture capacity of the different clay samples prepared, as well as on the impact of operating conditions on process performance. The results will allow identifying the most promising materials and the optimal conditions to maximize the effectiveness of the adsorption process.

4.1 Results of clay treatment

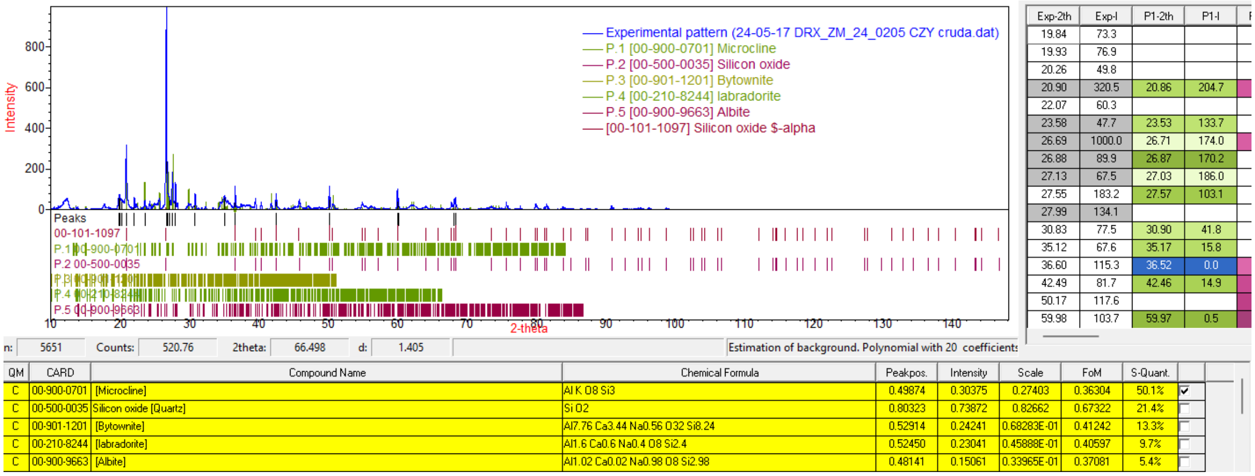
Initially, the clays that were available in the laboratory were chosen. However, cleaning and treatment with sodium hexametaphosphate were carried out to improve their properties and purify them for the CO_2 capture process. Characterization tests were carried out on the DRX equipment before and after the purification treatment.

Table 5. *Results of analysis performed on raw clays using X-ray diffraction*

Sample	Location	Mineral Phases
CZY-305	Zamora Chinchipe	Quartz (20,0%), kaolinite (22,0%), Antigorite (19,0%), Microcline (29,6%)
CZY-306	Zamora Chinchipe	Quartz (9,0%), kaolinite (63,4%), Muscovite (10,3%), Nacrite (17,3%)
COL-308	Morona Santiago	Quartz (39,1%), kaolinite (57,6%), Dickite (3,4%)

The CZY-305 clay was chosen, since it was the most abundant in the study and after carrying out several characterization tests, the following results were shown:

X-ray diffraction (XRD) analysis of the CZY-305 clay sample identifies the mineralogical composition based on the peaks of the experimental pattern compared to the crystallographic databases as indicated in the following figure.



Exp-2th	Exp-I	P1-2th	P1-I
19.84	73.3		
19.93	76.9		
20.26	49.8		
20.90	320.5	20.86	204.7
22.07	60.3		
23.58	47.7	23.53	133.7
26.69	1000.0	26.71	174.0
26.88	89.9	26.87	170.2
27.13	67.5	27.03	186.0
27.55	183.2	27.57	103.1
27.99	134.1		
30.83	77.5	30.90	41.8
35.12	67.6	35.17	15.8
36.60	115.3	36.52	0.0
42.49	81.7	42.46	14.9
50.17	117.6		
59.98	103.7	59.97	0.5

n: 5651 Counts: 520.76 2theta: 66.498 d: 1.405 Estimation of background. Polynomial with 20 coefficients

QM	CARD	Compound Name	Chemical Formula	Peakpos.	Intensity	Scale	FoM	S-Quant.	
C	00-900-0701	[Microcline]	Al K O8 Si3	0.49874	0.30375	0.27403	0.36304	50.1%	☑
C	00-500-0035	Silicon oxide [Quartz]	Si O2	0.80323	0.73872	0.82662	0.67322	21.4%	☐
C	00-901-1201	[Bytownite]	Al7.76 Ca3.44 Na0.56 O32 Si8.24	0.52914	0.24241	0.68283E-01	0.41242	13.3%	☐
C	00-210-8244	[labradorite]	Al1.6 Ca0.6 Na0.4 O8 Si2.4	0.52450	0.23041	0.45888E-01	0.40597	9.7%	☐
C	00-900-9663	[Albite]	Al1.02 Ca0.02 Na0.98 O8 Si2.98	0.48141	0.15061	0.33965E-01	0.37081	5.4%	☐

Figure 31. *X-ray diffraction pattern of raw clay CZY-305*

Where: Experimental pattern (blue line): Represents the experimental spectrum obtained from the raw CZY clay sample. On the X axis is the diffraction angle (2θ) and on the Y axis, the intensity of the diffracted X-rays.

Reference patterns (colored lines below the spectrum): These lines correspond to the reference crystallographic patterns for different minerals, facilitating the identification of the compounds present in the sample.

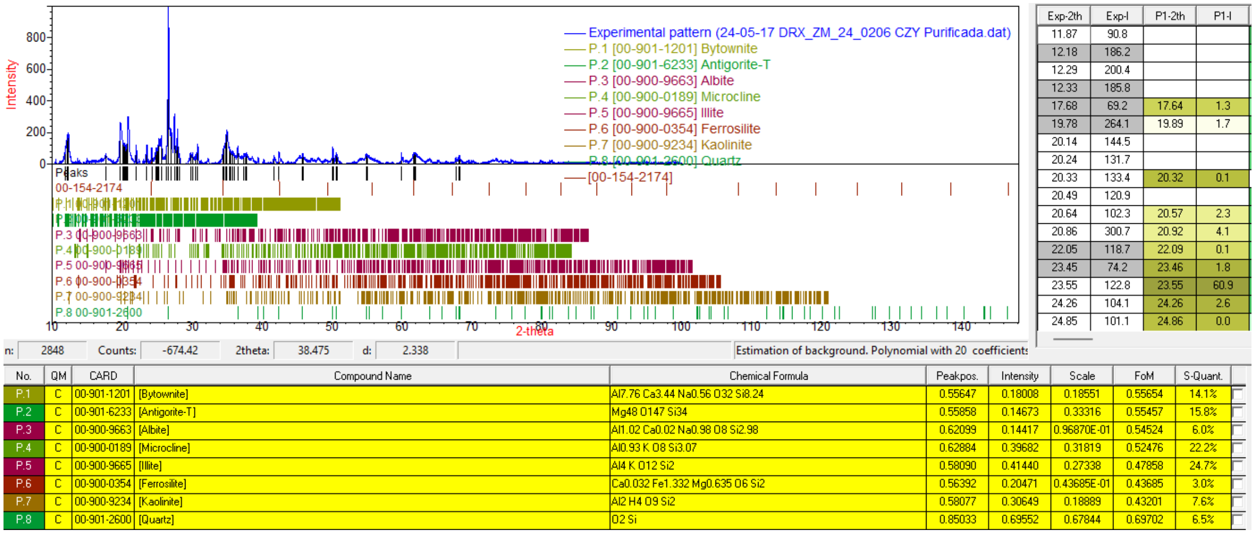
- Microcline (green): Peaks marked with P_1.
- Quartz (yellow): Peaks marked with P_2.
- Bytownite (pink): Peaks marked with P_3.
- Labradorite (purple): Peaks marked with P_4.
- Albite (red): Peaks marked with P_5.

The list of identified minerals, chemical formulas and parameters related to the analysis, such as the intensity of the peaks, is also shown, and the most important ones in percentage of occupation are placed in the following table.

Table 6. *Chemical composition of raw clay CZY-305*

Sample	Chemical Formula	S-Quant
Microcline	$AlKO_8Si_3$	50,1 %
Quartz:	SiO_2	21.4 %
Bytonite:	$Al_{7.76}$ $Ca_{3.44}$ $Na_{0.56}$ O_{32} $Si_{8.24}$	13.3%
Labradorite	$Al_{1.6}$ $Ca_{0.6}$ $Na_{0.4}$ O_8 $Si_{2.4}$	9.7 %
Albite	$Al_{1.02}$ $Ca_{0.02}$ $Na_{0.98}$ O_8 $Si_{2.98}$	5.4 %

After the washing, sieving and purification process, the following results were obtained, in which the appearance of new phases and the elimination of heavy materials, such as quartz, can be seen in the following figure:



Exp-2th	Exp-I	P1-2th	P1-I
11.87	90.8		
12.18	186.2		
12.29	200.4		
12.33	185.8		
17.68	69.2	17.64	1.3
19.78	264.1	19.89	1.7
20.14	144.5		
20.24	131.7		
20.33	133.4	20.32	0.1
20.49	120.9		
20.64	102.3	20.57	2.3
20.86	300.7	20.92	4.1
22.05	118.7	22.09	0.1
23.45	74.2	23.46	1.8
23.55	122.8	23.55	60.9
24.26	104.1	24.26	2.6
24.85	101.1	24.86	0.0

n: 2848 Counts: -674.42 2theta: 38.475 d: 2.338

Estimation of background. Polynomial with 20 coefficients

No.	QM	CARD	Compound Name	Chemical Formula	Peakpos.	Intensity	Scale	FoM	S-Quant.	
P.1	C	00-901-1201	[Bytownite]	Al7.76 Ca3.44 Na0.56 O32 Si8.24	0.55647	0.18008	0.18551	0.55654	14.1%	☐
P.2	C	00-901-6233	[Antigorite-T]	Mg48 O147 Si34	0.55858	0.14673	0.33316	0.55457	15.8%	☐
P.3	C	00-900-9663	[Albite]	Al1.02 Ca0.02 Na0.98 O8 Si2.98	0.62099	0.14417	0.96870E-01	0.54524	6.0%	☐
P.4	C	00-900-0189	[Microcline]	Al0.93 K O8 Si3.07	0.62884	0.39682	0.31819	0.52476	22.2%	☐
P.5	C	00-900-9665	[Illite]	Al4 K O12 Si2	0.58090	0.41440	0.27338	0.47858	24.7%	☐
P.6	C	00-900-0354	[Ferrosilite]	Ca0.032 Fe1.332 Mg0.635 O6 Si2	0.56392	0.20471	0.43685E-01	0.43685	3.0%	☐
P.7	C	00-900-9234	[Kaolinite]	Al2 H4 O9 Si2	0.58077	0.30649	0.18889	0.43201	7.6%	☐
P.8	C	00-901-2600	[Quartz]	O2 Si	0.85033	0.69552	0.67844	0.69702	6.5%	☐

Figure 32. *X-ray diffraction pattern of purified CZY-305 clay*

The figure 32, presents an X-ray diffraction (XRD) analysis of the Purified CZY-305 sample, showing the experimental spectrum compared to reference crystallographic patterns to identify the minerals present after purification. This analysis is used to determine the mineralogical composition and evaluate how it changed from the original sample.

Reference patterns (colored lines below the spectrum): These lines correspond to the reference crystallographic patterns for different minerals, facilitating the identification of the compounds present in the sample

They correspond to the crystallographic patterns of different minerals, helping to identify the phases present.

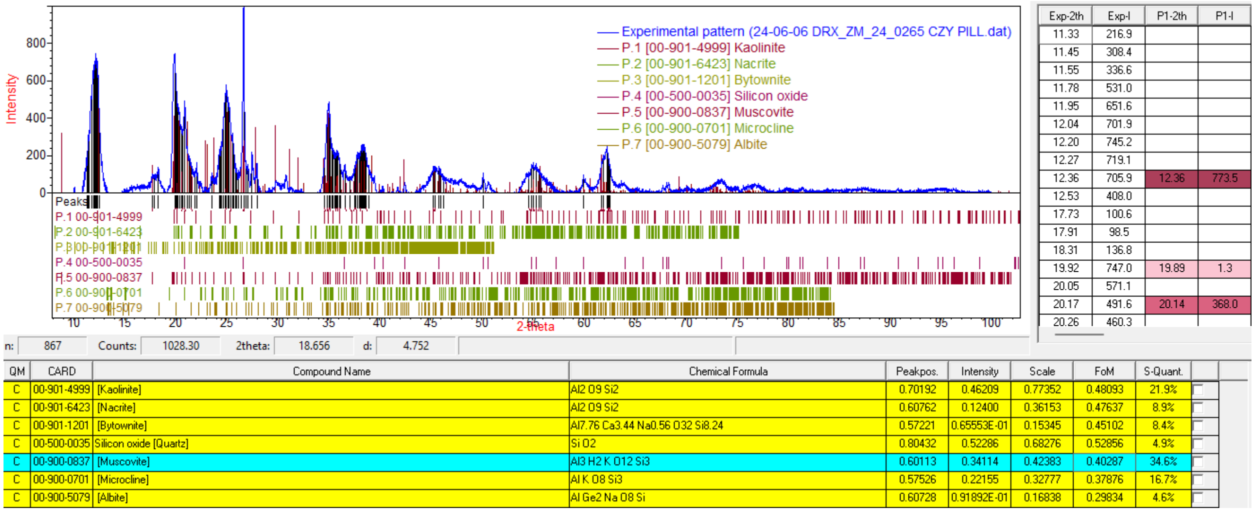
- Bytownite (green): Peaks marked as P_1.
- Antigorite-T (orange): P_2.
- Albite (yellow): P_3.
- Quartz (pink): P_8.

The list of identified minerals, chemical formulas and parameters related to the analysis, such as the intensity of the peaks, is shown. The most important ones are placed in the following table in terms of percentage of occupation, where it can be verified that there is a large amount of purification since the percentage of quartz is very low in relation to the raw clay CZY-305.

Table 7. *Chemical composition of purified clay*

Sample	Chemical Formula	S-Quant
Microcline	$Al_{0.93}\,K\,O_8\,Si_{3.07}$	22.2 %
Illite	$Al_4\,K\,O_{12}\,Si_2$	24.7 %
Antigorite T	$Mg_{48}\,O_{147}\,Si_{34}$	15.8 %
Bytownite	$Al_{7.76}\,Ca_{3.44}\,Na_{0.56}\,O_{32}\,Si_{8.24}$	14.1 %
Kaolinite	$Al_2\,H_4\,O_9\,Si_2$	7.6 %
Albite	$Al_{1.02}\,Ca_{0.02}\,Na_{0.98}\,O_8\,Si_{2.98}$	6 %
Quartz	$O_2\,Si$	6.5 %
Ferrosilite	$Ca_{0.032}\,Fe_{1.332}\,Mg_{0.635}\,O_6\,Si_2$	3.0 %

After having carried out the procedures to clean, sift and purify the CZY-305 clay, the pillaring of the same was carried out, which was carried out in accordance with the guidelines established in the methodology, giving us the following figure as a result.



Exp-2th	Exp-I	P1-2th	P1-I
11.33	216.9		
11.45	308.4		
11.55	336.6		
11.78	531.0		
11.95	651.6		
12.04	701.9		
12.20	745.2		
12.27	719.1		
12.36	705.9	12.36	773.5
12.53	408.0		
17.73	100.6		
17.91	98.5		
18.31	136.8		
19.92	747.0	19.89	1.3
20.05	571.1		
20.17	491.6	20.14	368.0
20.26	460.3		

n: 867 Counts: 1028.30 2theta: 18.656 d: 4.752

QM	CARD	Compound Name	Chemical Formula	Peakpos.	Intensity	Scale	FoM	S-Quant.	
C	00-901-4999	[Kaolinite]	Al2 O9 Si2	0.70192	0.46209	0.77352	0.48093	21.9%	☐
C	00-901-6423	[Nacrite]	Al2 O9 Si2	0.60762	0.12400	0.36153	0.47637	8.9%	☐
C	00-901-1201	[Bytownite]	Al7.76 Ca3.44 Na0.56 O32 Si8.24	0.57221	0.65553E-01	0.15345	0.45102	8.4%	☐
C	00-500-0035	Silicon oxide [Quartz]	Si O2	0.80432	0.52286	0.68276	0.52856	4.9%	☐
C	00-900-0837	[Muscovite]	Al3 H2 K O12 Si3	0.60113	0.34114	0.42383	0.40287	34.6%	☐
C	00-900-0701	[Microcline]	Al K O8 Si3	0.57526	0.22155	0.32777	0.37876	16.7%	☐
C	00-900-5079	[Albite]	Al Ge2 Na O8 Si	0.60728	0.91892E-01	0.16838	0.29834	4.6%	☐

***Figure 29**. X-ray diffraction pattern of pillarized CZY-305 clay*

This image corresponds to the X-ray diffraction (XRD) analysis of a sample of pillared clay (CZY PIL), which allows to identify the minerals present after the pillaring process and to evaluate the structural changes that this treatment has generated.

Main elements of the graph:

Experimental pattern (blue line): Represents the spectrum obtained after the XRD analysis, where the X axis shows the diffraction angle (2θ) and the Y axis, the intensity of the diffracted X-rays.

Reference patterns (colored lines below): The colors indicate the minerals identified by comparing the experimental peaks with reference crystallographic patterns.

- Kaolinite (green): Peaks marked as P_1.
- Nacrite (orange): P_2.
- Quartz (yellow): P_4.
- Muscovite (light blue): P_6.

***Table 8**. Composition of materials*

Sample	Chemical Formula	S-Quant
Microcline	$Al\ K\ O_8\ Si_3$	18.3 %
Muscovite	$Al_3\ H_2\ K\ O_{12}\ Si3$	37.9 %
Bytownite	$Al_{7.76}\ Ca_{3.44}\ Na_{0.56}\ O_{32}\ Si_{8.24}$	9.2 %
Kaolinite	$Al_2\ O_9\ Si_2$	24.1 %
Albite	$A_{l1.02}\ Ca_{0.02}\ Na_{0.98}\ O_8\ Si_{2.98}$	5 %
Quartz	$O_2\ Si$	5.4 %

The analysis shows that the pillared clay retains a significant proportion of minerals such as kaolinite and bytownite, which are essential for their high adsorption capacity. A significant content of microcline is also observed, which could provide structural stability to the material. There is also a reduction in quartz, compared to untreated samples (such as raw or purified ones), the quartz content is reduced, which is desirable, since quartz has less utility in adsorption applications due to its limited reactivity.

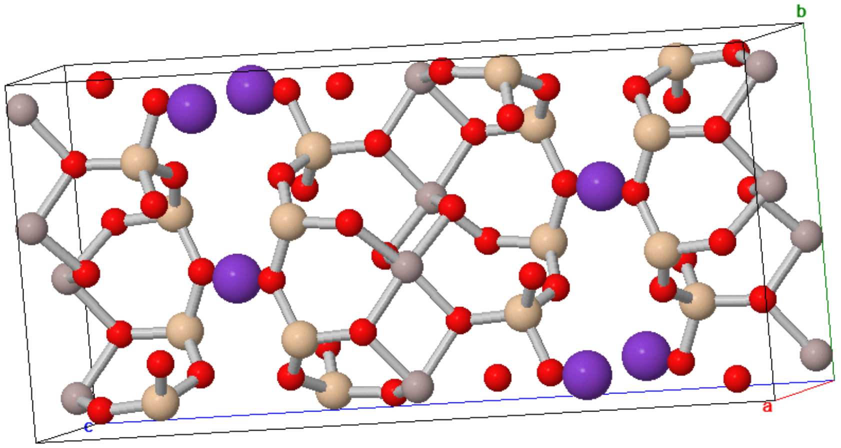


***Figure 33**. Structure of muscovite*

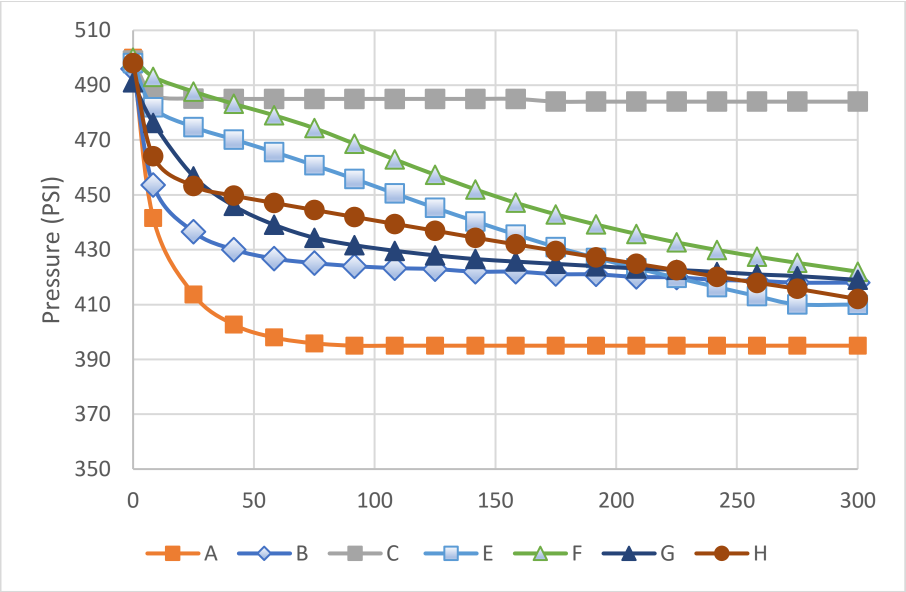
The presence of these minerals muscovite and albite, although in smaller quantities, can contribute to the porosity and thermal stability of the material.

Implications for adsorption: The increase in minerals such as kaolinite and bytownite, together with the reduction of impurities such as quartz, indicates that pillarization has improved the material's capacity for CO_2 capture applications by increasing porosity and surface accessibility. This analysis confirms that the pillarization process has optimized the properties of CZY-305 clay for use as an adsorbent, improving the proportion of active phases and reducing less useful phases.

4.2 Thermodynamic and kinetic analysis

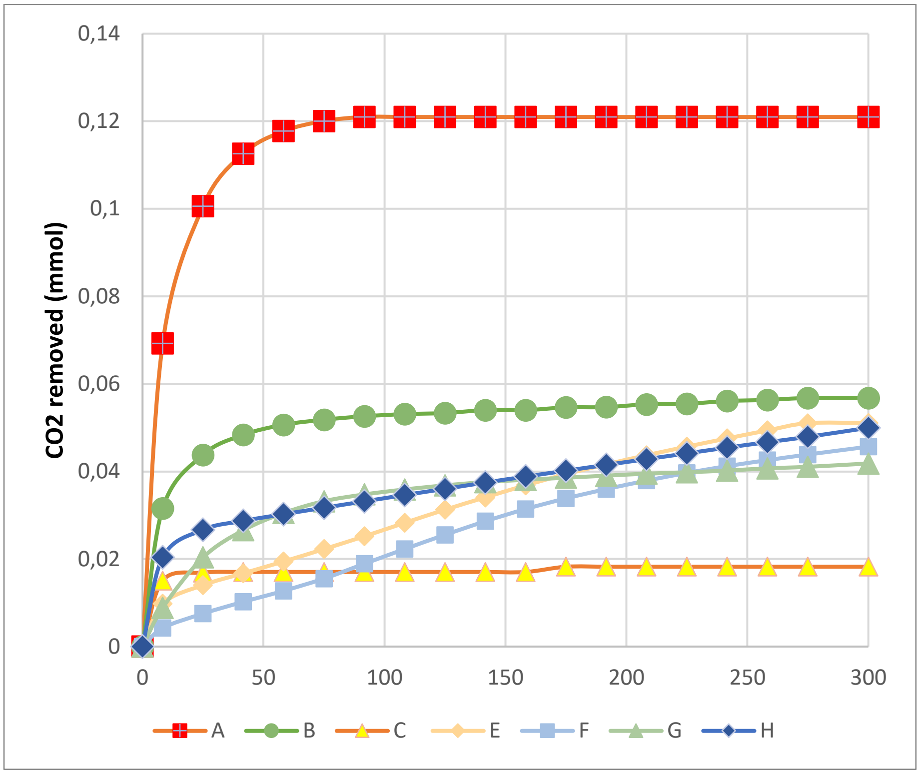
Tests were performed at temperatures of 25 °C – 30 °C on CZY-305, CZY-306 and Bentonite clays, with a pressure of 500 PSI supplied with CO_2 in the stirred and non-stirred reactor, which yielded the following results as shown below.

Non-stirred reactor



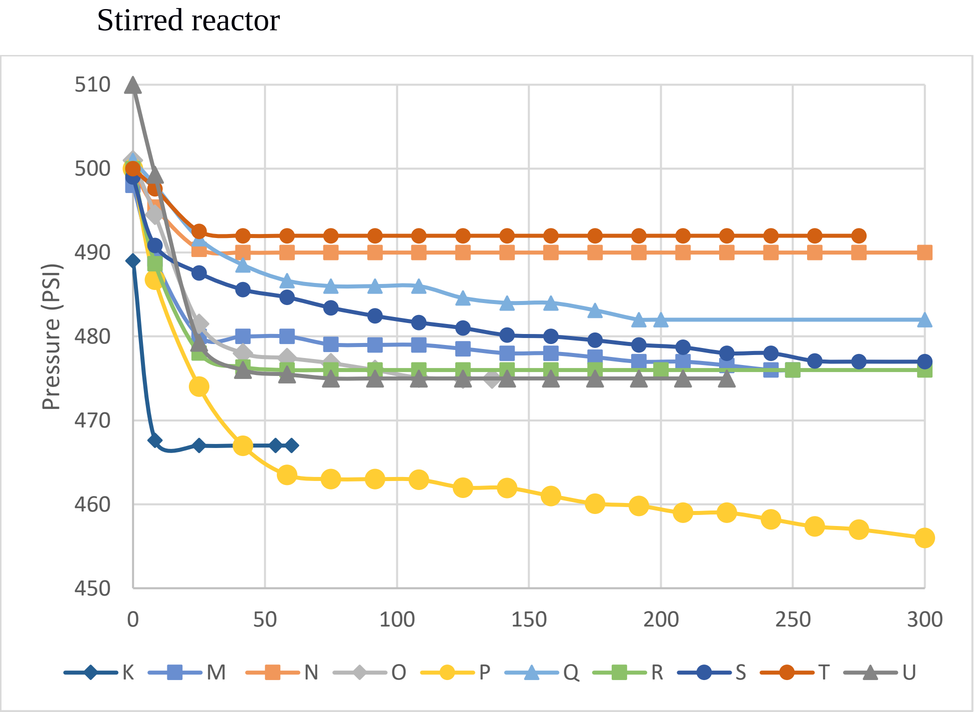
A: *H2O purified*
B: *CZY-305 + H_2O*
C: *CZY-305 + H_2O potable*
E: *CZY-305 + H_2O purified*
F: *COL-308 + H2O potable*
G: *COL-308 + H2O purified*
H: *CZY-305 + DETA*

Figure 34. *Gas phase pressure in clays in a stirred reactor*



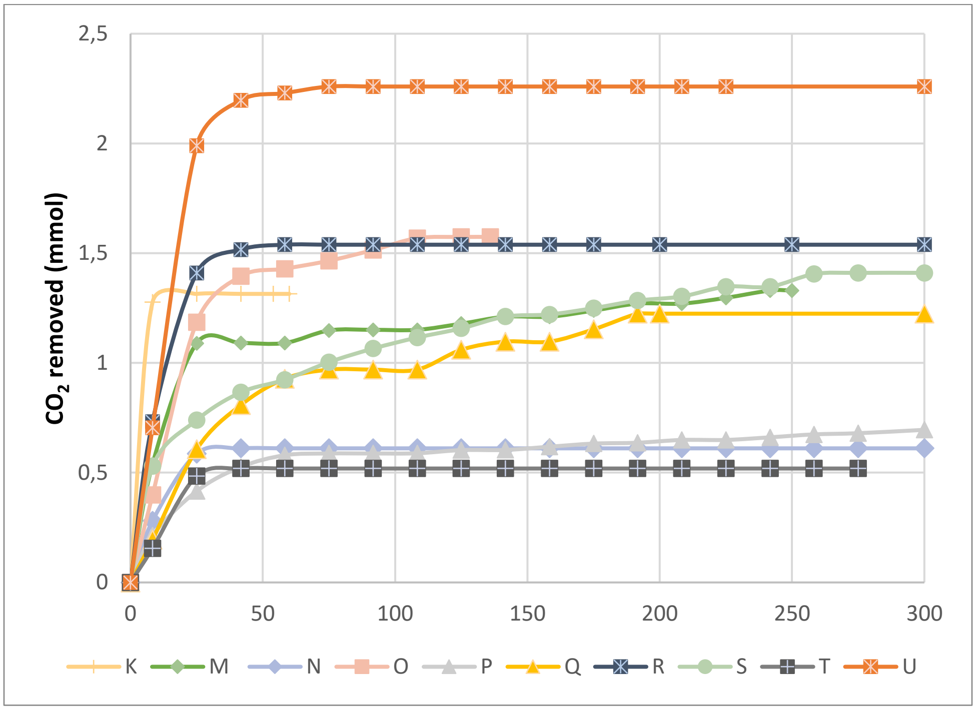
A: *H2O purified*
B: *CZY-305 + H_2O*
C: *CZY-305 + H_2O potable*
E: *CZY-305 + H_2O purified*
F: *COL-308 + H2O potable*
G: *COL-308 + H2O purified*
H: *CZY-305 + DETA*

Figure 35*. CO_2 removed versus time in a stirred reactor*



K: *Bentonite*
M: *Muscovite*
N: *Raw Muscovite*
O: *CZY-306*
P: *COL-308 + H2O (potable)*
Q: *COL-308 + H2O (purified)*
R: *CZY-305 + DETA*
S: *CZY-306 purified*
T: *Pillarized mica*
U: *Calcined pillarized mica*

Figure 36*. Gas phase pressure in clays in a non-stirred reactor*



K: *Bentonite*
M: *Muscovite*
N: *Raw Muscovite*
O: *CZY-306*
P: *COL-308 + H2O (potable)*
Q: *COL-308 + H2O (purified)*
R: *CZY-305 + DETA*
S: *CZY-306 purified*
T: *Pillarized mica*
U: *Calcined pillarized mica*

Figure 37. *CO_2 removed versus time in a non-stirred reactor*

The results indicate that the reaction rate during the first 100 minutes is the most optimal for the process. However, in this study data has been recorded up to 300 minutes in order to check the stability of the values in each of the tests carried out.

Below is a table that compiles the data from reviewed articles that have been obtained in the tests carried out with different types of clays, allowing a detailed comparison of their behavior.

Table 9. CO_2 adsorption capacity of raw clay minerals

Clay mineral	**CO_2 Adsorption capacity (mg CO_2/g) - (mmol CO_2/g)**	**Adsorption conditions**	**Ref**
Kaolinite	3 – 0.06	25 °C, 1 bar	[72]
Kaolinite	0 - 0	25 °C, 1 bar	[73]
Bentonite	6 – 0.13	25 °C, 1 bar	[74]
Bentonite	5 – 0.11	25 °C, 1 bar	[75]
Bentonite	14 – 0.32	25 °C, 1 bar	[40]
Montmorillonite	10 – 0.28	45 °C, 1 bar	[40]
Montmorillonite	7 – 0.16	25 °C, 1 bar	[76]

Montmorillonite	22 – 0.50	10 °C, 1 bar, 90'	[77]
Saponite	15 – 0.34	45 °C, 1 bar	[40]
Sepiolite	41 - 0.93	45 °C, 1 bar	[40]
Sepiolite	65 – 1.48	25 °C, 1 bar	[78]
Sepiolite	137 – 3.11	25 °C, 120 bar	[79]
Palygorskite	12 – 0.27	45 °C, 1 bar	[40]
Palygorskite	18 – 0.41	25 °C, 1 bar	[78]

With the results obtained, a comparison is made with the reviewed bibliography.

The results of the adsorption tests were obtained with the reactor with clay agitation without water treatment and with a mass of approximately 500 gr.

Table 10*. CO_2 adsorption capacity of raw clay minerals with H_2O*

TAG	Material	CO_2 Adsorption capacity (mmol CO_2/g)	Adsorption conditions
A	H_2O D	0.12	30 °C, 500 PSI
B	CZY-305+ H2O D	0.05	30 °C, 500 PSI
C	CZY-305+H2O P	0.02	30 °C, 500 PSI
E	CZY-305 + H2O D	0.05	30 °C, 500 PSI
F	COL-308+H2O P	0.04	30 °C, 500 PSI
G	COL-308+H2O D	0.04	30 °C, 500 PSI
H	CZY-305+DETA40%	0.05	30 °C, 500 PSI

Results of adsorption tests with the reactor without agitation and untreated clays.

Table 11*. CO_2 adsorption capacity of raw clay*

TAG	Material	CO_2 Adsorption capacity (mmol CO_2/g)	Adsorption conditions
K	Bentonite	1.31	30 °C, 500 PSI
M	Muscovite	1.33	30 °C, 500 PSI
N	Muscovite	0.61	30 °C, 500 PSI
P	CZY-305 R	0.69	25 °C, 500 PSI
Q	CZY-305 R	1.22	25 °C, 500 PSI

Results of adsorption tests with the reactor without agitation and clays with purification treatment and pillared with a mass of approximately 5 gr. CO_2 adsorption capacity of raw clay minerals.

Table 12. *CO_2 adsorption capacity of purified clay*

TAG	**Material**	**CO_2 Adsorption capacity (mmol CO_2/g)**	**Adsorption conditions**
R	Mica Pill	1.53	25 °C, 500 PSI
S	Mica Pill	1.41	25 °C, 500 PSI
T	Mica Pill	0.51	25 °C, 500 PSI
U	Mica Pill	2,25	25 °C, 500 PSI

The results obtained from the different clay samples show that by carrying out the previous treatment such as cleaning, purification, calcination and pillaring, the adsorption properties are significantly improved and it can be compared that it is within the established limits of the references cited in this document.

Ddeducing that muscovite and bentonite are materials suitable for good adsorption of CO_2 with (1.3 and 1.33) mmol CO_2/g respectively, in the same way when pillaring they become micas with a high adsorption capacity of (1.31) mmol CO_2/g since by improving their pores they have a greater adherence of CO_2

Influence of temperature and pressure

CO_2 adsorption in clays will be more efficient at low temperatures, while adsorption capacity decreases at high temperatures. Pressure positively influences adsorption, but the relationship between pressure and capacity is more marked in expansive clays such as montmorillonite.

CO_2 adsorption capacity

The results show that pillared CZY-305 clay has the highest CO_2 adsorption capacity compared to previously purified muscovite and bentonite. It is observed that clay is more efficient at low pressures, while kaolinite is more stable at low temperatures

Chapter 5

Conclusions and Recommendations

- Experimental tests were carried out to capture CO_2 in the installed equipment, demonstrating that they can work under different operating conditions for different tests and samples, so in this study the temperature range was 25-30 °C and a pressure of 500 PSI of carbon dioxide.

- The study focused on selecting the clays available from the School of Chemistry to carry out CO_2 adsorption tests, which were taken from the INEDITA Project called "Clays of Ecuador" in which the CZY-305, CZY-306, COl-308 clays were considered in their natural state without any type of activation.

- A cleaning, screening, calcining and purification process of the czy-305 clays was carried out to improve their mechanical and thermal capacities in which it was observed that the presence of quartz was eliminated.

- This analysis confirms that the pillaring process has optimized the properties of CZY clay for use as a CO_2 adsorbent, improving the proportion of active phases and reducing the less useful phases such as quartz.

- It was observed that clays adsorb a greater amount of CO_2 at low temperatures such as 25 °C, as established in most of the literature. They are not suitable for work at high temperatures, however, for the storage phase the desorption method can be applied.

- It was determined that the adsorption of CO_2 in clays is quite high, so it is recommended to try to process filters or catalysts that help in the fight against environmental pollution and to apply it more in the industrial area, which is the largest generator of these greenhouse gases.

- For future research, it is recommended to carry out a more detailed study of the clay purification process to optimize time and costs.

References

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