UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY

Escuela de Ciencias Químicas e Ingeniería

CLAYS EVALUATION IN CO_2 CAPTURE PROCESSES: A STATE-OF-ART

Trabajo de integración curricular presentado como requisito para la obtención de título como Petroquímico

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RESUMEN

El proyecto INEDITA se encuentra actualmente en desarrollo en la Universidad Yachay Tech (UYT). Este proyecto busca utilizar las arenas y arcillas ferruginosas del Ecuador para la captura de gases ácidos de la industria de hidrocarburos. La UYT cuenta con un sistema experimental, en el cual, es posible estudiar la captura de dióxido de carbono (CO_2), tal como la adsorción de este por arcillas. En la actualidad, no se cuenta con una revisión bibliográfica en la cual detallen las condiciones operacionales y los parámetros característicos relacionados al mineral arcilloso y al montaje experimental que tengan una influencia significativa en la captura de CO_2. Por este motivo, se propone el presente trabajo planteándose como objetivo el mencionado anteriormente. Los parámetros característicos revisados relacionados al mineral arcillosos fueron: origen de la muestra, propiedades estudiadas con técnicas de caracterización, pre-tratamiento de la muestra, tamaño de poro y presencia de agua. Los parámetros característicos revisados relacionados al sistema experimental fueron: sistema experimental, tipo de gas, características del montaje y el modo de operación. Las condiciones operacionales revisadas fueron: capacidad de adsorción de CO_2, presión, temperatura y selectividad. El análisis de la revisión señaló que los minerales arcillosos de origen artificial no presentan una capacidad de adsorción considerablemente superior a las de origen natural. Por otra parte, el parámetro característico más influyente en la adsorción de CO_2 es el pre-tratamiento de la muestra. Se ha revisado que los tipos de pre-tratamientos favorecen la captura de CO_2 en el siguiente orden decreciente: impregnación de amina, materiales preparados con minerales arcillosos, injerto de amina, pre-tratamiento con ácido y minerales arcillosos sin pre-tratamiento. Se ha revisado que el aumento de porosidad y la ausencia de agua en el mineral favorece la capacidad de adsorción de CO_2. Por otro lado, se establecieron a las condiciones operacionales como presión (P) y temperatura (T), altas (H) y bajas (L). Se revisó que las condiciones operacionales favorecen la capacidad de adsorción de CO_2 en minerales arcillosos en el siguiente orden decreciente: (HP, LT), (LP, LT), (HP, HT) y (LP, HT).

Palabras claves: minerales arcillosos, adsorción de CO_2, condiciones operacionales, parámetros característicos

ABSTRACT

The INEDITA project is currently under development at Yachay Tech University (UYT). This project seeks to use the ferruginous sands and clays of Ecuador for the capture of acid gases from the hydrocarbon industry. The UYT count with an experimental system, in which it is possible to study the capture of carbon dioxide (CO_2), such as its adsorption by clays. At present, there is no bibliographic review in which is detailed the operational conditions and characteristic parameters related to the clay mineral and the experimental setup that have a significant influence on CO_2 capture. For this reason, the present work is proposed considering the objective mentioned. The revised characteristic parameters related to the clay mineral were: sample origin, properties studied with characterization techniques, sample pre-treatment, pore size and water presence. The revised characteristic parameters related to the experimental system were: experimental system, type of gas, characteristics of the assembly and the mode of operation. The operational conditions reviewed were: CO_2 adsorption capacity, pressure, temperature and selectivity. The analysis of the review indicated that clay minerals of artificial origin do not have a considerably higher adsorption capacity than those of natural origin. On the other hand, the most influential characteristic parameter on CO_2 adsorption is the sample pre-treatment. It has been reviewed that the types of pre-treatments favor the capture of CO_2 in the following decreasing order: amine impregnation, materials prepared with clay minerals, amine grafting, pre-treatment with acid and clay minerals without pre-treatment. It has been reviewed that the increase in porosity and the absence of water in the mineral favors the CO_2 adsorption capacity. On the other hand, the operational conditions such as pressure (P) and temperature (T), high (H) and low (L) were established. It was reviewed that the operational conditions favor the CO_2 adsorption capacity in clay minerals in the following decreasing order: (HP, LT), (LP, LT), (HP, HT) and (LP, HT).

Keywords: clay minerals, CO_2 adsorption, operational conditions, characteristic parameters

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ABBREVIATIONS

AEP	1-(2-Aminoethyl)piperazine
CH_4	Methane
CO_2	Carbon dioxide
DEA	Diethanolamine
DIPA	Diisopropylamine
DMPZ	1,4-Dimethylpiperazine
FTIR	Fourier Transform Infrared Spectroscopy
H_2S	Hydrogen Sulphur
LULUCF	Land use, land-use change, and forestry
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MOFs	Metal-organic frameworks
MSB	Magnetic Suspension Balance
SBA	Sec-butylamine
SEM	Scanning Electron Microscope
TAETA	Tris(2-aminoethyl)amine
TETA	Triethylenetetramine
TGA	Thermogravimetric analysis
YTU	Yachay Tech University
XRD	X-ray diffraction

CHAPTER I

1. INTRODUCTION

The carbon dioxide (CO_2) emissions in the environment constitute a great problem for humanity. Research studies suggest that if atmospheric CO_2 concentrations increase from current levels near 385 parts per million by volume (ppmv) to a peak of 450 – 600 ppmv, it would mean irreversible impacts on climate change (Solomon, Plattner, Knutti, & Friedlingstein, 2009). The largest CO_2 global emissions result from carbon oxidation when fossil fuels are burned (Rubin, Meyer, & de Coninck, 2004). At the same time, fossil fuel global combustion sources are related mainly to power plants, oil refineries and large industrial facilities. In the case of Ecuador, in 2016, it emitted 2.49 tons of CO_2 to the environment per capita (The world bank, 2021). These emissions come, in decreasing order, from the sector of land use, land-use change and forestry (LULUCF), energy sector, and the industrial process sector (Guevara, Bravo, Molina, & Cadilhac, n.d.). Emissions from any activity related to industrial oil and natural gas processing are included in the energy sector. The increasing global emission of CO_2 from the oil industry has meant that research on technologies for CO_2 capture has intensified in recent years. A technology that has shown many potential advantages, compared to other conventional ones that use aqueous amine solvents, are the solid sorbents capable of capturing CO_2 from flue gas streams (Samanta, Zhao, Shimizu, Sarkar, & Gupta, 2012).

A variety of solid sorbents have been studied, such as activated carbonaceous materials, microporous/mesoporous silica or zeolites, carbonates, and polymeric resins loaded with or without nitrogen functionality, and metal-organic frameworks (MOFs) (Samanta et al., 2012). Additionally to these sorbents, several works suggest clays as potential solid sorbents for CO_2 capture. It is largely due to the great abundance, accessibility, and low cost of some clays. Ecuador contains a wide availability of non-metallic occurrences. Among the occurrences of clay minerals, the presence of some type of clays are notable such as the following: common clays, smectitic clays, halloysitic clays, kaolins and feldspars. These clay occurrences represent around 20% of the country's non-metallic mineral wealth (Uribe, 2015).

Regarding the use of the valued clay mineral wealth, it was evidenced that 50% goes to the artisanal manufacture of bricks and tiles and 15% to the industrial sector. It indicates a potential clay mining resource to be exploited in the country. At the Yachay Tech University (YTU), the INEDITA project is under development. This project seeks to study the possibilities of using ferruginous sands and clays from Ecuador to capture acid gases – CO_2, H_2S – from the hydrocarbon industry. The university, in its laboratory, counts on a high-pressure experimental system to carry out CO_2 capture tests. The present work is proposed for the realization of a state of the art to detail the operational conditions and characteristic parameters related to clay minerals and the experimental system used to capture CO_2 from acid gas streams.

1.1. Problem approach

The INEDITA project is currently under development at Yachay Tech University (UYT). This project seeks to use the ferruginous sands and clays of Ecuador for the capture of acid gases from the hydrocarbon industry. The UYT has an experimental system, in which it is possible to study the capture of carbon dioxide (CO_2), such as its adsorption by clays. At present, there is no bibliographic review in which the operational conditions and characteristic parameters related to the clay mineral and the experimental setup that have a significant influence on CO_2 capture are detailed. A work with the mentioned approach is necessary to evaluate clay minerals as potential solid sorbents. In this case, it is proposed to evaluate the clays of Ecuador. This is how the present work is proposed, considering the aforementioned approach as its objective.

1.2.Objectives

1.2.1. General objective

Development of a state of the art for the evaluation of clay minerals for CO_2 capture in order to evaluate the clays available in Ecuador as potential solid sorbents.

1.2.2. Specific objectives

- Review the main characteristics of the technologies available for CO_2 capture.
- To identify the last 20-years publication trends of clay minerals, which improves the capture process of CO_2.
- To know the properties and characteristics of clays for their potential application as a solid sorbent, and link these properties to Ecuadorian clays.
- To identify the characteristic parameters that influence CO_2 capture process using clay minerals and classify them according their CO_2 adsorption capacity.
- To know the most favorable magnitudes of the operational conditions in the CO_2 capture using clay minerals.

1.3. Keywords, relevance and methodology

In this work, the bibliographic search in databases was carried out using keywords according to the specific objectives of the study. The selection of key words was carried out according to a methodology. This methodology consisted of taking a base word related to the topic addressed in each chapter, adding a first keyword and then another. In this way it was possible to simplify the search results. After reviewing some scientific articles, the keywords were classified into specific and variable words. The specific words were related to the main topic of this study. The variable words were based on the topic addressed in each chapter. The word CO_2 was common to all the chapters (Table 1). The databases consulted were Scopus, Science Direct and Google Scholar. Access to the databases was possible through the permission granted by YTU.

Table 1. *Keywords employed for the information research.*

Organization	Specific words	Variable words
Chapter II	CO_2 CO_2 capture	Sources, combustion gases, fossil fuel, industrial, technologies
Chapter III	Clay minerals CO_2 capture	Fundamentals, properties, advantages, founded in Ecuador
Chapter IV	CO_2 capture CO_2 adsorption CO_2 sorption Clay minerals	Capacity, process, properties

Consultation of these databases resulted in the identification of 45 scientific articles published in the last twenty years which, in our opinion, reflect the state of the art in the central theme of this research and allowed us to meet the proposed objectives. Figure 1 shows the distribution, by every five years of publication, of the 45 scientific articles used in this work. During the period of time considered, an increasing trend of scientific publications on the subject was observed, with this trend being significant in the last five years, which reflects the importance given to this subject by the scientific community.

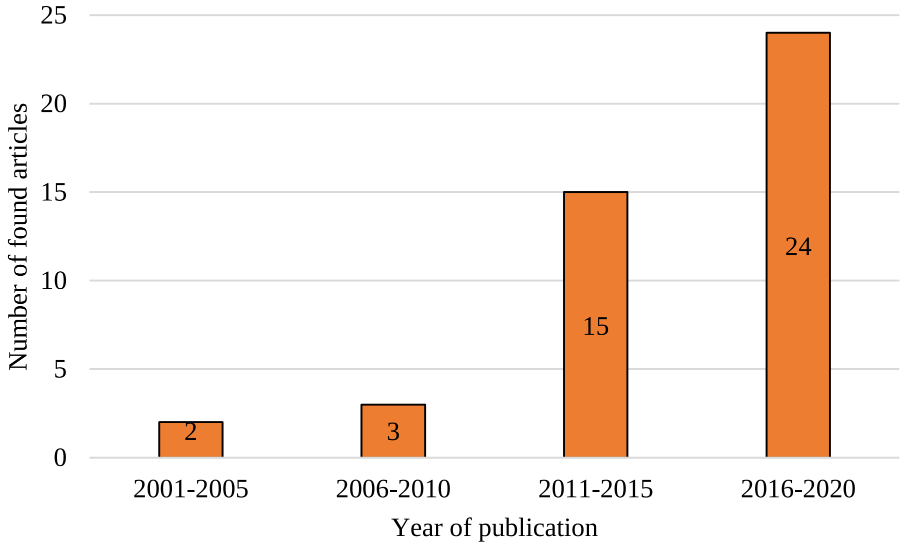


***Figure 1**. Number of articles found for every five years of publication.*

This work took the form of a state of the art as reported by Molina (2005). The methodology applied in this work is detailed in Figure 2. The clay minerals and experimental system characteristic parameters was made taking into account the following: parameters commonly studied in industrial processes and experimental systems; the literature review of parameters affecting CO_2 capture using mineral clays; and the frequency of such parameters in the articles reviewed. The selected characteristic parameters and operating conditions are shown in Figures 3 and 4, respectively.

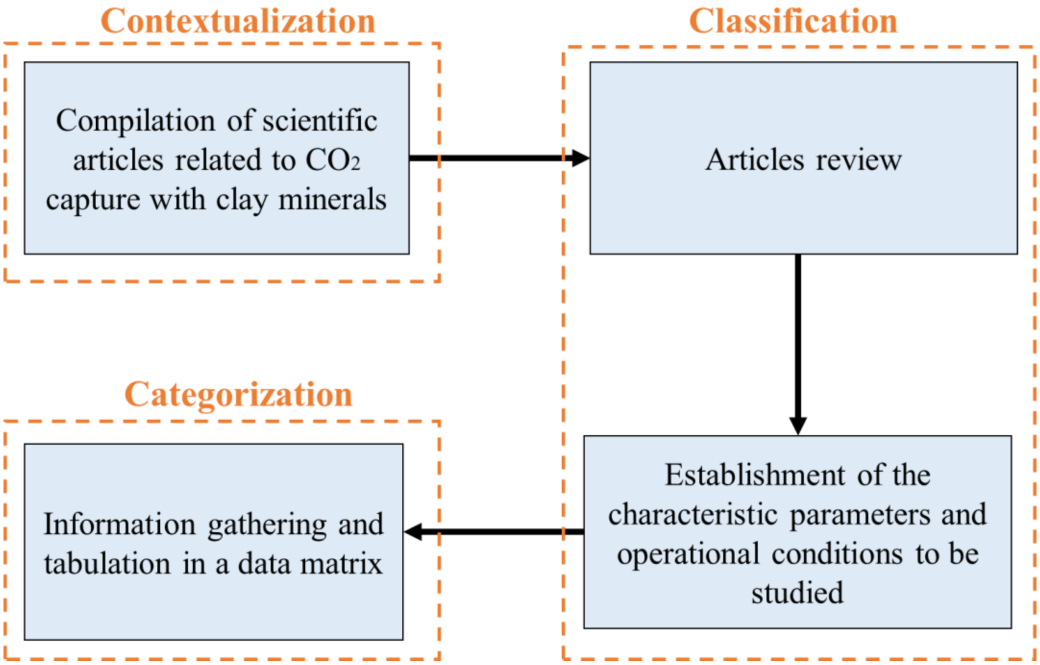


Figure 2. *State-of-the-art methodology adapted for the present work.*

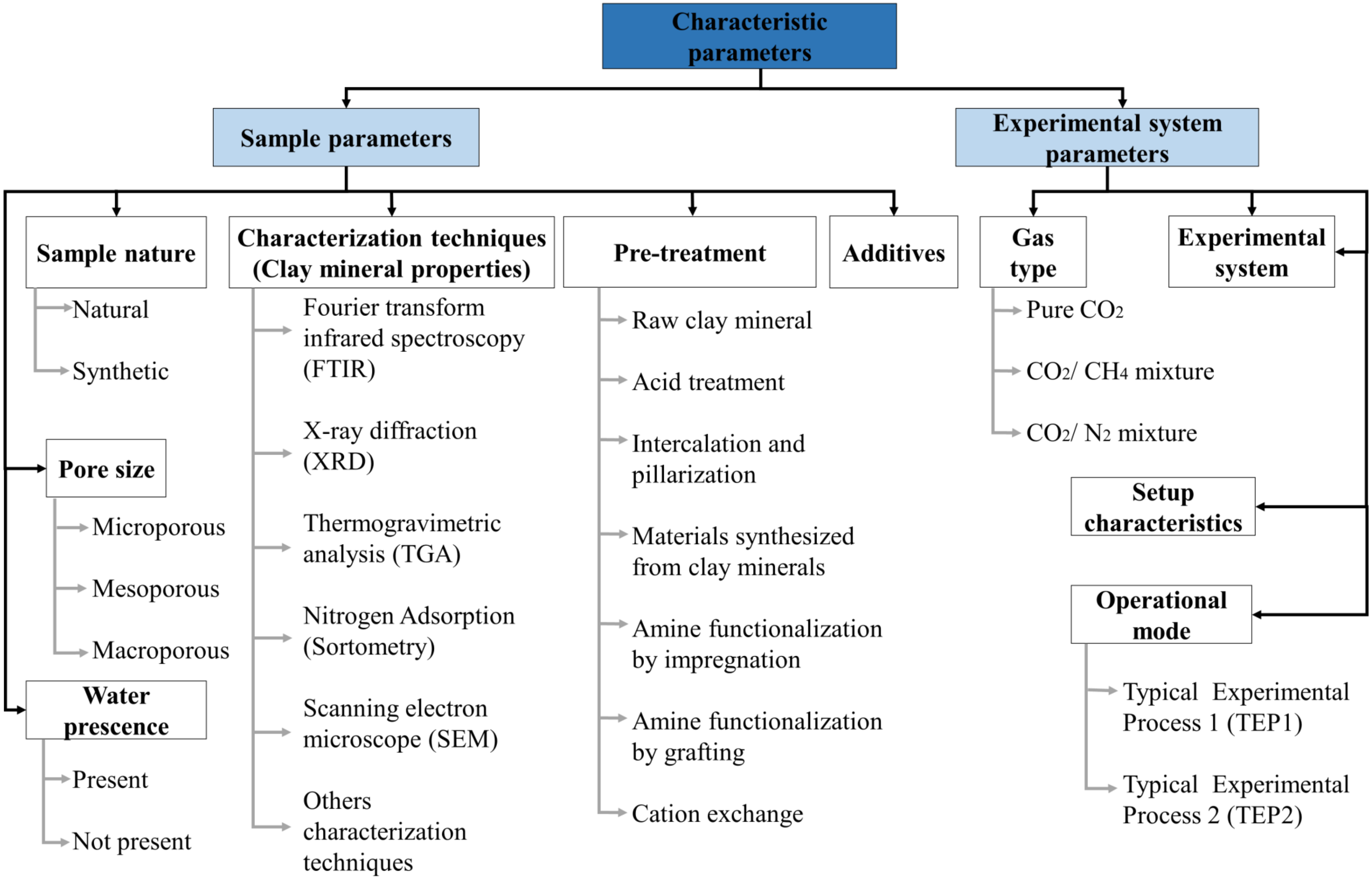


Figure 3. *Sample and experimental system characteristic parameters reviewed.*

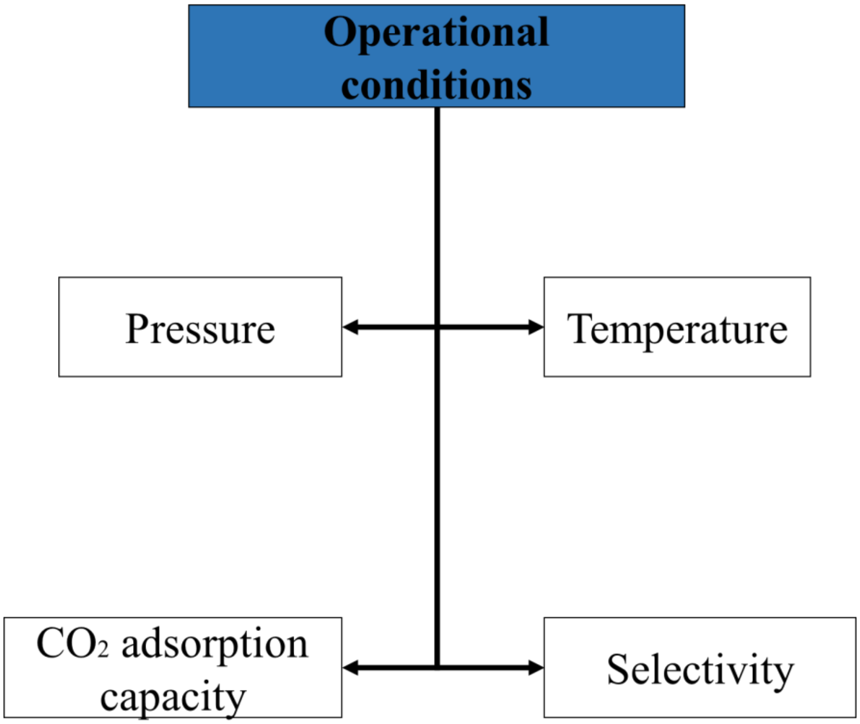


Figure 4. *Operational conditions reviewed.*

CHAPTER II

2. CO_2 CAPTURE: FUNDAMENTALS

The main application of CO_2 capture is likely to be at large scale processes, which are fossil fuel power plants, fuel processing plants, and other industrial plants, particularly for the manufacture of iron, steel, cement, and bulk chemicals (Thambimuthu, Soltanieh, & Abanades, 2005). The usage of carbon capture technologies in these processes can reduce the world's greenhouse gas emissions. The large-scale processes in which carbon separation/capture technologies have been operational for decades are natural gas facilities and fertilizer industries. It also has recently become operational in the power sector (Global CCS Institute, 2018). CO_2 capturing directly from small sources in the transportation, residential and commercial building sectors had been demonstrated to be more complex and expensive. For the mentioned reasons, it is necessary to carry out studies related to the CO_2 capture mainly from industrial complexes.

2.1. CO_2 capture types

The CO_2 capture systems are classified into four basic ones, shown in Figure 5, from fossil fuels or biomass usage. These systems are the following: capture from industrial process streams; post-combustion capture; oxy-fuel combustion capture; and pre-combustion capture.

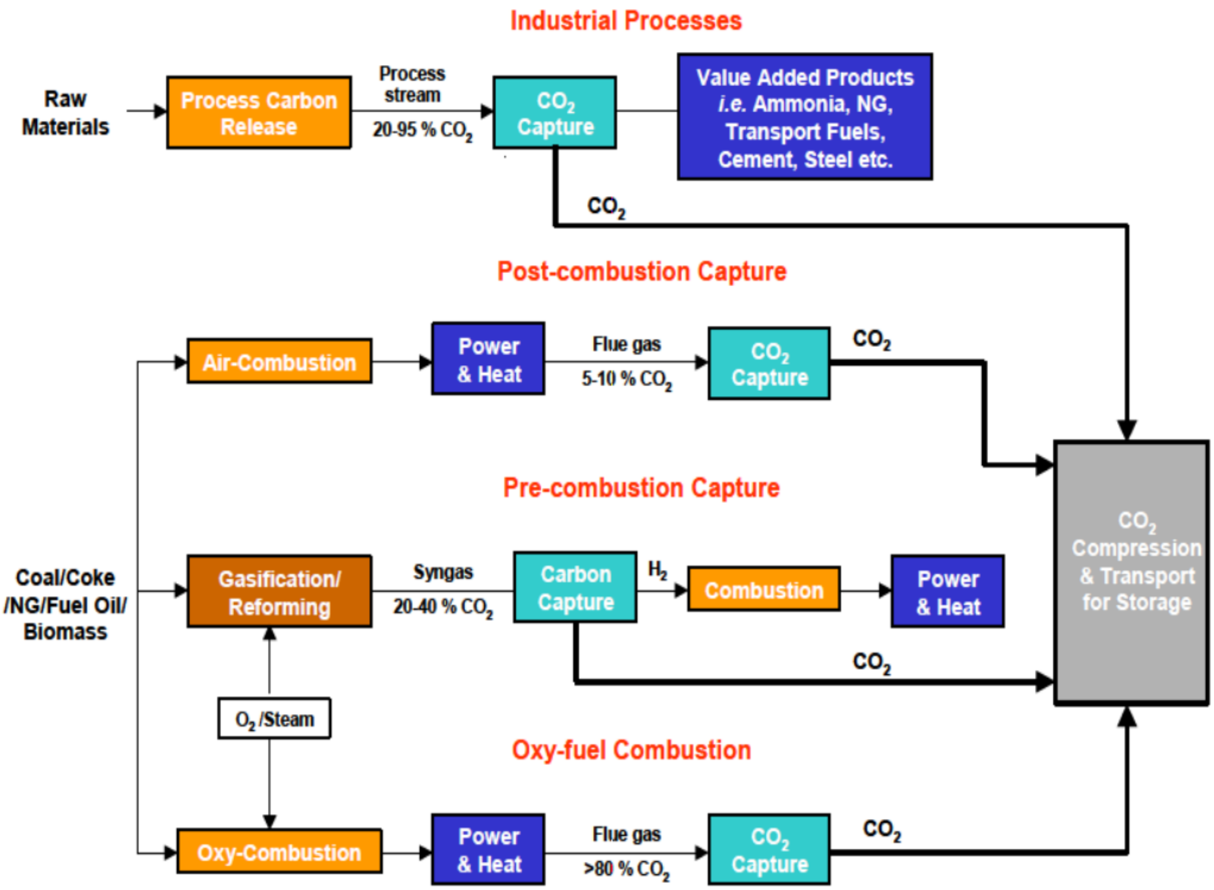


Figure 5. *CO_2 capture systems.*
Source: (Ofori, 2017)

Industrial process streams CO_2 have been captured for several decades, although most of the CO_2 that is captured is released into the atmosphere because there is no incentive or requirement to store it. The purification of natural gas and hydrogen-containing syngas production to manufacture ammonia, alcohols, and synthetic liquid fuels are current examples of CO_2 capture from process streams. (Thambimuthu et al., 2005).

Pre-combustion processes transform fuel into a gas mixture of hydrogen and CO_2. The obtained hydrogen is burnt without producing CO_2. The CO_2 obtained from the gas mixture can be compressed for transport and storage. The pre-combustion process is more complex than post-combustion, making the technology more difficult to apply to existing power plants (Global CCS Institute, 2018).

Post-combustion processes capture CO_2 from the exhaust flue gases released from power plants. Usually, the flue gases exit at atmospheric pressure to then be captured. This technique is applied in the existing power plants without a significant change in the plant. For this reason, it has the advantage of easier retrofitting compared to the other CO_2 capture and storage processes. It is the simplest technique to capture CO_2. (Sifat & Haseli, 2019)

Oxy-fuel combustion processes use oxygen instead of air for the combustion of fuel. This process produces exhaust gas that is mainly water vapor and CO_2, easily removed to produce a high purity CO_2 stream (Global CCS Institute, 2018).

2.2. CO_2 capture technologies

CO_2 capture systems use different types of CO_2 capture technologies. They are integrated into the four basic systems for CO_2 capture discussed. A description of these CO_2 capture methods is given below.

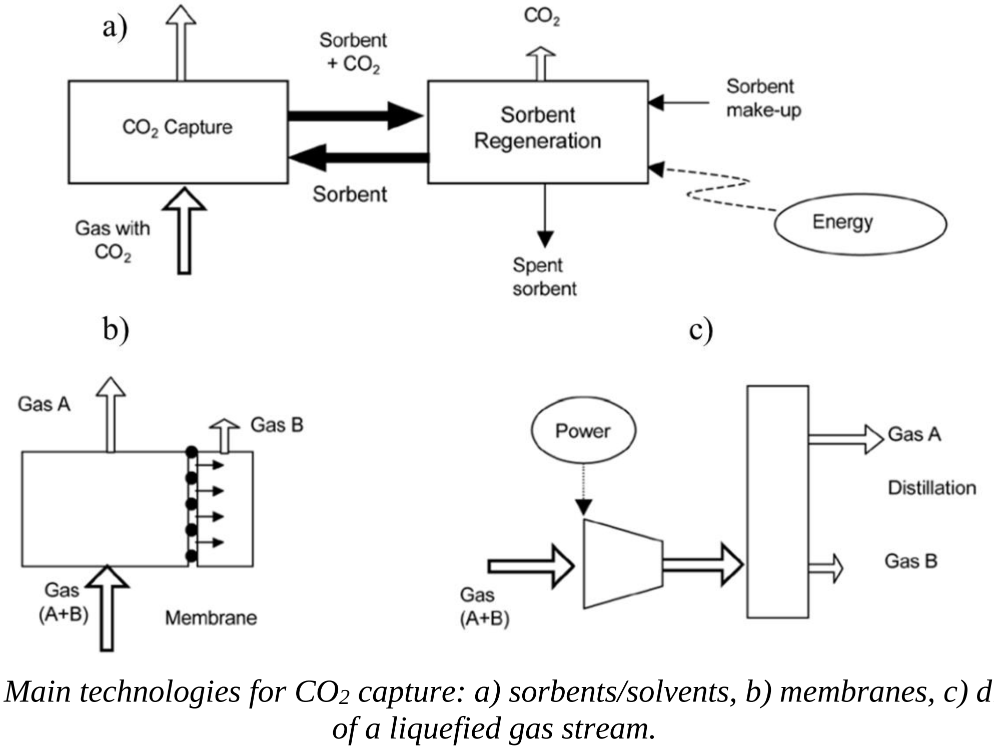


Figure 6. *Main technologies for CO_2 capture: a) sorbents/solvents, b) membranes, c) distillation of a liquefied gas stream.*
Source: (Thambimuthu et al., 2005)

2.2.1. CO_2 capture with sorbents/solvents

The separation is carried out by contacting the CO_2-containing gas with a liquid absorbent or solid sorbent, capable of capturing the CO_2. In the general scheme of Figure 6, the sorbent loaded with CO_2 is transported to a different vessel, where it releases CO_2, achieving regeneration. Regeneration happens after the sorbent passes through heating, a pressure decrease, or any other conditions change. (Thambimuthu et al., 2005).

The most conventional technology in the CO_2 capture process is the use of aqueous amine solvents. A traditional aqueous-amine industrial process is shown in Figure 7. Aqueous solutions of amines such as monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA), among others, are commonly used. However, absorption exhibits important drawbacks, e.g., relatively low CO_2 adsorption capacity, potential toxic byproduct release, operational instability and frequent equipment maintenance due to excessive corrosion of the amine system (Zhou et al., 2014), amine loss due to evaporation and, mainly, high energy consumption during solvent regeneration (Gómez-Pozuelo et al., 2019). Therefore, it is desirable to study new strategies to capture CO_2 from flue gas.

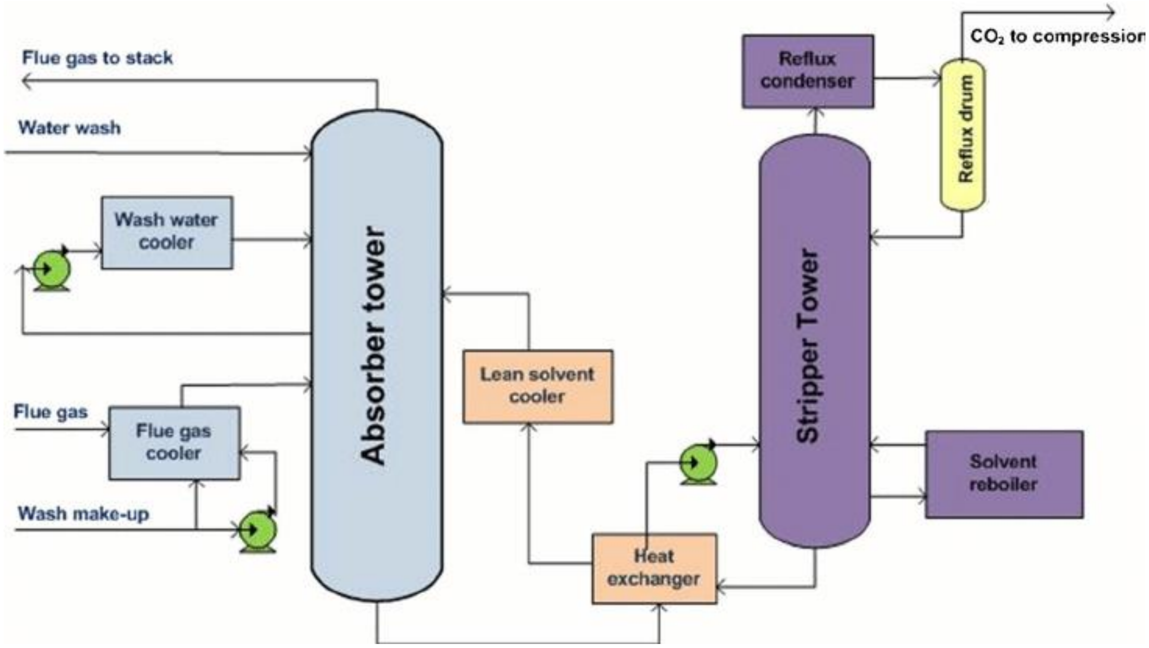


Figure 7. *Process flow diagram for CO_2 recovery from flue gas by amine chemical absorption.*
Source: (Sabouni, Kazemian, & Rohani, 2014)

2.2.2. CO_2 capture with membranes

Membranes are manufactured materials that allow the selective permeation of gas through them. The pressure difference across the membrane usually drives the flow of gas through the membrane. (Thambimuthu et al., 2005). This method is attracted to the scientific community due to its high CO_2 capture efficiency, simple process design, easy scale-up, low energy consumption, and lower capital cost (Mustafa, Farhan, & Hussain, 2016).

2.2.3. CO_2 capture with the distillation of a liquefied gas stream

A liquid stream can be turned into gas after compression, cooling, and expansion processes. Once in liquid form, gas components can be separated in a distillation column. Cryogenic CO_2 capture is often considered an unrealistic CO_2 capture technology due to expected high cooling costs. So far, the required cold for CO_2 separation can be obtained by integration with other processes (Knapik, Kosowski, & Stopa, 2018). Oxygen can be separated from the air following the scheme of Figure 6 and be used in a range of CO_2 capture systems like oxyfuel combustion and pre-combustion capture.

2.3. CO_2 capture using clay minerals

The CO_2 technologies explained are applied in the four basic CO_2 capture systems mentioned. These technologies can have very particular characteristics depending on the system to which it is adapted. A simplified scheme of the classification of the CO_2 capture technologies by the type of system is shown in Table 2. It can be seen that clay minerals are present. From there, it can be inferred that clay minerals as an emerging technology. The study of this technology has been increasing in recent years. As will be discussed in Chapter III, clay minerals are presented as a technology for the adsorption of CO_2 from gas streams. In this way, it would be placed mainly in Table 2 as an emerging technology to capture gases from process streams and post-combustion processes in the part of solid sorbents.

Table 2. *Current and emerging CO_2 capture technologies.*
Source: (Thambimuthu et al., 2005)

CO_2 capture task	**Process streams**		**Post-combustion capture**		**Oxy-fuel combustion capture**		**Pre-combustion capture**	
	CO_2/CH_4		**CO_2/N_2**		**O_2/N_2**		**CO_2/H_2**	
CO_2 capture technologies	**Current**	**Emerging**	**Current**	**Emerging**	**Current**	**Emerging**	**Current**	**Emerging**
Solvents (Absorption)	Physical solvents Chemical solvents	Improved solvents Novel contacting equipment Improved design of process	Chemical solvents	Improved solvents Novel contacting equipment Improved design of process	n.a.	Biomimetic solvents, e.g., hemoglobin-derivates	Physical solvents Chemical solvents	Improved solvents Novel contacting equipment Improved design of process
Membranes	Polymeric	Ceramic Facilitated transport Carbon Contactors	Polymeric	Ceramic Facilitated transport Carbon Contactors	Polymeric	Ion transport membranes Facilitated transport	Polymeric	Ceramic Palladium Reactors Contactors
Solid sorbents	Zeolites Activated carbon	**Clays minerals**	Zeolites Activated carbon	Carbonates Carbon-based sorbents **Clays minerals**	Zeolites Activated carbon	Adsorbents for O_2/N_2 separation, Perovskites Oxygen chemical looping	Zeolites Activated carbon Alumina **Clays minerals**	Carbonates Hydrotalcites Silicates **Clays minerals**
Cryogenic	Ryan-Holmes process		Liquefaction	Hybrid processes	Distillation	Improved distillation	Liquefaction	Hybrid processes

CHAPTER III

3. CLAY MINERALS AS SOLID SORBENTS

3.1. Clay minerals fundamentals

The term "clay" refers to a natural origin material composed mainly of fine-grained minerals, which are generally plastic with appropriate water content and will harden if dried or cooked. Although clay generally contains phyllosilicates. It may contain other materials that impart plasticity and harden when dried or cooked. Associated phases in clay may include materials that do not impart plasticity and organic matter. The term "clay mineral" refers to phyllosilicate minerals and minerals that impart plasticity to clay and harden when dried or burned. (Guggenheim et al., 1995). In clay minerals in the soil, packing the large O^{2-} ions together in space results in two distinct structural features within their crystalline structures. The first consists of four packed O^{2-} ions, three of these are arranged in a triangle with the fourth O^{2-} ion in the dimple formed by the other three. The centers of the four O^{2-} ions shape the apices of a regular tetrahedron, and a small central space is called a "tetrahedral site." The structure explained is showed in Figure 8-a. The second structural feature is formed by six very compact O^{2-} ions. The centers of the six ions form the apices of a regular octahedron, and the small central space is called the "octahedral site." (Schulze, 2005). The structure is shown in Figure 8-b. The explained structures form layers that conform the basic structure of phyllosilicate minerals.

Clay minerals are a group of hydrous layer aluminosilicates that form the greater part of the minerals' phyllosilicate family. The different clays vary greatly in chemical, mineralogical, and physical characteristics, but a common characteristic is their crystalline laminar structure, as shown in Figure 9.

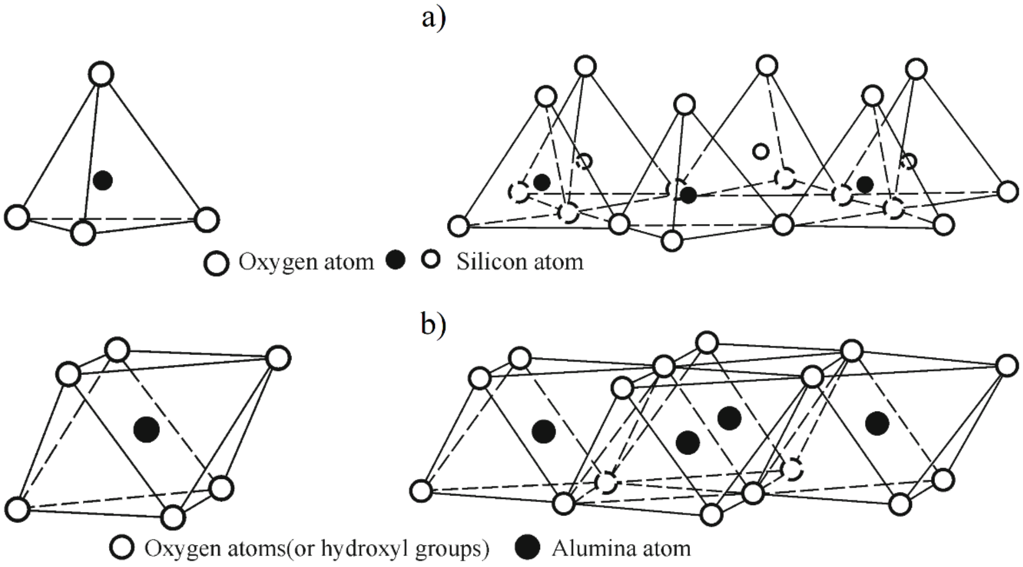


***Figure 8**. Clay mineral basic structures: a) Tetrahedral forming tetrahedral layer, b) octahedral forming octahedral layer.*
Source: (Dai & Zhao, 2018)

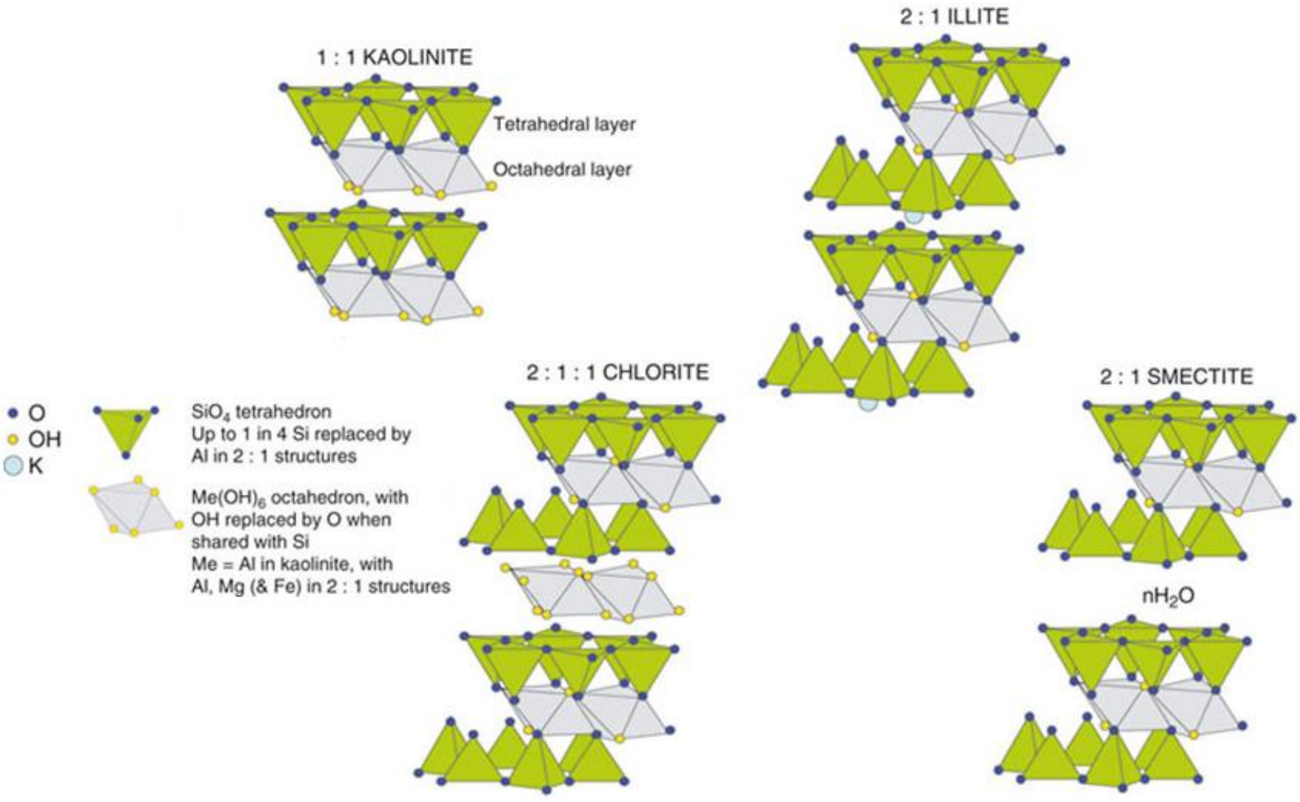


***Figure 9.** Chemical structure of some clay minerals.*
Source: (Chesworth, 2008)

Clay minerals classification can be very complex. However, a simple classification can be made based on the different arrangements of tetrahedral and octahedral layers (Chesworth, 2008). Table 3 gives a simplified classification scheme.

Table 3. *Simplified classification of clay minerals.*
Source: (Chesworth, 2008)

Layers arrangement	**GROUP TYPE**	
	Dioctahedral	**Trioctahedral**
1:01	Kaolinite (Al)	Serpentine (Mg)
2 : 1 Nonexpanded	Illite (Al) Glauconite (Fe)	"Biotite" (Fe, Mg)
2 : 1 (Low charge) Expanded Smectites	Montmorillonite (Si) Beidellite (Al) Nontronite (Fe)	Saponite (Mg) Hectorite (Li)
2 : 1 (High charge)	Vermiculite (Al)	Vermiculite (Mg, Fe)
2:01:01	Chlorite (Al)	Chlorites (Mg, Fe)
Mixed layer	Intergrowth of any two or three of the clay minerals listed above	-
Chain structure	Palygorskite (Al, Mg)	Sepiolite (Mg)

Clay minerals present chemical and physical properties. Its chemical properties present ion exchange capacity, interactions with inorganic and organic compounds, and clay-water interactions. Regarding physical properties, it presents different textural properties, high-temperature reactions, and solubility.

Ion exchange is referred to the clay mineral capacity to adsorb cations and anions and held them around the outside of the crystal structural unit in an exchangeable state, usually without affecting the basic silicate structure. Ion exchange capacity depends on the deficiency in the positive or negative charge balance (locally or overall) of mineral structures.

Clay mineral water retention depends on some factors. Clay materials can retain water in several forms. The water can be retained in pores, clay mineral surface, interlayer positions, or within structural channels. The water can be separated by drying at ambient conditions. Specific surface is generally proportional to water retention capacity. Plasticity is also a parameter that increases with water retention.

Interaction with inorganic/organic compounds is an important chemical property of clay minerals. Clay minerals that interact with inorganic compounds can accommodate relatively large, inorganic cations between layers. This multivalency causes the interlayer space to be only partially occupied by such inorganic cations distributed in the space. Organic interactions can be used to functionalize clay minerals to be used as a catalyst.

Textural properties of clay minerals are various. A clay mineral's size and shape is an important parameter since it can affect the adsorption reactions. Clay minerals can present different shapes like well-formed minerals, six-sided flakes, tubular form, and mosaic sheets. Clay minerals also have other textural properties such as large specific surface area, high porosity, surface charge, and surface functional groups.

Clay minerals can have important high-temperature reactions. A temperature increase beyond dehydroxylation can mean that the clay mineral structure may be destroyed or just modified. It also depends on the clay mineral composition and structure. Information about high-temperature reactions is important in other areas like ceramic science and industry.

Clay minerals solubility is a parameter that can establish in which mediums it can react. The solubility of clay minerals in acids varies with the acid's nature and its concentration, acid-clay ratio, temperature, duration, and clay composition. Acid treatment is an important matter of study since it is a technique that usually improves clay mineral CO_2 adsorption capacity. In alkaline solutions, clay mineral solubility depends on the same factors as those stated for acid. (Grim & Kodama, 2014).

The properties mentioned above of clay minerals correspond to general properties of these that can influence the capture of CO_2. However, other properties make a solid sorbent suitable for this. These properties are the following: high CO_2 sorption capacity, selectivity towards CO_2 adsorption, regeneration efficiency, high availability, and low cost (Lutyński, Sakiewicz, & González, 2014).

The CO_2 adsorption capacity in mineral clays can be high and comparable with other technologies used, such as absorption with amine solvents. The adsorption capacity of clay minerals can be comparable and even exceed some values of those achieved by amine solvents. This characteristic will be analyzed in more detail in Chapter IV. Selectivity towards CO_2 in clay minerals shows relatively high values. Despite this, more research needs to be done regarding clay minerals and amine solvents' selective ability. In this way, a comparison could be made, and clay minerals' efficiency concerning their selectivity could be known. Some authors have studied the efficiency in the regeneration of clay minerals (Cai et al., 2015; Horri et al., 2019; Sanz, Calleja, Arencibia, & Sanz-Pérez, 2010; Stevens et al., 2013). These authors studied the regeneration process of bentonite, halloysite nanotubes and montmorillonite. The studies showed that these clay minerals could maintain relatively high adsorption capacities for several cycles. This means that most of these minerals have high regeneration efficiency. The availability of clay minerals is wide. As will be mentioned later, in Ecuador, mineral clay occurrences represent 20 % of non-metallic occurrences. The clays' cost would be of great economic accessibility since, as mentioned, there are several mineral occurrences in Ecuador. Occurrences are those deposits of resources that have not been economically valued.

3.2. Improvements in the CO_2 capture process

A technology that has shown many potential advantages, compared to the conventional CO_2 capture using aqueous amine solvents, is the adsorption processes using solid sorbents capable of CO_2 capture from flue gas streams. In this context, adsorption on solid materials is considered an attractive alternative, and, consequently, much effort has been made to develop appropriate solid adsorbents. Materials are generally selected in terms of low-cost raw materials, low heat capacity, fast kinetics, high CO_2 adsorption capacity, high CO_2 selectivity, thermal, chemical, and mechanical stability (Gómez-Pozuelo et al., 2019).

A variety of solid sorbents have been an object of studies, such as activated carbonaceous materials, microporous/mesoporous silica or zeolites, carbonates, and polymeric resins loaded with or without nitrogen functionality and MOFs (Samanta et al., 2012). Activated carbonaceous materials and zeolites are structures with narrow pore sizes, so these materials also reach high CO_2

adsorption values (Chouikhi et al., 2019). Regarding MOFS, the main disadvantages of these structures are the relatively low thermal stability required in the regeneration stage and the high cost required to produce them on a larger scale. Additional to these sorbents, several works suggest clay minerals as potential solid sorbents for CO_2 capture. Clay minerals are abundant, inexpensive, and generally safe materials for the environment. It is necessary to develop adsorbents with these characteristics to obtain more economical and sustainable processes at an industrial scale. Thus, clay minerals have become an alternative in processes like adsorption and catalysis. Clay minerals present material properties such as large specific surface area, high porosity, surface charge, and surface functional groups, making clay minerals function as adsorbents, filters, flocculates, and carbon stabilizers. Further, the surfaces of clay minerals can be modified from hydrophilic to hydrophobic, for example, making them good adsorbents and carriers of non-ionic organic compounds (Yuan, Theng, Churchman, & Gates, 2006)

3.3. Clays available in Ecuador

Ecuador encompasses a broad availability of non-metallic occurrences. Among the occurrences of clay minerals, as: common clays, smectitic clays, halloysitic clays, kaolins, and feldspars are predominant in different Ecuador provinces; these occurrences are detailed in Table 4. These occurrences represent around 20% of the country's non-metallic mineral wealth. Regarding the use of the valued clay mineral wealth, it was evidenced that 50% goes to the artisanal manufacture of bricks and tiles and 15% to the industrial sector (Uribe, 2015). The clay minerals reviewed in this work were kaolinite, bentonite, montmorillonite, saponite, sepiolite, palygorskite, laponite, kaolinite/limestone, halloysite, smectite, fluorohectorite (smectite type), and illite. After analyzing Table 4, the clay minerals of kaolinite, smectite, halloysite, and illite will be emphasized, as these clay minerals are the ones found in the greatest quantity in Ecuador.

Table 4. *Mineralogical nature of predominant clays in Ecuador.*
Source: (Uribe, 2015)

Clay	Description
Kaolinitic clays	This type of clay has in its composition important proportions of free quartz and high plasticity. Mineralogically these clays are a mixture of minerals from the kaolinite group, with abundant quartz and traces of illite and amorphous substances (allophane). The deposits are the result of weathered rocks; kaolin is residual or little transported. In Ecuador, some companies use them as a substitute for imported ball clay.
Common clays	Under this name are included all primary clays, which are mostly composed of impure clay or silt, which come from the weathering of rocks very close to the surface. They are not suitable for the manufacture of fine ceramics. These types of clays are burned for brick production, meeting local and provincial demands. They are generally alluvial deposits of clayey sands, as well as weathering products of crystalline granite shales. These raw materials are exploited manually by shoveling. The clay is mixed and homogenized, which in many cases is mixed with sawdust or rice husks. Subsequently, the pieces are manually shaped (bricks - tiles), and after drying in the air and sun, the pieces are taken to the wood-fired ovens for at least 24 hours.
Esmectitic clays	This type of clay is found with preference in sedimentary formations, in which high levels of acidic tufts and tufts are evident. Contain smectite as the main component. They are high plasticity clays that come from the alteration of andesitic lavas, with sterile rock clasts, hematite, and goethite. In some cases, there are outcrops with traces of cristobalite and mica. These clays have a good chance of being used in red ceramic.
Halloystic clays	Clays in which the main component is halloysite. This type of clay is the product of the weathering of the Altar group's volcanic deposits, is characterized by the mineral presence of halloysite and probably allophane as major components and remains of feldspar quartz, cristobalite, and hematite.
Kaolin	Kaolin is a rock composed mostly of kaolinite, is a pure white clay that comes from the decomposition of feldspar rocks. It is the raw material of countless industries; its applications vary and range from the ceramic industry to the paper industry. In the occurrences of the provinces of Azuay, El Cañar, Morona Santiago, Zamora Chinchipe, and Loja, given their mineralogical nature, several adjustments must be made in terms of their benefit as raw material, to improve its characteristics both in dry crude and after cooking. Drying attitudes should also be considered, as the behavior is very critical.
Feldspars	Important deposits of this raw material exist in the Provinces of Azuay, Bolívar, Cañar, Chimborazo, El Oro and Zamora Chinchipe. Usually, an intrusive acid rock emerges with a light grey granoblastic texture, which has undergone weathering processes, forming interesting accumulations of feldspar.

CHAPTER IV

4. CLAYS FOR CO_2 CAPTURE: STATE-OF-THE-ART

4.1. Characteristic parameters

4.1.1. Sample nature

In the work of Uribe (2015) the occurrences of clay minerals from Ecuador are dated, which were described in Table 4. As they are occurrences, all these clays are of natural origin. Despite this fact, the decision was taken to establish the nature/origin of the sample as a characteristic parameter. As mentioned below, synthetic clays have significant advantages that can convert them into potential materials for CO_2 adsorption. In addition to this, very few authors study the use of synthetic clay minerals specifically for CO_2 adsorption (Cavalcanti, Kalantzopoulos, Eckert, Knudsen, & Fossum, 2018; Michels et al., 2015). Most of the reviewed clay minerals in this work are of natural origin, except for the synthetic clay mineral fluorohectorite.

Fluorohectorites are synthetic clay minerals that have been used as a representative and clean model system of natural smectite clays (Cavalcanti, Kalantzopoulos, Eckert, Knudsen, & Fossum, 2018). Synthetic clay minerals can be tailored to promote specific properties (D. Zhang, Zhou, Lin, Tong, & Yu, 2010). In this way, synthetic nano-silicate clays had acquired some characteristics that vantage their CO_2 adsorption capacity over their natural counterparts. Some of these characteristics are the following: fewer impurity content (e.g., carbonates, (hydr)oxides, silica, and organic matter); more homogenous charge distribution, leading to well-defined intercalation states (Michels et al., 2015); harmless in the adsorption reaction; less expensive to produce than other high-performance porous synthetic materials considered for CO_2 captures, such as MOFs (Michels et al., 2015).

Cavalcanti et al. (2018) showed that the nano silicate Nickel Fluorohectorite was able to capture one of the highest capacities of CO_2 ever achieved. This capacity was compared to the capacity of some of the best CO_2 adsorption materials reported to date. These materials were Montmorilonite, Zeolite 13X, functionalized polymers, activated carbons, MOF–aminoclay composites, and MOF-210. The results showed that MOFs reported the highest gravimetric capacity records because of their low density. However, fluorohectorite showed exceptional results on CO_2 capture, calling attention to the diversity of characteristics among all materials that could be combined for a viable carbon capture and storage solution.

4.1.2. Sample characterization

Materials characterization techniques are methodologies used to analyze the structures and composition of materials. In this way, the qualitative and quantitative magnitudes of the properties of a material can be known. In this case, the material of interest is clay minerals. The characterization techniques frequently used to study the physical and chemical materials structures are shown in Table 5.

***Table 5**. Characterization techniques.*

Structure studied	**Technique**	
Physical structure	Low-Temperature Physisorption	
	X-ray Diffraction	
Chemical structure	Static Chemisorption	
Other characterization techniques	Atomic Absorption Spectroscopy	Transmission Electron Microscopy
	Infrared Spectroscopy	Thermogravimetric Analysis
	Nuclear Magnetic Resonance	Desorption at Programmed Temperature
	Raman Spectroscopy	Reduction to Programmed Temperature
	Scanning Electron Microscopy	Reaction to Programmed Temperature

It is proposed to study the critical properties of clay minerals, together with the characterization techniques used, that may affect the capture of CO_2. For this reason, the characterization techniques were established as a characteristic parameter. Clay mineral properties can directly favor the CO_2 capture by increasing the CO_2 adsorption capacity, for example the following: amine presence, thermal stability, or favorable textural properties (i.e. high specific surface area, porosity and pore volume). The mineral properties can also contribute to the study of its CO_2 adsorption capacity, for example the following: material identification, chemical composition before and after chemical pre-treatment, or CO_2 adsorption capacity. In the literature reviewed, the most applied characterization techniques and the properties most studied with these techniques are expressed in Table 6.

Table 6. *Reviewed properties in CO_2 adsorption studied with characterization techniques.*

Characterization technique	Properties studied
FTIR, XRD	Amine presence in clay Material identification Composition before and after clay pre-treatment and CO_2 adsorption
TGA	Thermal stability CO_2 adsorption capacity
Nitrogen adsorption	Adsorption equilibrium equations obtention CO_2 adsorption capacity
SEM	Material morphology Grain distribution Chemical composition

The techniques presented in Table 6 correspond to those reviewed in the scientific articles. At YTU, the laboratory equipment where these techniques can be performed belongs to different schools. The laboratory techniques, along with the school where the respective equipment for its execution is located, are the following: XRD, School of Chemical Sciences and Engineering; SEM, School of Earth and Environmental Sciences; FTIR, School of Biological Sciences; TGA, the equipment for the application of this technique is in the purchasing process. It can be seen that most of the equipment is available at the university, except for the equipment necessary for the adsorption and desorption of gases.

4.1.3. Sample pre-treatment

4.1.3.1. Raw clay mineral

Many authors have reported the CO_2 adsorption capacity by raw clay minerals (Gómez-Pozuelo et al., 2019; Grekov, Suzuki-Muresan, Kalinichev, Pré, & Grambow, 2020; Pajdak, Skoczylas, Szymanek, Lutyński, & Sakiewicz, 2020; Cecilia et al., 2018). These studies aim to compare the CO_2 capture capacity between raw clay minerals and the modified ones. The study of raw clay minerals adsorption capacity is also important because investigates the effects of environmental conditions in clays structure. Clay minerals and the genesis conditions change, so each material displays an inherent chemical composition and specific textural properties, supposing different adsorption capacity (Chouikhi et al., 2019).

4.1.3.2. Acid treatment

Acid treatment or activation constitutes a step for the synthesis of a catalyst (Figure 10) and consequently, for the synthesis of many adsorbents. Normally, metals are incorporated into a catalyst on a given substrate by a preparation method. The transformation of the metal phase into an active catalytic phase is carried out through an activation process usually carried out using an acid.

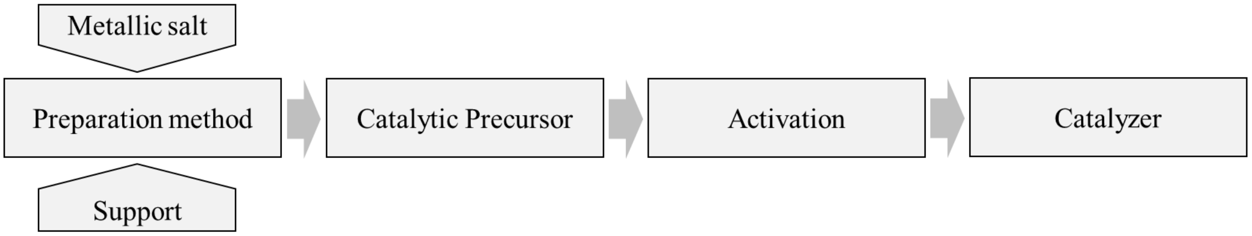


***Figure 10**. Steps for the synthesis of a catalyst.*

Acid activation has been studied as a chemical treatment method for the improvements of the textural and chemical properties of a clay mineral. (Wang et al., 2013). Regarding the textural properties, acid treatment can improve the CO_2 capture efficiency because of the higher surface area and pore volume it produces in the material. Also, the formation of an amorphous phase displays a higher CO_2 affinity of the clay (Horri et al., 2019). The modification of textural properties by acid treatment is studied by several authors, as shown in Figure 11.

Regarding chemical properties, acid treatment increases the number of acid sites. This means an enhanced catalytic and adsorptive process. The activation of a clay mineral by acid treatment is an easy and fast way to increase the porosity due to partial leaching of a phyllosilicate framework. However, despite being a cheap technology, is a technique that had not been applied to CO_2 capture processes until the last decade. (Chouikhi et al., 2019)

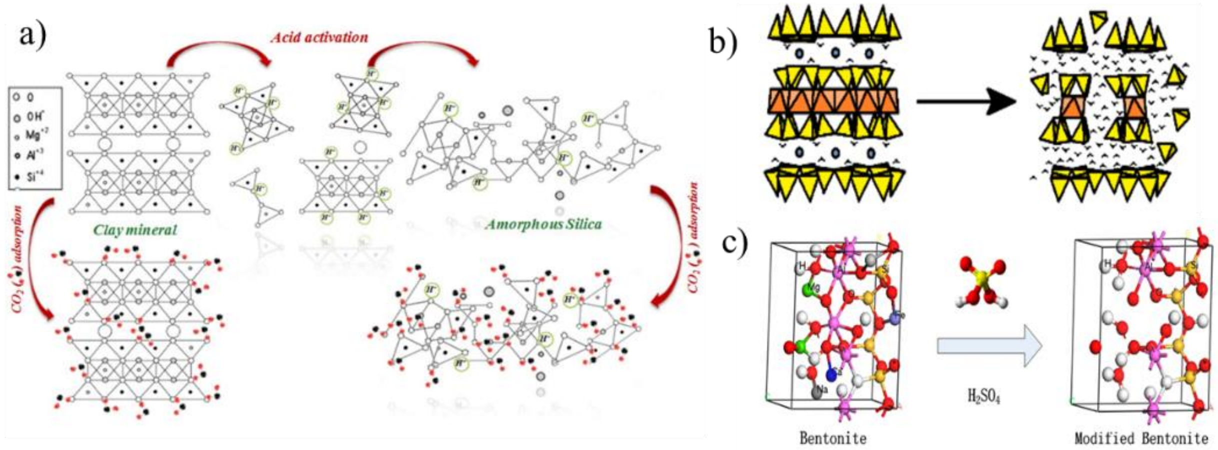


***Figure 11**. Modification of textural properties by acid treatment.*
Source: a) (Horri et al., 2019), b) (Chouikhi et al., 2019), c) (Wang et al., 2013)

4.1.3.3. Intercalation and pillarization

Intercalation compounds are formed from the more or less reversible insertion of a "host" species that can be atoms, ions, or molecules into a solid crystalline network called the host matrix. The network retains its structural integrity in intercalation and disintegration. That is, it is a topotactic process. These reactions occur at temperatures close to ambient temperature, which contrasts with most solid-state synthesis pathways, which occur at generally very high temperatures. (Rojas, 2019).

Usually, organic compounds are intercalated in clay minerals, forming organoclays, as shown in Figure 12. This chemical species can enhance CO_2 adsorption capacity by achieving the following: increase in the interlayer space; interaction between the weak base -OH sites and the CO_2 molecules; and strong affinity between the dendrimer and the CO_2 molecules.

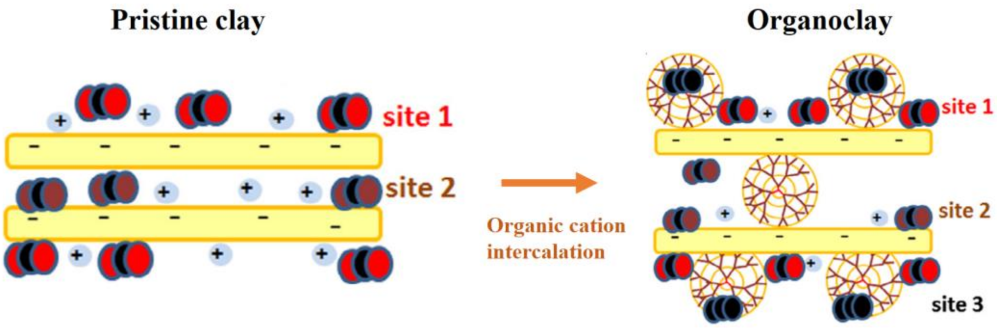


Figure 12. *Intercalation of an organic compound on smectite clay.*
Source: (Shah & Imae, 2016)

Pillared clays are related to the intercalation process. The pillarization can be a successive reaction to the intercalation. The pillared reactions consist of introducing certain types of voluminous polycations between the clay layers, which are consolidated as metal oxides by subsequent heating. The metal oxides species are anchored as pillars between the clay layers, providing a large microporosity to the clay (Rojas, 2019). The intercalation and pillarization reactions are shown in Figure 13.

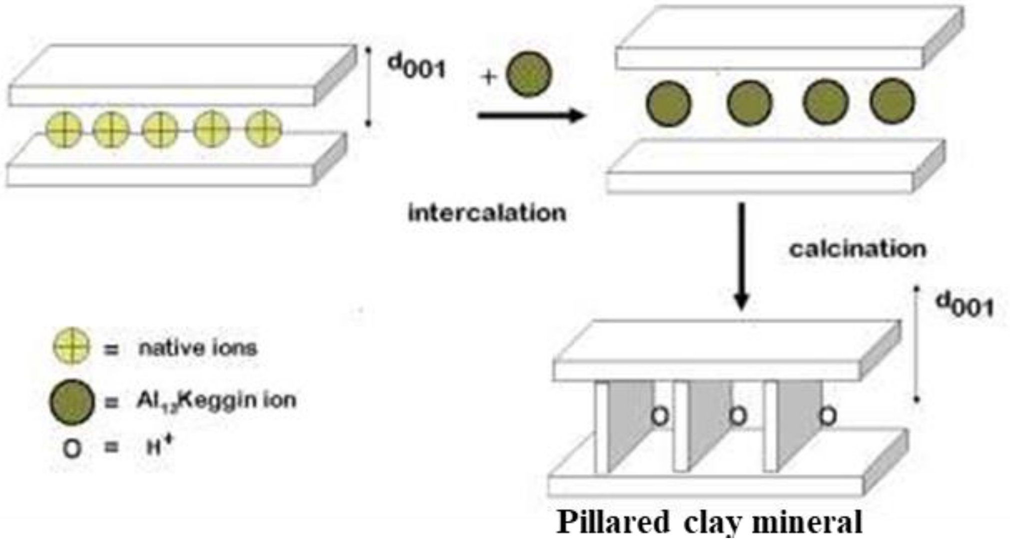


Figure 13*. Clay mineral intercalation reaction followed by a pillarization.*
Source: (Fatimah, Narsito, & Wijaya, 2011)

4.1.3.4. Materials synthesized from clay minerals

Clay minerals are abundant and low-cost materials with suitable properties to synthesize other adsorbents with a better CO_2 adsorption capacity than itself. Several works study the synthesis of zeolites from clay minerals. These materials present a high potential for CO_2 adsorption since the cage of zeolites (shown in Figure 14) can display appropriate dimensions to capture the CO_2 molecules through quadrupole interactions. Clay minerals can also synthetizes other materials like pillared clays (Gil, Trujillano, Vicente, & Korili, 2007) or other minerals, like gehlenite/stilbite (Bkour, Faqir, Shawabkeh, Ul-Hamid, & Bart, 2016).

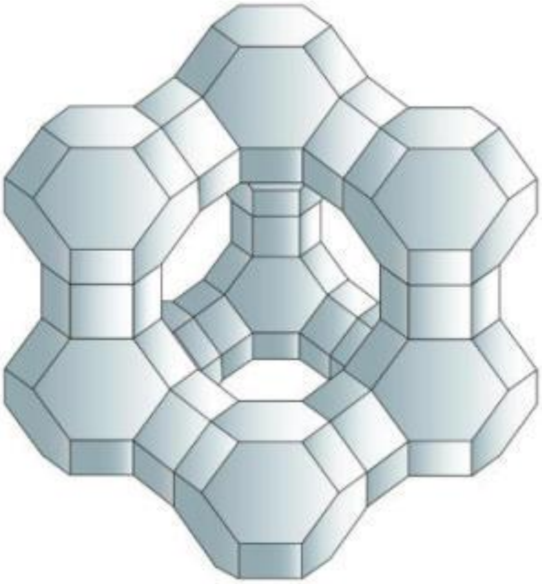


***Figure 14**. Zeolite structure.*

4.1.3.5. Functionalization with amine

The CO_2 adsorption capacity of clay can be improved by incorporating amine-species on its surface, which favors the chemical interactions with the CO_2 molecules. Several methodologies have been described to incorporate the amine species; the most common of these is the functionalization by grafting and the impregnation with an amine-rich polymer.

- **Grafting**

The grafting process is based on the formation of a covalent bond between the silanol groups of the surface of the adsorbent and aminosilane species to obtain hybrid adsorbents with high thermal stability, high water tolerance, and high selectivity towards CO_2. (Horri et al., 2019). This methodology is well described by authors like (Hiyoshi, Yogo, & Yashima, 2005). In the grafting process, hydrogen bonds are probably responsible for stabilizing the aminated compound with surface silanol groups, although CO_2 adsorption is restricted by diffusional considerations (Sanz et al., 2010). A simplified illustration of a grafting reaction is showed in Figure 15.

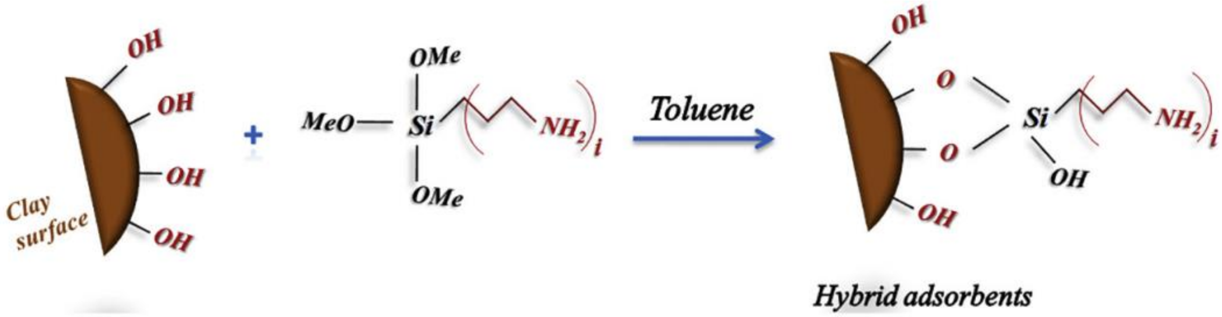


Figure 15. *Amine functionalization grafting procedure.*
Source: (Horri et al., 2019)

- **Impregnation**

The impregnation method consists of the incorporation of chemical species in the surface of the clay. This process constitutes a preparation method of a catalyst, as shown in Figure 16. Metals are typically incorporated into another chemical species called the support to form the catalyst. However, the impregnation of an amine-rich polymer using clay minerals as supports to disperse is a methodology that has been applied in recent years. This methodology has been widely described also for porous silicas or zeolites (Chouikhi et al., 2019).

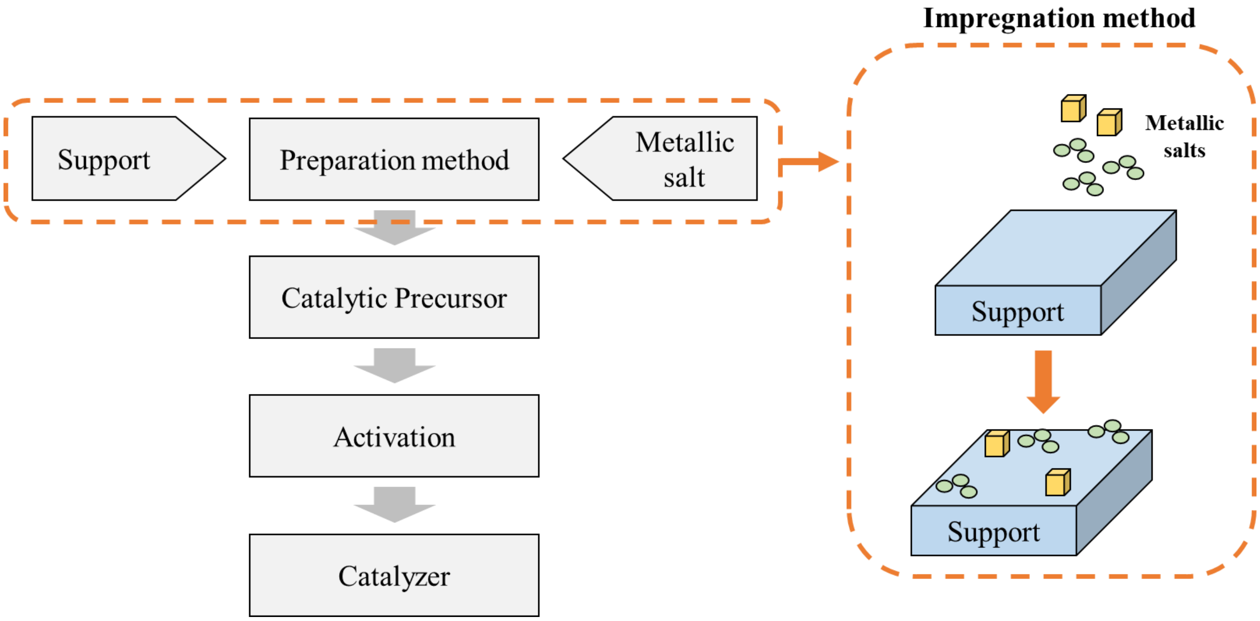


Figure 16. *Impregnation method as a preparation method of a catalyst.*

4.1.3.6. Cation exchange

Clay minerals have ions that can be exchangeable. When the ions are exchanged, variable loads are induced in the mineral responsible for the retention of anions. Due to their larger size, anions have lower mobility than cations, which is particularly important in the case of phosphate, or low solubility cations; in this case, it is more about fixation than exchange (García & Suaréz, 2014). A clay mineral cation exchange capacity occur for the following reasons: isomorphic substitutions within the structure, showed in Figure 17; existence of edges (decompensated surfaces) (García & Suaréz, 2014); dissociation of OH from basal layers, showed in Figure 17; and Van der Waals bonds.

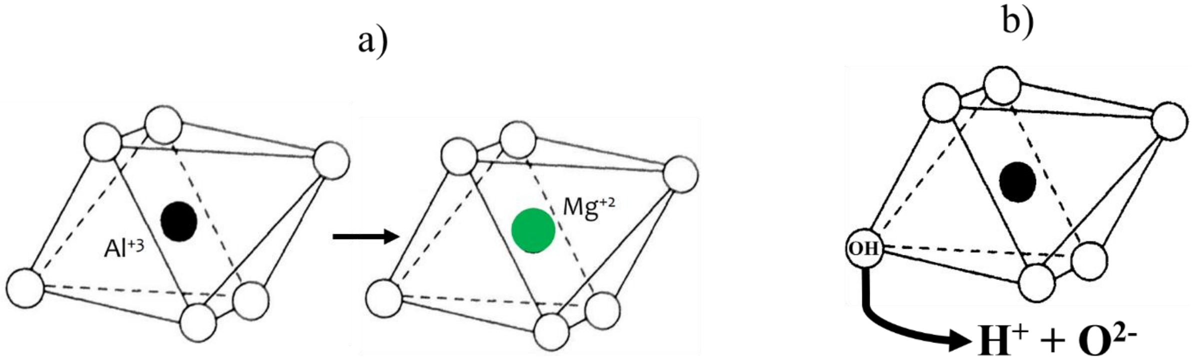


Figure 17. *Clay mineral exchanging cations: a) Isomorphic substitutions within the structure, b) dissociation of OH from basal layers.*
Source: a) (Patel, 2017)

The cation exchange effect on CH_4 and CO_2 adsorption capacity has been studied by several authors and concluded that the cation exchange increases CO_2 adsorption, especially at low pressure, but has a negligible effect on the overall CH_4 adsorption. (J. Zhang et al., 2016; Elkhalifah, Maitra, Bustam, & Murugesan, 2013; Grekov et al., 2020). The process of cation exchange by the various exchange salts positively affects the BET surface area and, thus, on CO_2 clay adsorption capacity. Combining exchange salt selection and optimization of exchange reaction conditions should be possible to achieve higher levels of gas retention (Melnitchenko, Thompson, Volzone, & Ortiga, 2000).

4.1.4. Pore size

Clay mineral is a material that presents porosity. The increase in porosity is a parameter that directly affects the CO_2 adsorption capacity. Shale, being a rock rich in clay minerals, is presented as a porous material. For this reason, authors such as G. Chen et al. (2016); Ross & Marc Bustin (2009) have studied the effect of pores on the CO_2 adsorption capacity of mineral clays and shales in general. These authors have established that the relationship between a clay mineral's porosity and its CO_2 adsorption capacity is affected by various physical-chemical and structural properties. For that reason, it can be said that this relationship can be very complex. In general, the CO_2 adsorption capacity of a clay mineral is favored the higher its porosity. In this work, clay minerals will be classified according to their porosity to determine if there is any relationship with CO_2

adsorption capacity. Their pore size can classify materials as macro-, meso- and microporous. The pore size can be obtained from different data analyses such as pore size distribution or the type of adsorption isotherm obtained. These and other textural properties of can be obtained through sortometry studies.

4.1.4.1. Sortometry

The sortometry is based on a high-performance analytical system to perform research-grade measurements of physical adsorption isotherms, using N_2, helium, argon, CO_2, or other non-corrosive gas as adsorbate; and to determine specific surface area, volume and total pore area and pore size distribution.

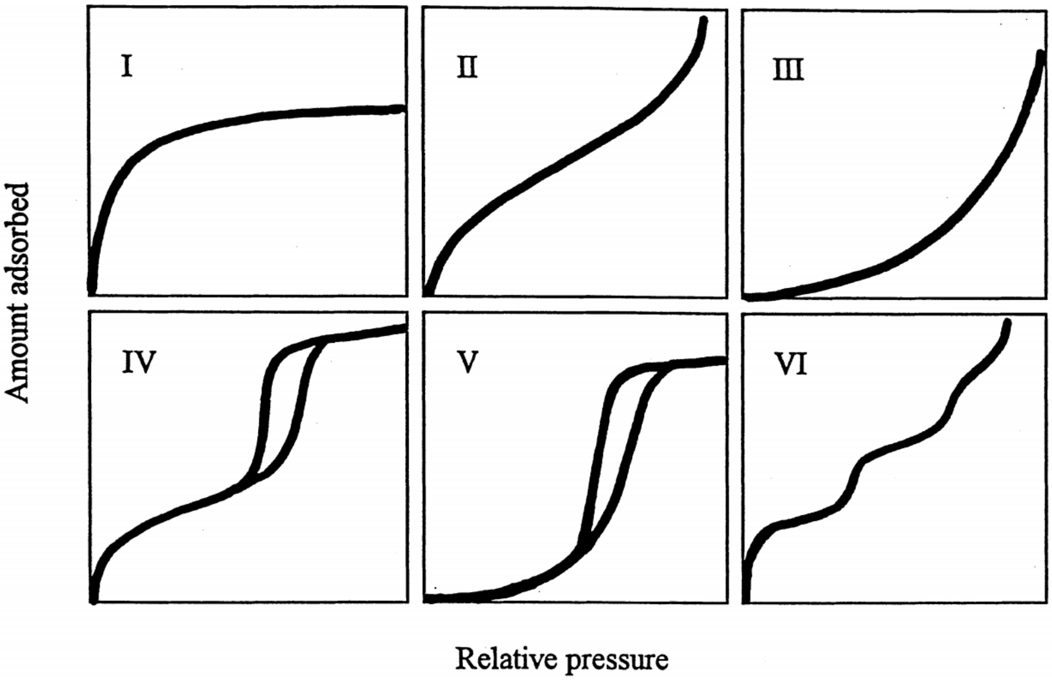


Figure 18. *Isotherm adsorption types.*
Source: (Donohue & Aranovich, 1998)

The experimental process of sortometry basically consists on adsorbing the gas on the material to be studied. From these data, an adsorption isotherm of any type can be obtained, shown in Figure 18. The type of isotherm obtained can establish the material's pore size, as shown in Table 7.

Table 7. *Isotherm types according to material porosity*

Material porosity	**Diameter**	**Isotherm type**
Microporous	d < 2 nm	I
Mesoporous	2 nm < d < 50 nm	IV, V
Macroporous	d > 50 nm	II, III
Non-porous	-	VI

The data obtained from sortometry can also be adjusted to adsorption equilibrium models such as the Langmuir, Brunauer, Emmett and Teller (BET), Freundlich model, among others. From these models, it is possible to obtain the measurement of other textural properties of the material, like the pore size distribution (Figure 19) and others, which are not of particular interest in this review.

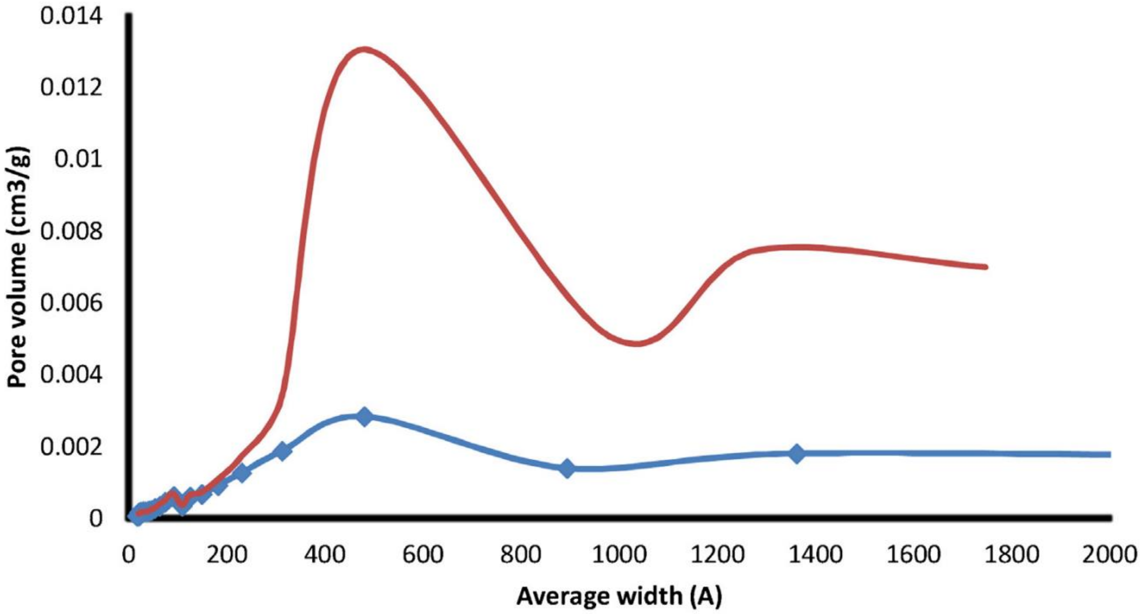


Figure 19. *Example of a sample pore size distribution.*
Source: (Bkour et al., 2016)

4.1.5. Water presence

The presence of water is an important characteristic parameter in the CO_2 adsorption capacity of clay minerals. Shale deposits are an alternative for CO_2 storage, and some of them are saturated with water. Shale is composed mainly of clay minerals and also organic matter. For this reason, it is important to study the influence of water on clay minerals. Several studies suggest that preloaded water in clay-rich shales significantly reduces gas sorption, and even in organic-rich shales, gas sorption capacity can be considerably reduced because of the moisture. The reason for this is that generally, clay minerals are hydrophilic. In this way, water can be easily adsorbed onto clay mineral surfaces, reducing the shale's total gas sorption capacity.

Hydrophilicity produces pore space saturation with water in shale media. Consequently, CO_2 sorption in clay nanopores is greatly reduced because of water presence. This occurs because water molecules cover the clay surfaces forming a water adsorption layer due to the hydrophilic clay surfaces. Water can reduce CO_2 sorption in clay nanopores even at very low water concentration in the exterior reservoir. (Jin & Firoozabadi, 2014).

4.1.6. Type of gas adsorbed

The type of gas adsorbed is a significant characteristic parameter to study as different industrial plants release different gas compositions. In this way, knowing the type of gas studied, it is possible to know in which industrial area the clay minerals reviewed in this work can be used. The gases reviewed in the literature were pure CO_2, CO_2/CH_4 mixtures, CO_2/N_2 mixtures, and $CO_2/CH_4/N_2$ mixtures. The CO_2 sources are mainly the burning of fossil fuels from the following types of industry, in decreasing order according to quantity: energy industry, cement production, refineries, iron and steel industry, petrochemical industry, oil and natural gas processing, among others. It then comes from biomass burning, coming from the industrial plants that produce bioethanol and bioenergy. The CH_4 sources are the following types of industry, in decreasing order according to the amount emitted: production and waste from the agricultural sector, production and use of fossil fuels, and burning of biomass and biofuel. The revised N_2 corresponds to the nitrogen used for the sortometry study.

4.1.7. Experimental system

The experimental system used to study CO_2 adsorption was reported. The importance of this is because from knowing the experimental system used, it can be known other characteristics that can affect CO_2 capture. These characteristics can be features of each experimental system. This parameter is detailed later. Experimental systems are used more frequently to study CO_2 capture. The types of CO_2 adsorption experimental systems reviewed were several. Among them, it was frequent the use of TGA equipments; Gravimetric Analysis equipments; sortometers, such as ASAP Apparatus 2020 (Micromeritics), Quantachrome Isorb Instrument HP1 or VTI Scientific Instruments; and lab-designed experimental systems, showed in Figure 20. The adsorption measurements obtained from studies by computer simulations were also reviewed. The most widely used simulation software is the Grand canonical Monte Carlo simulation.

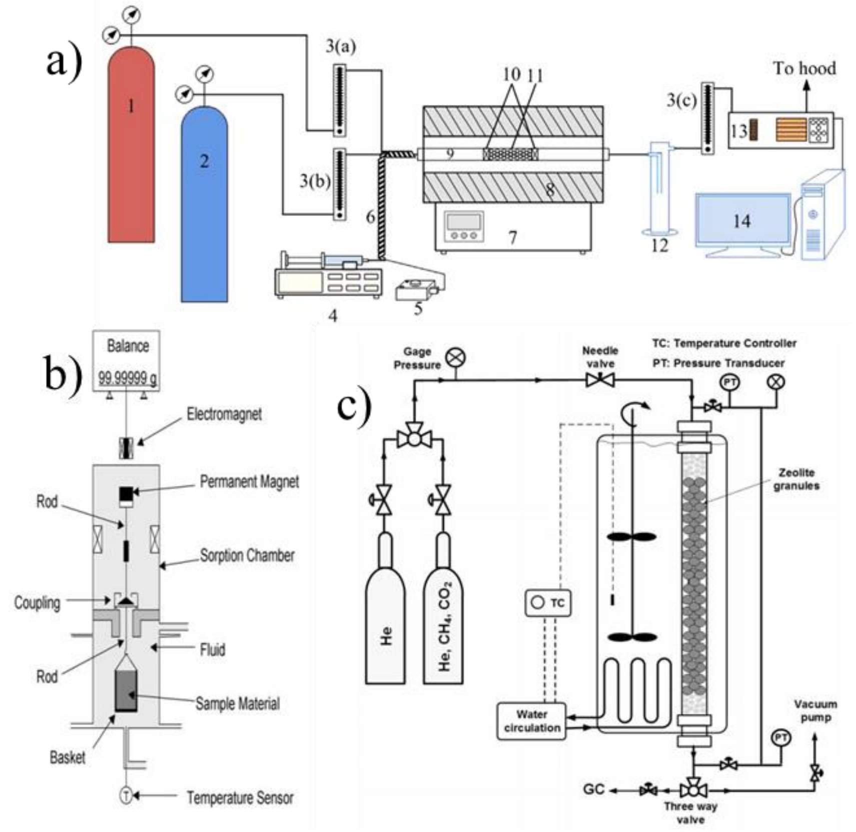


Figure 20. *Lab-designed CO_2 adsorption experimental systems with different devices: a) quartz tube reactor, b) magnetic suspension balance, c) adsorption column.*

Source: a) (Irani et al., 2015), b) (Elkhalifah, Bustam, Shariff, & Murugesan, 2014), c) (Arefi Pour, Sharifnia, Neishabori Salehi, & Ghodrati, 2016)

- **Setup characteristics**

The setup characteristics were taken as a characteristic parameter since each experimental system can have its particular characteristic that can influence the CO_2 adsorption capacity of the clay mineral. A magnetic suspension balance (MSB) was applied to measure the sample changes in weight. As shown in Figure 20-b, an MSB is a gravimetric device that makes it possible to weigh samples contactless under nearly all environments. Several authors used this technique (Atilhan et al., 2016; Bkour et al., 2016; Elkhalifah et al., 2014, 2013; Jeon, Choi, Yun, & Lee, 2014). The use of an adsorption column was not conventional at a laboratory scale. In Arefi Pour, Sharifnia, Neishabori Salehi, & Ghodrati (2016) work, an adsorption column, shown in Figure 20-c, packed with the clay sorbent, was used to analyze its chemical composition after adsorption. In some studies, the measured adsorption data is not in equilibrium since the sample's weight still showed an increasing trend after a long time after adsorption begins, likely due to a slow adsorption rate (Y. H. Chen & Lu, 2014; Wang et al., 2013). An important characteristic of the experimental systems reviewed was that in order to measure the amount of adsorbed CO_2, the change in the weight of the clay was measured (Cai et al., 2015; Y. H. Chen & Lu, 2014, 2015; Horri et al., 2019; Ouyang et al., 2018; Pajdak et al., 2020). The use of other apparatus in experimental systems was also characteristically, like using a quartz tube reactor, shown in Figure 20-a (Irani et al., 2015); a quartz crystal microbalance (Schaef et al., 2015), pressure transducers and temperature sensors.

4.1.8. Operating mode

The experimental processes reviewed mostly correspond to batch-type processes. This is because any adsorption reactor is sealed before adsorption occurs. After this, adsorption is normally allowed to occur for a period of time. Finally, the system can be opened to release gas that has not been adsorbed. All the experimental processes reviewed share some characteristics in general. In this way all the processes have been classified into two types of processes, these are described in Table 8.

Table 8. *Typical experimental processes in the reviewed literature.*

Experimental Process	General description	Observations
TEP1 : Typical Experimental Process 1	1. Heating and/with gas purge/purge gas to remove impurities or moisture. After that, the purge gas can be retired to achieve vacuum. 2. Temperature decrease to the desired one to adsorption occur. 3. Heating and gas purge injection to desorb CO_2.	Usually, N_2 is used to increase temperature and purge gas, i.e., remove impurities. Helium and argon are used just as purge gas.
TEP2 : Typical Experimental Process 2	1. Heating and pressure decrease to vacuum to remove impurities and moisture. 2.Temperature decrease to the desired one to adsorption occur. 3. Heating and pressure decrease to desorb CO_2.	

4.2. Operational conditions

4.2.1. Clay minerals CO_2 adsorption capacity

The CO_2 adsorption capacity of a clay mineral was taken as a reference operational condition. In this way, according to this value magnitude, the most favorable characteristic parameters and operational conditions will be categorized. From the data on this property provided by the literature, the efficiency of clay minerals in capturing CO_2 can be verified. As already mentioned, the use of aqueous amine-based absorbents is used as a conventional technology for CO_2 capture. In this way, in the Table 9 is showed the values of the CO_2 adsorption capacity using amine solvents with and clay minerals for comparison purposes. It can be seen in Table 9 that the CO_2 capture values with amine solvents are, in general, higher than those using clay minerals. However, the CO_2 capture values of clay minerals such as saponite, and improved palygorskite exceed most of those using amine solvents. Those amine solvent values that greatly outperform all others, including the other amines themselves, are the multiamines and cycloamines of TETA, TAEA, and AEP. In this way, the great potential that clay minerals have for CO_2 adsorption can be observed. All the values reviewed were reported in the units of milligrams of CO_2 adsorbed per grams of adsorbent because it was the most used unit in the articles reviewed.

Table 9. *CO$_2$ capture values using clay minerals and amine solvents.*
Source: Clay minerals data (Gómez-Pozuelo et al., 2019); Amine solvents data (Bernhardsen & Knuutila, 2017)

Clay mineral (45 ºC, 0.1 Bar)		**CO$_2$ adsorption capacity (mg CO$_2$/g adsorbent)**	**Amine solvents (30 ºC, 0.1 Bar)**		**CO$_2$ absorption capacity (mg CO$_2$/g solution)**
Raw clay minerals	Bentonite	25	Primary amines	MEA	58
	Saponite	35		SBA	65
	Sepiolite	50	Secondary amines	DEA	57
	Palygorskite	13		DIPA	50
Amine impregnated clay minerals	Bentonite	33	Multiamines	TETA	170
	Saponite	85		TAEA	168
	Sepiolite	59	Cyclemines	AEP	118
	Palygorskite	73		2.5 DMPZ	33

4.2.2. Pressure

Le Chatelier's principle states that if a gaseous system's pressure increases in equilibrium, the system moves towards fewer moles. The adsorption of molecules on an adsorbent reduces the number of moles in the system. In this way, at higher pressure, an increasing amount of molecules will be adsorbed. The relationship between magnitude of adsorption and pressure can also be expressed mathematically by the Freundlich Adsorption equilibrium equation, shown as Eq. (1).

$$\frac{x}{m} = Kp^{1/n} \qquad (1)$$

where: x is the amount of gas adsorbed per unit mass of adsorbent at pressure p; K and n are constantly depending in the nature of gas and the adsorbent. The value of n is less than 1; and therefore, a does not increase as rapidly as p.

The variation of the adsorption extent with pressure at a given constant temperature is showed graphically by adsorption isotherms, showed in Figure 18. In the adsorbent, there are a limited number of active sites, in which adsorption can occur. It means initially the rate of adsorption will get increased until a point is reached when all the active sites are filled. After this the rate of adsorption becomes independent of the pressure.

In order to evaluate the efficiency of the characteristic parameters, it is desired to know the value of the CO_2 adsorption capacity, under different characteristic parameters, at the same operating conditions. In the case of pressure, the CO_2 adsorption capacity value was taken at 1 bar, or the closest to it.

4.2.3. Temperature

Le Chatelier's principle states that increasing temperatures favor the endothermic direction of the reaction. Adsorption is an exothermic process, as shown in Eq. (2), so the increase in temperatures disfavor adsorption.

$$Gas\ (adsorbate) + Solid\ (adsorbent) = Gas\ adsorbed\ on\ solid + Heat \tag{2}$$

It can be seen that the relation between temperature and the adsorbed quantity is inversely proportional. This can also be demonstrated by plotting the amount absorbed at different temperatures at constant pressure. The equation that describes the adsorption rate, under the conditions mentioned, is given by a complex expression (Morrison, 1990). The graph of this expression is shown in Figure 21. This graph corresponds to the physisorption in a temperature range at constant pressure, which corresponds to an isobar. It this way, it can also be seen graphically that the relation between temperature and the adsorbed quantity is inversely proportional.

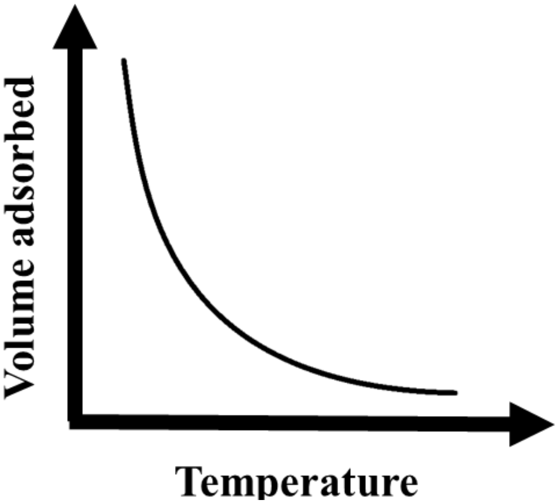


Figure 21. *Physisorption isobar*
Source: Adapted from Morrison (1990)

To evaluate the efficiency of the characteristic parameters, it is desired to know the value of the CO_2 adsorption capacity, under different characteristic parameters, at the same operational conditions. In the case of temperature, the CO_2 adsorption capacity value was taken at 25 ºC or the closest to it.

4.2.4. CO_2 selectivity

Selectivity refers to how much of the desired product (CO_2) was adsorbed relative to the product (s) that are not desired to be adsorbed (CH_4, N_2). In the study of CO_2 capture from a gas mixture, the clay mineral should count with CO_2 selectivity. Some factors can influence the CO2 selectivity in the clay mineral, such as moisture content, pressure, temperature, pore size/shape and others. The selectivity of CO_2 over CH_4 declines with the rise of moisture content (Jin & Firoozabadi, 2014). The increase in pressure means the CO_2 selectivity decreases logarithmically and is lower with a higher temperature at the same pressure (Kang, Zhang, Kang, Guo, & Zhao, 2020). It has been previously reported that, for porous sorbents, CO_2 adsorption selectivity over other gas species is controlled by a combination of factors such as the pore size/shape, thermodynamics and relative gas densities of adsorbed species (Nicholson & Gubbins, 1996).

CHAPTER V

5. REVIEWED DATA ANALYSIS

5.1. Characteristic parameters

In this work, several characteristic parameters that influence CO_2 adsorption capacity in clay minerals have been reviewed. These characteristic parameters are the nature of the sample, properties studied with characterization techniques, sample pre-treatment; pore size, water presence, and other experimental parameters. All these characteristic parameters will not be analyzed since some have been revised to study additional experimental process details. In the analysis of the results, only the following characteristic parameters will be discussed in the next order of importance: sample pre-treatment, additives, presence of water, pore size and nature of the sample. In general, in Table 10, there is a similar pattern for all clay minerals concerning the sample pre-treatment type due to its CO_2 adsorption capacity. In this way, a general order can be established in which the sample pre-treatment favor the CO_2 adsorption capacity in the following decreasing order:

Amine functionalization by impregnation > Materials Synthesized from clay minerals > Amine functionalization by grafting > Acid activation > Raw clay mineral

The nature of the sample, pore size, and water presence, unlike sample pre-treatment, do not present a similar pattern. For this reason, a direct relationship between the mentioned parameters cannot be established with CO_2 adsorption capacity. The additives used and the presence of water will be taken into account to analyze each type of mineral clay as follows:

Kaolinite, in Table 10, first presents a sample raw clay sample; this data is inconsistent. This is due to the favorable operational conditions (50 bar, 25 °C) of this sample. The other sample pre-treatment types follow the color pattern.

Bentonite, as can be seen in Table 10, complies with the established color pattern.

Montmorillonite partially follows the established color pattern. It can be seen that in third place, there is an organic compound intercalated sample; in the case of smectite, this sample pre-treatment type comes first. For this reason, it can be said that this process can moderately favor CO_2 adsorption capacity. The efficiency of the intercalation could depend significantly on the additive intercalated. It can be seen that in the fourth place, there is an impregnated sample; however, the impregnated species is NaOH, not an amine as usual. Thus it can be seen that an impregnated mineral clay is most favored if the impregnated additive is an amine. Concerning pillarization, a sample treated in this way is presented in the seventh and eighth places, corresponding to intermediate positions. The halloysite also contains a pillared sample in the intermediate places. This fact could indicate that pillarization moderately favors CO_2 adsorption capacity. However, there is no water present in these three data, which favors the CO_2 adsorption capacity, and more data should be available to know more exactly how favorable the pillarization process is for the CO_2 adsorption capacity. Concerning the cation exchange samples, in montmorillonite and smectite, they are located behind other pre-treatment types that moderately favor CO_2 adsorption capacity. In this case, there are a total of five samples, which is a significant number. For this reason, it could be said that the cation exchange pre-treatment favors the CO_2 adsorption capacity to a lesser extent.

Table 10. *Sample pre-treatment types ordered by their CO_2 adsorption capacity.*

Clay mineral	**SAMPLE PRE-TREATMENT TYPE**													
	<—————————————————— CO_2 ADSORPTION CAPACITY													
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
Kaolinite	Raw clay	Amine functionalization by Impregnation	Materials Synthesized from Clay Minerals (Zeolite Y)	Raw clay	Raw clay	Activated by Acid Treatment	Raw clay							
Bentonite		Materials Synthesized from Clay Minerals (Zeolite 13X)	Acid treatment and impregnation	Amine functionalization by impregnation	Amine Impregnation	Amine functionalization by grafting	Acid activation and grafting	Activated by Acid Treatment	Raw clay					
Montmorillonite		Materials Synthesized from Clay Minerals (Zeolite A)	Amine functionalization by impregnation	Organic compound intercalation	Impregnation	Amine functionalization by grafting	Pillarization + Cation exchange	Pillarization	Acid activation	Raw clay	Raw clay	Carion exchange	Cation exchange	Grafting + Impregnation
Halloysite	Raw clay	Amine functionalization by impregnation	Impregnation	Acid treatment	Pillarization	Raw clay	Amine functionalization by grafting	Acid treatment						
Saponite		Amine functionalization by impregnation	Materials Synthesized from Clay Minerals (Pillared clays, PILCs)	Amine functionalization by grafting	Raw clay									
Sepiolite		Amine functionalization by impregnation	Raw clay	Amine functionalization by grafting	Grafting + Impregnation	Activated by Acid Treatment								
Palygorskite		Amine functionalization by impregnation	Amine functionalization by grafting	Grafting + impregnation	Activated by Acid Treatment	Raw clay								
Smectite		Intercalation	Cation exchange	Cation exchange	Cation exchange	Acid and Thermal treatment								

LEGEND	**COLOR**
Most favorable	🟧 🟩
Moderately favorable	⬜
Less favorable	🟨 🟥
Rejected because of their favorable Operational Conditions	⬛
Rejected for lack of sense	🟦
Common color pattern	🟧 🟩 ⬜ 🟨 🟥

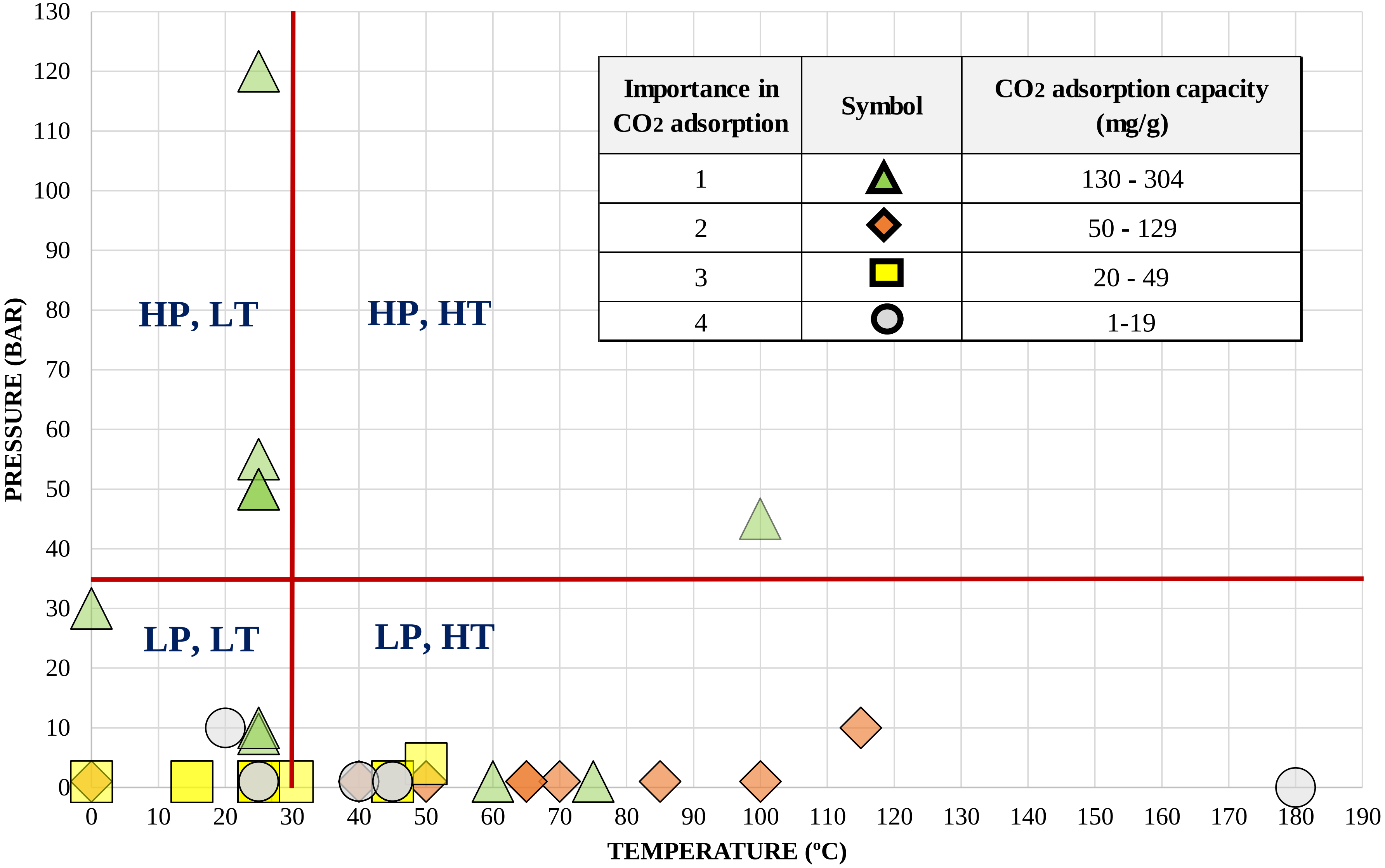
Halloysite partially follows the established pattern. It can be seen that in the first place, there is a raw clay sample, this data is inconsistent; this is due to its favorable operational conditions (30 bar, 0 ºC). Acid treatment is in third place; despite being already mentioned as one of the least favorable sample pre-treatment type. In all cases where the acid treatment is classified as an ineffective pre-treatment type, acids such as H_2SO_4, HCl or HNO_3 were used. In this case, ethylenediaminetetraacetic acid (EDTA) is used, which is clearly a better additive than the other acids mentioned because it better favors CO_2 adsorption capacity. It can be seen that the samples treated with pillarization and amine grafting are found to be moderately favorable pre-treatment types.

Saponite follows the established color pattern.

Sepiolite shows in second place a raw clay sample; this data is inconsistent; this is due to the favorable operational conditions (120 bar, 25 ºC) of this sample. The other pre-treatment types partially follow the established color pattern.

5.2. Operational conditions

The experimental system at YTU laboratory can reach pressures and temperatures up to 35 bar and 30 ºC, as reported by Villarroel (2020). Thus, these values will be taken as high pressures and high temperatures. In the analysis of results, a cartesian plane divided into four quadrants will be established, according to whether they present High (H) or Low (L) Pressure (P) or Temperature (T). In this way, the quadrants will be named as (HP, LT), (LP, LT), (HP, HT) and (LP, HT). In the Cartesian plane, the data obtained from the review will be placed and in this way, the samples' operational conditions will be displayed according to their CO_2 adsorption capacity. The Figure 22 presents the aforementioned Cartesian plane.



Importance in CO2 adsorption	Symbol	CO2 adsorption capacity (mg/g)
1	▲	130 - 304
2	◆	50 - 129
3	■	20 - 49
4	●	1-19

***Figure 22**. Operational conditions reviewed data.*

The data presented in the previous figure will be quantified in Table 11 to perform the following analysis

Table 11. *Operational conditions analysis.*

Importance in CO_2 adsorption	Operational Conditions	Quadrant	Symbol	Number of appearances
1	> 35 BAR , < 30 °C	**HP, LT**	▲	5
			🔶	0
			🟨	0
			⚪	0
2	< 35 BAR , < 30 °C	**LP, LT**	▲	7
			🔶	5
			🟨	11
			⚪	5
3	> 35 BAR , > 30 °C	**HP, HT**	▲	1
			🔶	0
			🟨	0
			⚪	0
4	< 35 BAR , > 30 °C	**LP, HT**	▲	2
			🔶	10
			🟨	4
			⚪	8

In the quadrant (HP, LT) exists by theory the most favorable operational conditions for the CO_2 adsorption capacity, as already mentioned before. It can be seen that there exists in (HP, LT) a significant number of green triangles. This is not the highest number; however, it is acceptable. In the quadrant (LP, LT), there is the largest number of green triangles. As already mentioned, the CO_2 adsorption capacity values were taken at 1 bar and 25 °C, or the closest to this. In this way, in

(LP, LT) there will be the highest number of points of all classes. In this way, this quadrant corresponds to the operational conditions that most favor the CO_2 operational conditions.

It can be seen that in the quadrant (LP, LT) there are the largest number of green triangles, orange diamonds and yellow squares. As already mentioned, this is because all the data close to the conditions of 1 bar and 25 ºC were taken. Despite this, these operational conditions (Low pressures and temperatures) are taken as the second most favorable for the CO_2 adsorption capture due to their high number of triangles and rhombuses.

In the quadrant (HP, HT), there is the least number of data than all the quadrants. However, this quadrant's only data corresponds to the sample with the second-highest CO_2 adsorption capacity (295 mg / g). For this reason, it could be said that the High Pressure and Low-Temperature conditions are the following favorable conditions for CO_2 adsorption capacity.

It can be seen that in the quadrant (LP, HT) there is the greatest amount of gray circles. This fact makes sense since this quadrant corresponds to the least favorable conditions.

In general, it can be said that the operational conditions favor the CO_2 adsorption capacity in the following order:

(HP, LT) > (LP, LT) > (HP, HT) > (LP, HT)

An analysis by the type of clay mineral can be made by analyzing Figure 23. In the figure, the operational conditions of the individual clay minerals are showed, from this figure, the following can be established:

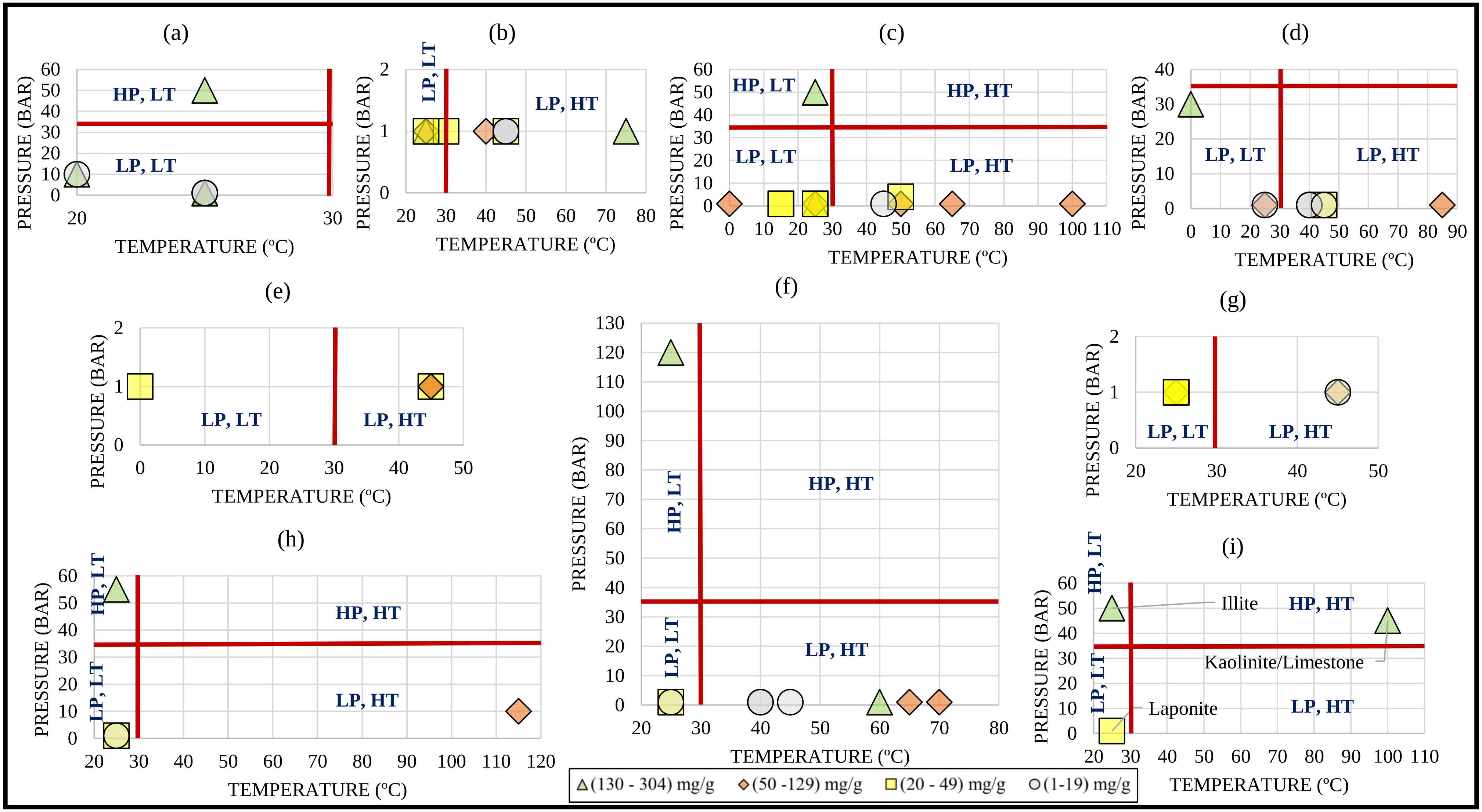


Figure 23. *Operational conditions reviewed for each clay mineral: a) Kaolinite, b) Bentonite, c) Montmorillonite, d) Halloysite, e) Saponite, f) Sepiolite, g) Palygorskite, h) Smectite, i) Other clay minerals.*

Figure 23-a, c, h show triangles in the most favorable area (HP, LT) which is logical. Figure 23-e, g show a square in a favorable zone, (LP, LT), which also follows the established logic of operational conditions.

In Figure 23-b, there are some bentonite samples inconsistent with the aforementioned. There is a triangle and a rhombus in the least favorable conditions, (LP, HT). This is because the triangle sample exhibits an amine impregnation pre-treatment and acid treatment. In the same way, whe rhombus sample shows amine impregnation. In Figure 23-d, the halloysite shows a sample of a rhombus in the least favorable area, (LP, HT). This sample is treated with amine impregnation. The sepiolite, in Figure 23-f, has two rhombuses in the least favorable part, (LP, HT). This is because these samples are functionalized with amine, by impregnation and grafting.

In the clay mineral kaolinite / limestone diagram, in Figure 23-i, shows a sample represented with a triangle in the least favorable part, (LP, HT). The mentioned sample is justified because it has a favorable pre-treatment, it is a material synthesized from clay minerals.

It can be seen that in Figure 23 that in no case is there a gray circle in the most favorable area (HP, LT). This fact makes it even clearer that these conditions are the most favorable for CO_2 capture. There are triangles and diamonds in less favorable areas, but as explained above, this is due to the types of pre-treatments applied. These pre-treatments normally correspond to the most beneficial one, the amine impregnation pre-treatment.

CONCLUSIONS AND RECOMMENDATIONS

- The main characteristics of CO_2 capture technologies have been reviewed and the characteristics of clay minerals that make them a potential emerging technology in this area have been pointed out.

- It has been shown that the scientific community is interested in the development of clay minerals as a technology for this field due to the increase in studies on this topic since the year 2001.

- The main properties and characteristics that make clays potential candidates for CO_2 adsorption are their low cost, high availability and high CO_2 adsorption capacity. The Ecuadorian clays indicated in the work count with these properties.

- The characteristic parameter with the highest influence on CO_2 adsorption is the sample pre-treatment. This is because in most clay minerals, the different pre-treatment types contribute in almost the same way to increase the clay mineral CO_2 adsorption capacity.

- The pre-treatments types favor the clay mineral CO_2 adsorption capacity of in the following decreasing order: amine impregnation, materials prepared with clay minerals, amine grafting, pre-treatment with acid and clay minerals without pre-treatment

- The characteristic parameters of the nature of the sample, pore size and presence of water do not have a considerable influence on the CO_2 adsorption capacity. Despite this, its influence is evident, even if it is minor

- The other characteristic parameters studied, such as properties studied with different characterization techniques, experimental system; setup characteristics; and the operation mode, were reviewed, established and will serve to facilitate the investigation of clay minerals for CO_2 capture.

- The favorable clay mineral operational conditions for CO_2 capture were established, and these are, in decreasing order according to their contribution to the mineral CO_2 adsorption capacity: (HP, LT), (LP, LT), (HP, HT) and (LP, HT).

- It is recommended, for future research on this subject, not only to quantify the characteristic parameter of the CO_2 absorption capacity to categorize a clay mineral as a potential solid sorbent. In addition to these, quantify other important parameters that a solid sorbent should have, such as regeneration capacity, availability, price, kinetics, chemical and mechanical stability.

- It is recommended for future work on this topic to make use of this work so that it serves as a guide for the investigation of clay minerals in the capture of CO_2.

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APPENDIX

Table A.1*. Reviewed data matrix*

					CHARACTERISTIC PARAMETERS															**OPERATIONAL CONDITIONS**			
Scientific article					**Sample features**											**Experimental system**							
Nº	**Title**	**Authors**	**Year**	**Clay mineral studied**	**Samples nature**	**Characterization techniques**						**Samples preparation and pre-treatment**	**Additives**	**Pore size**	**Water presence**	**Type of gas**	**Experimental system**	**Operating mode**	**Setup characteristics**	**Pressure (bar)**	**Temperature (ºC)**	**CO_2 adsorption capacity (mg CO_2/g adsorbent)**	**Selectivity (for mixtures)**
						FTIR	**XRD**	**TGA**	**N_2 Adsorption**	**SEM**	**Others**												

1	Adsorption Mechanism of CO_2/CH_4 in Kaolinite Clay: Insight from Molecular Simulation	Zhou, W. et al.	2019	**Kaolinite**	Natural							Raw clay	NA	Mesoporous	Present	CO_2/ CH_4 mixture	Software simulation (Grand canonical Monte Carlo simulation)	NA	NA	50	25	**220**	1.4

2	Amine modification on kaolinites to enhance CO_2 adsorption	Chen, Y. & Lu, D.	2014			x	x	x	x			Amine functionalization by Impregnation	MEA + DEA	Mesoporous	Not present	Pure CO_2	Thermogravimetric analyser/Semi-batch	TEP1 using N2 as purge gas	The change in the weight of the sample during adsorption/desorption processes, measured through TGA, was used to calculate CO_2 adsorption capacity. The adsorption capacity measured through TGA in our study is not an equilibrium adsorption capacity.	1	25	**144**	

3	CO_2 adsorption properties of ion-exchanged zeolite Y prepared from natural clays	Djeffal, N. et al.	2017		Natural	x	x		x	x		Materials Synthesized from Clay Minerals (Zeolite Y)	NA	Microporous	Present	Pure CO_2	ASAP 2020 (Micromeritics) apparatus/Semi-batch	TEP2	NA	1	25	**130**	
4	N2 and CO_2 Adsorption by Soils with High Kaolinite Content from San Juan Amecac, Puebla, México	Quiroz-Estrada, K. et al.	2016		Natural		x		x			Raw clay	NA	Microporous and mesoporous	Not present	Pure CO_2	GOW-MAC 350 gas chromatograph (GOW-MAC Instrument Co., Bethlehem, PA, USA)	TEP1 using He as purge gas	CO_2 adsorption was evaluated with a gas chromatograph provided with a thermal conductivity detector	0.02	180	**4.6**	

5	Amine modification on kaolinites to enhance CO_2 adsorption	Chen, Y. & Lu, D.	2014		Natural	x	x	x	x			Raw clay	NA	Mesoporous	Not present	Pure CO_2	Thermogravimetric analyser	TEP1 using N2 as purge gas	The change in the weight of the sample during adsorption/desorption processes, measured through TGA, was used to calculate CO_2 adsorption capacity. The adsorption capacity measured through TGA in our study is not an equilibrium adsorption capacity.	1	25	**3**	

6	CO_2 capture by kaolinite and its adsorption mechanism	Chen, Y. & Lu, D.	2014		Natural		x	x	x	x		Activated by Acid Treatment	H2SO4	Mesoporous	Not present	Pure CO_2	Thermogravimetric analyser/Semi-batch	TEP1 using N2 as purge gas	On the basis of the change in the weight of the sample, measured using TGA, the CO_2 adsorption capacity of the sample was calculated	1	25	**3**	
7	Effect of Pressure and Temperature on CO_2 CH_4 Competitive Adsorption on Kaolinite by Monte Carlo Simulations	Kang, G. et al.	2020		Natural							Raw clay	NA	NA	Not present	CO_2/ CH_4 mixture	Software simulation (Grand canonical Monte Carlo simulation)	NA	NA	10	20	**1.56**	6
8	CO2 capture using zeolite 13X prepared from bentonite	Chen, C., Park, D. & Ahn, W.	2013				x		x	x		Materials Synthesized from Clay Minerals (Zeolite 13X)	NA	Microporous	Not present	CO2/N2 mixture	SCINCO thermal gravimeter S-1000/Semi-batch	TEP1 using He as purge	The sample was loaded into an alumina sample pan.	1	25	**211**	37

9	Sulfuric Acid Modified Bentonite as the Support of Tetraethylene pentamine for CO2 Capture	Wang, W. et al.	2013		Natural		x	x	x	x		Acid treatment and impregnation	H2SO4 and TEPA	Mesoporous	Present	Pure CO2	thermogravimetric analyzer (TGAQ600SDT) and Fixed-Bed Flow System	TEP1 using N2 as purge gas	Sorption capacity measured by TGA in this study is not an equilibrium sorption capacityThe amount of water introduced in the flue gas was measured using a water bubbling temperature controller	1	75	**190**	

10	Carbon Dioxide Retention on Bentonite Clay Adsorbents Modified by Mono-, Di- and Triethanolamine Compounds	Elkhalifah, Ali. et al.	2014	**Bentonite**	Natural		x					Amine functionalization by Impregnation	MEA	NA	Not present	Pure CO2	Sorption chamber/Semi-batch	TEP2	A magnetic suspension balance was used to measure the changes in weight of the sample.	1	25	**129**	
11	Liquid-Impregnated Clay Solid Sorbents for CO2 Removal from Postcombustion Gas Streams	Siriwardane, R. & Robinson, C.	2009		Natural							Amine Impregnation	MEA	Mesoporous	Present	Pure CO2	Thermogravimetric analyzer	TEP1 using N2 as purge gas	Usage of an apparatus (Cahn 500 Thermomax 500 unit) to obtain the fractional CO2 conversions and rate of CO2-uptake information.	1	40	**92.4**	

12	CO2 adsorption on amine-functionalized clays	Gómez-Pozuelo, G. et al.	2019	Natural	x	x		x		T-plot method	Amine functionalization by grafting	(3-aminopropyl)-trimethoxysilane	Mesoporous	Present	Pure CO2	VTI Scientific Instruments HVPA-100/Semi batch	TEP2	Cyclic adsorption-desorption measurements were carried using argon as purge gas. For this, a fix bed reactor coupled to a mass spectrometer was applied.	1	45	**43**	
13	Amine grafting of acid-activated bentonite for carbon dioxide capture	Horri, N. et al.	2019	Natural	x	x		x		Elemental analyses	Acid activation and grafting	HCl, Amino-propyl and diethylene-triamine	Mesoporous	Present	Pure CO2	thermal gravimetric analyzer (SDT Simultaneous 2960, TA Instruments apparatus)/	TEP1 using N2 as purge gas	Based on the weight increases/decreases during the adsorption process	1	30	**29.2**	

14	Modified bentonitic clay minerals as adsorbents of CO, CO2 and SO2 gases	Venaruzzo, J.L. et al.	2002	Natural		x		x		plasma emission spectroscopy (PES)	Activated by Acid Treatment	HCl	Microporous and mesoporous	Not present	Pure CO2	Standard volumetric apparatus/Semi-batch	TEP2	Gases were dried by passing through presorbers before entering the system	1	25	**24**	
15	CO2 adsorption on amine-functionalized clays	Gómez-Pozuelo, G. et al.	2019	Natural	x	x		x		T-plot method	Raw clay	NA	Mesoporous	Present	Pure CO2	VTI Scientific Instruments HVPA-100/Semi-batch	TEP2	Cyclic adsorption-desorption measurements were carried using argon as purge gas. For this, a fix bed reactorcoupled to a mass spectrometer was applied.	1	45	**14**	

16	Adsorption separation of CO2/ CH_4 on the synthesized NaA zeolite shaped with montmorillonite clay in natural gas purification process	Pour, A. et al.	2016	**Montmorillonite**	Natural	x	x		x	x		Materials Synthesized from Clay Minerals (Zeolite A)	NA	Mesoporous	Present	CO2/ CH_4 mixture	Lab designed experimental system/Semi-batch	TEP1 using He as purge gas	The experimental system was equipped with an fixed-bed column.	1	25	**220**	7.1
17	High-Pressure Methane, Carbon Dioxide, and Nitrogen Adsorption on Amine-Impregnated Porous Montmorillonite Nanoclays	Atilhan, M. et al.	2016		Natural	x		x		x	Elemental analysis	Amine functionalization by Impregnation	Dimethyl dialkyl (C14−C18) amine	Mesoporous	Present	CO2/ CH_4/N2 mixture	Micromeritics ASAP/Semi-batch	TEP2	Magnetic suspension apparatus (MSA) was used to obtain the gas quantity adsorbed by nanoclay materials	50	25	**213.44**	2:1:1

18	TPD study of the reversible retention of carbon dioxide over montmorillonite intercalated with polyol dendrimers	Azzouz, A. et al.	2009		Natural							Organic compound intercalation	Polyols	Mesoporous	Not present	Pure CO2	Thermal programmed desorption (TPD) column	TEP1 using N2 as purge gas	Slow injection was required to avoid pore obstruction due to quick gas accumulation at the pore entry	1	25	**110**	
19	Exploiting response surface methodology for experimental modeling and optimization of CO2 adsorption onto NaOH-modified nanoclay montmorillonite	Khajeh, M. & Ghaemi, A.	2019		Natural	x	x		x	x		Impregnation	NaOH	mesoporous	Not present	Pure CO2	Stainless steel reactor/	TEP1 with N2	Adsorbent samples are prepared in a powder form All data is stored during the adsorption including temperature (K), pressure (bar) and time (s) in Excel tables per second by computer.	1	65	**105.55**	

20	Preparation and CO2 adsorption of diamine modified montmorillonite via exfoliation grafting route	Stevens, L. et al.	2012		Natural		x	x			Flash elemental analysis. Diffuse reflectance Fourier transform infrared spectra (DRIFTS)	Amine functionalization by grafting (Exfoliated-montmorillonite)	N-2-aminoethyl-3-aminopropyl trimethoxysilane	Mesoporous	Present	Pure CO2	Thermogravimetric Analyser Q500 (TA Instruments)/Semi-batch	TEP1 using N2	The CO2 adsorption capacity was determined from the weight change in CO2	1	100	**105**	
21	Alkali metal-promoted aluminum-pillared montmorillonites High-performance CO2 adsorbents	Wu, K. et al.	2020		Natural		x		x			PillarizationCation exchange	AlCs	Microporous and mesoporous	Not present	Pure CO2	Thermogravimetric analyzer (STA449F5, NETZSCH, Germany)	TEP2	The sample was placed in an alumina oxide pan	1	50	**102.3**	

22	CO2 Adsorption by Several Types of Pillared Montmorillonite Clays	Wang, K., Yan, X. & Komarneni, S.	2018		Natural		x		x			Pillarization	TiO2 + SiO2	Mesoporous	Not present	Pure CO2	Quantachrome Autosorb-1 sorption analyzer/	TEP2	NA	1	0	**51.93**	
23	Efect of acid activation on the CO2 adsorption capacity of montmotillonite	Horri, N. et al.	2020		Natural	x	x	x	x		Elemental analyses Nuclear magnetic resonance (NMR)	Acid activation	HCl	Mesoporous	Not present	Pure CO2	Volumetric analyzer (Scientifc Instruments HPVA-100, VTI)/Semi-batch	TEP1 using N2	Dual-site Sips model was used to fit the experimental data of the functionalized material	1	15	**26.7**	

24	Preparation and CO2 adsorption of diamine modified montmorillonite via exfoliation grafting route	Stevens, L. et al.	2012		Natural		x	x			Flash elemental analysis. Diffuse reflectance Fourier transform infrared spectra (DRIFTS)	Raw clay	NA	Mesoporous	Present	Pure CO2	Thermogravimetric Analyser Q500 (TA Instruments)	TEP1 using N2 as purge gas	The CO2 adsorption capacity was determined from the weight change in CO2	1	25	**22**	
25	Thermodynamics analysis of the adsorption of CH_4 and CO2 on montmorillonite	Du, X. et al.	2020		Natural	NA						Raw clay	NA	Microporous and mesoporous	Not present	CO2/ CH_4 mixture	Intelligent Gravimetric Analyzer (IGAe100B, Hiden Isochema,Ltd., U·K)	TEP2	NA	1	15	**22**	4
26	Competitive Sorption of CO2 and H2O in 2:1 Layer Phyllosilicates	Schaef, H. et al.	2015		Natural		x				In situ IR	Carion exchange	Na+	Mesoporous	Present	Pure CO2	Standard Parr reactor/	TEP2	Gas adsorption measurements were conducted in a custombuilt quartz crystal microbalance	4	50	**22**	

27	N2 and CO2 Adsorption by TMA- and HDP-Montmorillonites	Volzone, C., Rinaldi, J. & Ortiga J.	2002		Natural		x					Cation exchange	Tetramethylammonium	NA	Not present	Pure CO2	Standard volumetric apparatus/	TEP2	NA	1	25	**21**	
28	CO2 adsorption on amine-functionalized clays	Gómez-Pozuelo, G. et al.	2019		Natural	x	x		x		T-plot method	Grafting + Impregnation	3-aminopropyltriethoxysilane/polyethyleneimine	Mesoporous	Present	Pure CO2	VTI Scientific Instruments HVPA-100	TEP2	Cyclic adsorption-desorption measurements were carried using argon as purge gas. For this, a fix bed reactor coupled to a mass spectrometer was applied.	1	45	**18**	
29	Halloysite nanotubes: Novel and eco-friendly adsorbents for high-pressure CO2 capture	Ramadass, K. et al.	2018	**Halloysite**	Natural	x	x		x	x	TEM X-ray	Raw clay	NA	Mesoporous	Present	Pure CO2	Quantachrome Isorb HP1 instrument	TEP2	NA	30	0	**268.46**	

30	Amine-Impregnated Mesoporous Silica Nanotube as an Emerging Nanocomposite for CO2 Capture	Niu, M. et al.	2016		Natural	x	x	x		x	TEMEDS	Amine functionalization by Impregnation	Polyethylenimine	Mesoporous	Not present	Pure CO2	TGA (STA449 F5 Netzsch Germany)/	TEP1 using N2 as purge gas	An alumina pan was used as sample container	1	85	**121**	
31	Preparation and characterization of novel carbon dioxide adsorbents based on polyethylenimine-modified Halloysite nanotubes	Cai, H. et al.	2014		Natural	x		x	x		TEM Dynamin Light Scattering (DLS)	Impregnation	Polyethylenimine	mesoporous	Present	Pure CO2	PE-TGA 7 thermal analyser/	TEP2	The weight change of the adsorbent was monitored to determine the adsorption and desorption performance of the materials	1	25	**54.8**	

32	Carbon dioxide sorption on EDTA modified halloysite	Waszczuk, P., Lutynski, M., González, M. et al.	2016		Natural							Acid treatment	EDTA	mesoporous	Present	Pure CO2	High-pressure manometric setup/		Setup is immersed in demineralized water with electronic temperature stabilization of 0.1°C The manometric setup consists of a sample cell, reference cell, valves, tubing, pressure transducers and temperature sensors	1	45	**35.2**	
33	Sorption of CO2 and CH_4 on Raw and Calcined Halloysite—Structural and Pore Characterization Study	Pajdak, A. et al.	2020		Natural				x	x	TEMEDS Gravimetric analysis	Pillarization	NA	Macro and mesoporous	Not present	CO2/ CH_4 mixture	IGA 001Gravimetric gas sorption analyser/	TEP2	The gravimetric measurement method records the changes of the sorbent weight during sorption under isobaric and isothermal	1	40	**8.8**	6.6

34	Sorption of CO2 and CH_4 on Raw and Calcined Halloysite—Structural and Pore Characterization Study	Pajdak, A. et al.	2020		Natural				x	x	TEM, EDS, Gravimetric analysis	Raw clay	NA	Macro and mesoporous	Not present	CO2/ CH_4 mixture	IGA 001 Gravimetric gas sorption analyser/	TEP2	The gravimetric measurement method records the changes of the sorbent weight during sorption under isobaric and isothermal	1	40	**8**	9
35	Halloysite Nanotubes Capturing Isotope Selective Atmospheric CO2	Jana, S. et al.	2015		Natural Halloysite Nanotubes	x		x	x	x	Field emission scanning electron microscopy (FESEM), EDX	Amine functionalization by grafting	3-aminopropyltriethoxysilane	Mesoporous	Not present	Pure CO2	Flask equipped with a fixed bed/	NA	The experiment was done at ambient condictions The amount of unadsorbed CO2 remain in the ambient air of the flask was determined by a laser-based ICOS technique.	1	25	**5**	

36	Halloysite as Mineral Adsorbent of Co2 – Kinetics and Adsorption Capacity	Lutynski, M., Sakiewicz, P. & González, M.	2014		Natural					x		Acid treatment	H2SO4	Microporous	Not present	CO2 pure	High-pressure manometric setup/	NA	Setup is immersed in demineralized water with electronic temperature stabilization of 0.1°CThe manometric setup consists of a sample cell, reference cell, valves, tubing, pressure transducers and temperature sensors	1	45	**3.2**	3

37	Adsorption of nitrogen, hydrogen and carbon dioxide on aluminapillared clays	Gil, A. et al.	2007	**Saponite**	Natural		**x**		**x**		T-plot method	Amine functionalization by Impregnation	Polyethylenimine	Mesoporous	Present	Pure CO2	VTI Scientific Instruments HVPA-100	TEP2	Cyclic adsorption-desorption measurements were carried using argon as purge gas. For this, a fix bed reactor coupled to a mass spectrometer was used.	1	45	**67**	
38	CO2 adsorption on amine-functionalized clays	Gómez-Pozuelo, G. et al.	2019		Natural	**x**	**x**		**x**		Elemental analysis Textural analysis	Materials Synthesized from Clay Minerals (Pillared clays, PILCs)	NA	Microporous	Not present	Pure CO2	Static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyser)/	TEP2	In the CO2 adsorption data, each point of adsorption was equilibrated for at least two hours	1	0	**48**	

39	CO2 adsorption on amine-functionalized clays	Gómez-Pozuelo, G. et al.	2019		Natural	**x**	**x**		**x**		T-plot method	Amine functionalization by grafting	3-aminopropyltriethoxysilane and N1-(3-trimethoxysilylpropyl) diethylenetriamine	Mesoporous	Present	Pure CO2	VTI Scientific Instruments HVPA-100	TEP2	Cyclic adsorption-desorption measurements were carried using argon as purge gas. For this, a fix bed reactor coupled to a mass spectrometer was used.	1	45	**39**	
40	CO2 adsorption on amine-functionalized clays	Gómez-Pozuelo, G. et al.	2019		Natural	**x**	**x**		**x**		T-plot method	Raw clay	NA	Mesoporous	Present	Pure CO2	VTI Scientific Instruments HVPA-100	TEP2	Cyclic adsorption-desorption measurements were carried using argon as purge gas. For this, a fix bed reactor coupled to a mass spectrometer was used.	1	45	**15**	

41	Modified nanosepiolite as an inexpensive support of tetraethylene pentamine for CO2 sorption	Irani, M. et al.	2014	**Sepiolite**	Natural	x	x	x		x	High Resolution Transmission Electron Microscope (HRTEM)	Amine functionalization by Impregnation	Tetraethylenepentamine	Mesoporous	Not present	Pure CO2	Lab designed experimental system/	NA	A quartz tube reactor was used. The liquid water was vaporized using heat tape before entering the gas stream. Each sorption test was carried out until the CO2 concentration in the outlet gas stream reached to the corresponding inlet CO2	1	60	**165**	
42	Sorption equilibrium and kinetics of CO2 on clay minerals from subcritical to supercritical conditions: CO2 sequestration at nanoscale interfaces	Jeon, P. et al.	2014		Natural		x		x			Raw clay	NA	Microporous and mesoporous	Not present	Pure CO2	Gravimetric sorption equipment	TEP1 using He as purge gas	A magnetic suspension balance is used.	120	25	**137**	

43	Textural properties determined CO2 capture of Tetraethylene pentamine loaded SiO2 nanowires from α-sepiolite	Ouyang, J. et al.	2017		Natural	x	x			x	energy dispersive X-ray spectroscopy (EDS)	Amine functionalization by grafting	3-aminopropyltriethoxysilane	Mesoporous	Present	Pure CO2	Thermogravimetric (TG) analysis (Netzsch STA-449 F5 instrument)	TEP1 using N2 as purge gas	The weight change was recorded.	1	70	**121**	
44	Evaluation of two fibrous clay minerals (sepiolite and palygorskite) for CO2 Capture	Cecilia, J.A. et al.	2018		Natural	x	x	x	x	x	Elemental analysis, DRIFT, TEM	Grafting + Impregnation	3-aminopropyltriethoxysilane/polyethyleneimine	Mesoporous	Present	Pure CO2	Micromeritics ASAP 2020 Analyzer (i.e., volumetrically)/	TEP2	Dual-site Sips model was used to fit the experimental data of the functionalized material	1	65	**91**	

45	Evaluation of two fibrous clay minerals (sepiolite and palygorskite) for CO2 Capture	Cecilia, J.A. et al.	2018		Natural	x	x		x	x	Elemental analysis, DRIFT, TEM	Activated by Acid Treatment	HNO3	Mesoporous	Present	Pure CO2	Micromeritics ASAP 2020 Analyzer (i.e., volumetrically)/	TEP2	Dual-site Sips model was used to fit the experimental data of the functionalized material	1	25	**41**	
46	CO2 capturing performances of millimeter scale beads made by tetraethylene pentamine loaded ultra-fine palygorskite powders from jet pulverization	Ouyang, J. et al.	2018	**Palygorskite**	Natural	x	x	x		x	energy dispersive X-ray spectroscopy(EDS)	Amine functionalization by Impregnation	tetraethylenepentamine	Mesoporous	Present	Pure CO2	Atmosphere and temperature controlled TGA (Netzsch STA449 F5 Germany)/	TEP1 using N2	An alumina pan was used as asample container	1	25	**110**	

47	CO2 adsorption on amine-functionalized clays	Gómez-Pozuelo, G. et al.	2019		Natural	x	x		x		T-plot method	Amine functionalization by grafting	3-aminopropyltriethoxysilane and N1-(3-trimethoxysilylpropyl) diethylenetriamine	Macroporous	Present	Pure CO2	VTI Scientific Instruments HVPA-100	TEP2	Cyclic adsorption-desorption measurements were carried using argon as purge gas. For this, a fix bed reactor coupled to a mass spectrometer was applied.	1	45	**57**	
48	Evaluation of two fibrous clay minerals (sepiolite and palygorskite) for CO2 Capture	Cecilia, J.A. et al.	2018		Natural	x	x		x	x	Elemental analysis, DRIFT, TEM	Grafting + Impregnation	3-aminopropyltriethoxysilane/polyet	Mesoporous	Present	Pure CO2	Micromeritics ASAP 2020 Analyzer (i.e., volumetrically)/	TEP2	Dual-site Sips model was used to fit the experimental data of the functionalized material	1	25	**46**	
49	Evaluation of two fibrous clay minerals (sepiolite and palygorskite) for CO2 Capture	Cecilia, J.A. et al.	2018		Natural	x	x		x	x	Elemental analysis, DRIFT, TEM	Activated by Acid Treatment	HNO3	Mesoporous	Present	Pure CO2	Micromeritics ASAP 2020 Analyzer (i.e., volumetrically)/	TEP2	Dual-site Sips model was used to fit the experimental data of the functionalized material	1	25	**43**	

50	Evaluation of two fibrous clay minerals (sepiolite and palygorskite) for CO2 Capture	Cecilia, J.A. et al.	2018		Natural	x	x		x	x	Elemental analysis, DRIFT, TEM	Raw clay	NA	Mesoporous	Present	Pure CO2	Micromeritics ASAP 2020 Analyzer (i.e., volumetrically)/	TEP2	Dual-site Sips model was used to fit the experimental data of the functionalized material	1	45	**12**	
51	A nano-silicate material with exceptional capacity for CO2 capture and storage at room temperature	Cavalcanti, L. et al.	2018	**Smectite**	Synthetic Nickel Fluorohectorite	N A						Intercalation	Nickel	mesoporous	Present	Pure CO2	Calibrated custom-made Sieverts apparatus	TEP2	CO2 gas was introduced to the reservoir and equilibrated for one hour, prior to allowing the expansion into the sample chamber and intercalation into the clay powder material	55	25	**283.86**	

52	Effects of exchanged ammonium cations on structure characteristics and CO2 adsorption capacities of bentonite clay	Elkhalifah, A. et al.	2013		Natural	x	x	x	x		CHNS elemental analysis	Cation exchange	monoethanolamine	mesoporous	Present	Pure CO2	Sorption chamber	TEP2	Adsorption equilibrium studies were carried out using a magnetic suspension balance.	10	25	**138.6**	
53	Intercalation and Retention of Carbon Dioxide in a Smectite Clay promoted by Interlayer Cations	Michels, L. et al.	2015		Synthetic Li-fluorohectorite		x					Cation exchange	Li+	Mesoporous	Present	Pure CO2	Calibrated in-house built (IFE, Kjeller) volumetric Sieverts-type apparatus	TEP2	NA	9	25	**140**	

54	Thermodynamic data of adsorption reveal the entry of CH_4 and CO2 in a smectite clay interlayer	Grekov, D. et al.	2020		Natural				x			Cation exchange	Mg-	Microporous and mesoporous	Present	CH_4/CO2 mixture	Lab-build manometric apparatus/	TEP2	A device (Keller LEX 1 digital pressure transducers) was used to continuously monitor the pressure and temperature conditions. The adsorbed amount was determined by mass balance calculated using the ideal gas law accounting for gas compressibility	10	115	**77**	11.5
55	O2, CH_4 and CO2 gas retentions by acid smectites before and after thermal treatment	Volzone, C. & Ortiga J.	2000		Natural		x		x		plasma emission spectroscopy (PES)	Acid and Thermal treatment	H2SO4	Microporous	Not present	Pure CO2	Standard volumetric apparatus/	TEP2	NA	1	25	**15.7**	

56	Analytical investigation of specific adsorption kinetics of CO2 gas on dendrimer loaded in organoclays	Shah, K. & Imae, T.	2015	Laponite	Natural							Organic compound intercalation	Polyamidoamine	Mesoporous	Not present	Pure CO2	Computer simulation		NA	1	25	**36**	
57	Synthesis of a Ca/Na-aluminosilicate from kaolin and limestone and its use for adsorption of CO2	Bkour, Q. et al.	2016	Kaolinite/Limestone	Natural	x	x		x	x	energy dispersive X-rayspectrometry (EDX)	Materials Synthesized from Clay Minerals (Gehlenite/Stilbite)	NA	Mesoporous	Present	Pure CO2	Gravimetric Analyzer/	TEP2	A magnetic suspensionbalance was used	45	100	**295**	
58	Methane and Carbon Dioxide Adsorption on Illite	Zhang, J. et al.	2016	Illite	Natural							Cation exchange	K+	Microporous	Not present	CH_4/CO2 mixture	Grand canonical Monte Carlo (GCMC) simulations	NA	NA	50	25	**304**	4.75

The information obtained from the scientific articles marked in orange color was taken in part from the review of Chouikhi et al. (2019) and in part of the article directly.