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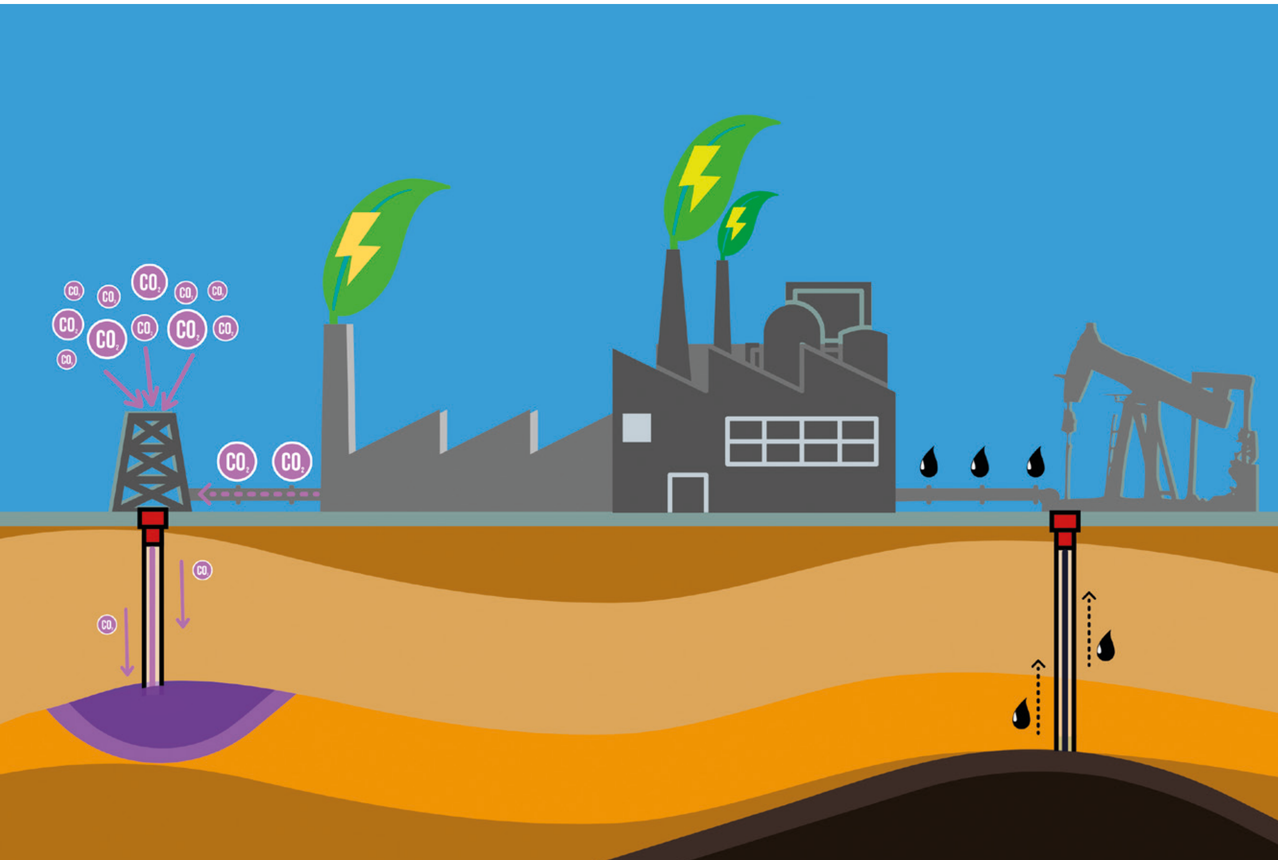
editors

PERSPECTIVES TO CO_2 GEOLOGICAL STORAGE AND GREENHOUSE GAS NEGATIVE EMISSIONS IN SOUTH-SOUTHEASTERN BRAZIL

Paraná and Santos Sedimentary Basins



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Research Centre for Greenhouse Gas Innovation

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1. Global warming

BOOK PRESENTATION

The global warming theory indicates that the global mean surface air temperature has increased during the last 200 years. This surface air warming is responsible for a worldwide phenomenon known as Climate Change. At its highest incidences of extreme climate events, it is modifying the rainfall regimes and, consequently, directly affecting our everyday life on the planet. The main cause of global warming is the increase of total greenhouse gas (GHG) concentrations in the atmosphere, where the carbon dioxide (CO_2) produced from anthropic activities is the primary contributor.

In this regard, the United Nations (UN), through various international agreements, recognised the need for urgent actions to address the effects of climate change. One of these international agreements is the Paris Agreement signed in 2015 by 157 countries, which aims to maintain the global temperature rise at a maximum of 2 °C above pre-industrial levels by decreasing greenhouse gas emissions (UNFCCC, 2015).

Among the available options for CO_2 emissions reduction, the technologies known as CCS (Carbon capture and storage) or CCUS (Carbon capture, utilisation and storage) are the most effective technique. CCS or CCUS technologies are considered essential parts of the lowest-cost paths to achieving the targets set during the Paris Agreement (Global CCS Institute, 2019). The

CCS technologies sequestrate carbon from the atmosphere by capturing CO_2 at its stationary emission sources and storing it during a long-time period or even permanently in rock formations. Therefore, the application of CCS technologies to the industrial and power generation sectors, the largest CO_2 emitters, is not just an option but an obligation to sustain the essential activities of humankind.

The south-eastern region of Brazil is the most industrial carbon-intensive zone of the country. It is one of the leading producers of oil, gas, and biofuels, thus the most greenhouse gas emitter. Therefore, the perception is that this region is the prefered location to apply CCS technologies, especially the CO_2 geological storage aspects. Subsequently, it is essential to conduct detailed evaluations to identify the most economically suitable and secure locations to store the captured CO_2.

The CO_2 geological storage is a compelling option because it allows safe storage for a long time, more than a thousand years, tremendous amounts of CO_2 compatible with the current greenhouse gas emissions. According to the IPCC (2005), the reservoir options for CO_2 geological storage are depleted oil and gas reservoirs, deep saline aquifers, mined salt caverns, unmineable coal seams, basaltic rocks, and organic-rich rock formations (Bachu, 2000; IPCC, 2005; Busch et al., 2008). All the above-stated options available in the south-eastern region of Brazil, with three of its sedimentary basins – Campos, Santos, and Paraná – already classified by Ketzer et al. (2014) as high prospective basins for CCS application.

Nevertheless, not all the previously commented rock formations are feasible CO_2 geological reservoirs. Potential reservoir rocks for CO_2 storage must exhibit the required characteristics to sustain large amounts of CO_2 injection during a time interval that is compatible with the CO_2 emissions and guarantees CO_2 reservoir retention for a long time (e. g., more than 1000 years). They should also have the appropriate conditions to avoid CO_2 leakage into the surface or nearby water bodies, with traps that confine the CO_2 storage reservoir, such as sealing rock formations (e. g., impermeable rock layers) or geological structures.

Specifically, potential reservoir rocks must demonstrate good porosity, permeability and adequate CO_2 geochemical trapping mechanisms such as gas sorption into organic matter and clay minerals (especially in coals and shales). Rocks containing Ca, Mg, and Fe (e. g., basalts) react with CO_2 to boost CO_2 storage because of their carbon mineralisation potentials. The interaction of CO_2 with mafic-to-ultramafic basaltic rocks enhances the permanent trapping of CO_2 in neoformed minerals.

Reservoir depths requirement for CO_2 storage is over 800m at formation pressures of at least 73.9 bar (IPCC, 2005; WRI, 2008; Herzog, 2018). Other factors must be carefully evaluated, including the reservoir CO_2 retention capacity, CO_2 storage volume, CO_2 injection capacity, and operational costs.

The most used method for CO_2 geological storage is CO_2 reinjection during enhanced oil or gas recovery operations in producing fields. The Pre-Salt offshore operations of the Santos sedimentary basin uses this method. Other efficient methods are the CO_2 injection in coal seams to enhance coalbed methane recovery and organic-rich black shales to enhance gas recovery. Paraná basin contains all the CO_2 geological storage options, such as basaltic rocks, coal seams, organic-rich black shales, saline aquifers, sandstones, and typical oil and gas reservoir-type rocks. It is also the largest onshore sedimentary Basin with a superficial area of 1,500,000 km2, including its extension to Paraguay, Argentina, and Uruguay (Milani et al., 2007). The Parana basin spreads across the carbon-intensive region of the country. Therefore, considering the locations, dimensions, geological settings, and reservoir stimulation suitability, Paraná and Santos sedimentary basins are the most favourable environments for CO_2 deep geological storage. In addition, considering that the CCS technologies are relatively new, the regulatory, legal, and environmental aspects must also be appropriately addressed and in full compliance with the planning and development of the CCS technologies during all stages of the future projects in the south-eastern region of Brazil.

Therefore, the book reflects the results of all the research studies developed during Project 36 (Perspectives for Carbon storage in onshore non-conventional oil reservoirs and offshore sedimentary basins in Southeast Brazil) of the Research Centre for Gas Innovation (RCGI) located at the Polytechnic School of the University of São Paulo and financed by SHELL and FAPESP. The chapters intend to discuss the topics related to the technologies involving CO_2 geological storage. Furthermore, they present the theoretical concepts and findings of the studies that preferentially focused on the organic-rich black shales of the Irati Formation, which is considered a potential geological unit for unconventional oil and gas reservoirs equivalent to those named in the United States of America. Overall, the book chapters present readers with a clear vision of the CCS-related techniques and the techno-economic potential of the CO_2 geological storage to mitigate greenhouse gas emissions in the southern-eastern region of Brazil.

Furthermore, the book presents the latest studies of the CNPq Research Group (Estudos para Armazenamento Geológico de Carbono - CCS) from the Institute of Energy and Environment (IEE) of the University of Sao Paulo. The results of the Research Group served as crucial findings for project 36 of the Research Center for Gas Innovation (RCGI) regarding the technical and regulatory issues for the implementation of Carbon, Capture and Storage (CCS) technologies, especially CO_2 geological storage in the Southeastern Region of Brazil, in the Paraná and Santos Basins. It provides an overview of the potential for secured long-term storage of CO_2 in south-eastern Brazil. The book also presents the academic findings related to CO_2 reservoir properties and criteria for selecting the best sites for CO_2 storage while looking to improve the decision-making process of the Brazilian CCUS development and contribute to the R&D (Research and Development) plan concerning greenhouse gas emissions mitigation.

The book focuses on the complete assessment of two of the most favourable locations within the prospective basins in Brazil, Paraná and Santos basins. The methodological approach involves geological evaluations and regulatory analyses. The geological aspect includes benchmarking, geochemical analyses, 3D modelling, petrophysical modelling, and statistical data analyses to characterise the CO_2 geological storage potential. It also includes numerical reservoir simulations for the calculation of CO_2 reservoir capacity. Meanwhile, the regulatory investigation consists of a descriptive method adopted to represent the state of the art stationary sources of CO_2 emissions in the southeast region of Brazil. The methodology to regulatory contents for the best practices exposition include:

1) analytical and deductive method;
2) systematic and teleological method;
3) hermeneutics;
4) the comparative method.

The research techniques are documentary and theoretical analysis, as well as institutional actions and composition descriptions. The most critical challenge our primary and secondary audiences face is the lack of geological evaluations, modelling data, and regulatory and legal certainty. Therefore, the book tends to address this challenge by answering the following questions:

a) Where are the most favourable area within prospective locations to implement CCUS projects in Brazil?

b) How to implement feasible CCUS projects in Brazil?

c) What are the required parameters for internal regulatory and legal compliance for feasible CCUS implementation in Brazil?

The novelty lies in directing the content to the non-specialised public to improve the decision-making process for development in south-eastern Brazil with an interdisciplinary assessment of its potential based on integrating geological, engineering, and regulatory checks. Furthermore, the innovation relies on selecting the best sites for both onshore and offshore CCS deployment and fully characterising the most prospective geological formations and their CO_2 reservoir capacity.

The editors
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CONTENTS

CHAPTER 1

MAIN STATIONARY CO_2 EMISSION SOURCES IN SOUTH-SOUTHEAST BRAZIL

Mariana Ciotta
Orlando da Silva
Raíssa Musarra

ABSTRACT

Adequate knowledge of the geographical location of stationary CO_2 emitting sources, the emission clusters impacts costs and the general viability of CCS projects is a fundamental part of planning a CCS project. This chapter seeks to comment on mapping the state of the art stationary sources of CO_2 emissions in the south-southeast region of Brazil. It presents a compilation of the data distributed by the state governments of South-southeastern Brazil on CO_2 emissions in five sectors: energy sector, industrial processes, agricultural sector, land use and waste. The origins of emissions in the south-southeast Brazilian states are distinct, suggesting different approaches for these locations. This effort aims to facilitate the dynamics of energy planning associated with CCS by promoting an understanding of the dynamics of emissions. Understanding emissions and their origins are one step closer to making a capture and storage project a reality.

Keywords: GEE inventory, CO_2 emission sources, CO_2 emission clusters.

1. INTRODUCTION

Understanding the geographical location of stationary CO_2 emitting sources is a fundamental part of planning a CCS (Carbon Capture, Transport and Storage) project (GALE et al., 2005). The reason is that the location of the CO_2 to be injected in geological reservoirs implies different costs, different transport procedures, different logistics, etc. There was a 9.6% increase in 2020 in gross greenhouse gas emissions released into the atmosphere: 2.17 billion tons of carbon dioxide equivalent (tCO_2e) compared to 1.98 billion in 2018. In the same year, the national GDP (greenhouse gas emissions produced to Gross Domestic Product) rose by 1. 1%, suggesting that Brazil's emissions are disconnected from wealth generation, unlike most other major economies (SEEG, 2020).

The difficulties approaching this endeavour arise from the lack of compilation and publication of Brazilian data on emissions. The data made available by the states governments in the south-southeast region of Brazil are not homogeneous and present different temporal and categorical relationships. This chapter depends on data obtained from the Ministry of Mines and Energy, information compiled by the energy research company, especially on the data of Brazilian emissions analysis developed by the climate observatory, and the System of Estimates of Emissions and Removals of Greenhouse Gases (SEEG, from the acronym in Portuguese). It allows identifying the sectors with the highest CO_2 emissions. Several pieces of information are compiled in this text to provide an overview of the situation of emissions in seven Brazilian states: Paraná, Santa Catarina, Rio Grande do Sul (formers in the southern region), São Paulo, Minas Gerais, Espírito Santo and Rio de January (trainers from the southeast region). These states are directly related to the sedimentary basins of Paraná and Santos with potential geological reservoir units for CO_2 storage; therefore, it reveals the need for knowledge of the emissions associated with these regions. This work aims to homogenise and standardise information regarding emissions from these regions as much as possible. The southern states (Paraná, Santa Catarina, and the Rio Grande do Sul) present a simplified analysis considering the absence of accurate data (in the case of Santa Catarina) and relatively lower levels of emission from industrial and energy processes in the data available to the other two states in the region (Paraná and the Rio Grande do Sul).

2. OBJECTIVES

The main objective of this chapter is to map the primary sources of CO_2 emissions in south-southeast Brazil. Thus, the aim is to understand the proximity of these CO_2 emission sources to possible geological storage sites to provide the basis for future CCS planning in the area. Therefore, the study involves compiling data on emissions in the south-southeastern Brazilian States published disorganizedly by state agencies and academic publications, understanding the relevance of the various sectors categorised in the total emissions, and defining critical areas for future carbon capture planning.

3. METHODOLOGY

The working methodology consists of the following steps: (i) literature review on the history of emissions in south-southeastern Brazil; (ii) search for data in the various state bodies; (iii) organisation of CO_2 emissions data relevant to the CCS universe; and (vi) data presentation.

4. THE HISTORICAL RECORD OF STATIONARY CO_2 EMISSIONS IN SOUTH-SOUTHEASTERN BRAZIL

Historically, South-southeastern Brazil has had a powerful influence on its economy and, therefore, has a long history of associated greenhouse gas emissions. The first efforts to map greenhouse gas emissions from the South-southeastern Brazilian states are recent, dating back to 2008. Moreover, it is essential to comment on the outdatedness of these data, which should have changed considerably within a decade.

The First Inventory of Anthropic Emissions of Direct and Indirect Greenhouse Gases in the State of São Paulo, a project coordinated and carried out by PROCLIMA/CETESB/SMA, with support from the British Embassy in Brazil, is a fundamental part of the commitment made by São Paulo to actively participate in efforts to protect the global climate system and to promote the transition to a low carbon economy in the state (CETESB, 2011). This document contains estimates of Greenhouse Gas (GHG) emissions in the São Paulo territory between 1990 and 2008, based on the methodology approved by the IPCC - Intergovernmental Panel on Climate Change.

In turn, the first inventory of greenhouse gas emissions in Minas Gerais was published in 2008 by the State Government, through the State Foundation for the Environment - FEAM, an entity of the State Secretariat of Environment and Sustainable Development - SEMAD (FEAM, 2008).

Espírito Santo's first greenhouse gas inventory was published in 2013 by the Espírito Santo State Government. It was published through the State Secretariat of Environment and Water Resources (Seama), the State Institute of Environment and Water Resources (Iema) and the Jones dos Santos Neves Institute (IJSN), in cooperation with the Foundation for the Coordination of Projects, Research and Technological Studies (Coppetec). Other associated bodies included the International Virtual Institute for Global Change of Coppe/UFRJ, linked to the Alberto Luiz Coimbra Institute (Coppe - UFRJ) and the National Agency for Technological to Economic and Social Development and Defense Environmental (Andesa) (LORENA et al., 2013).

The Inventory of Greenhouse Gas Emissions of the State of Rio de Janeiro was prepared based on the IPCC-2006 Guidebook (IPCC, 2006), a methodology conceived initially for countries. Although published at different times, these inventories follow a similar method and are the most reliable sources of emissions in Southeast Brazil.

Furthermore, the most recent effort to categorise Brazilian emissions came from the System of Greenhouse Gas Emissions and Removals Estimates (SEEG). SEEG is an initiative of the Climate Observatory which comprises the production of annual estimates of greenhouse gas emissions in Brazil, analytical documents on the evolution of emissions and an Internet portal to make the system's methods and data available simply and clearly. The Greenhouse Gas Emissions and Removals Estimates are generated according to the guidelines of the Intergovernmental Panel on Climate Change (IPCC) based on the methodology of the Brazilian Inventories of Anthropic Greenhouse Gas Emissions and Removals, prepared by the Ministry of Science, Technology and Innovation (MCTI), and on data obtained from government reports, institutes, research centres, sector entities and non-governmental organisations (SEEG, 2020).

5. STATIONARY CO_2 EMISSIONS IN SOUTH-SOUTHEAST BRAZIL

All five sectors that are sources of emissions - Agriculture and Livestock, Energy, Land Use Change, Industrial Processes and Waste - are evaluated with the same level of detail contained in the emission inventories. The data available in SEEG Collection 8 constitute a series covering the period from 1970 to 2019, except for the Land Use Change sector that has the series from 1990 to 2019.

The period before 1990 is not covered by the emission inventories (SEEG, 2020). The data that was accessed from other sources are broken down as such, with simplified data for the south region and in-depth data for the southeast region.

5.1. South Brazil States emissions

In terms of gross emissions allocation in the state, Santa Catarina has the amount of 7,750,278 $MtCO_2e$, placing it in the 26th position in the ranking of most CO_2 emitting states. The state of Rio Grande do Sul appears with 89,425,462 $MtCO_2e$, placing it in the7th position. The state of Paraná, in turn, shows the amount of 73,267,990 $MtCO_2$, which puts it in the 10th position in the ranking of most emitting states. The figure indicating the gross emissions statistics of the state of Santa Catarina has been omitted due to the unavailability of data.

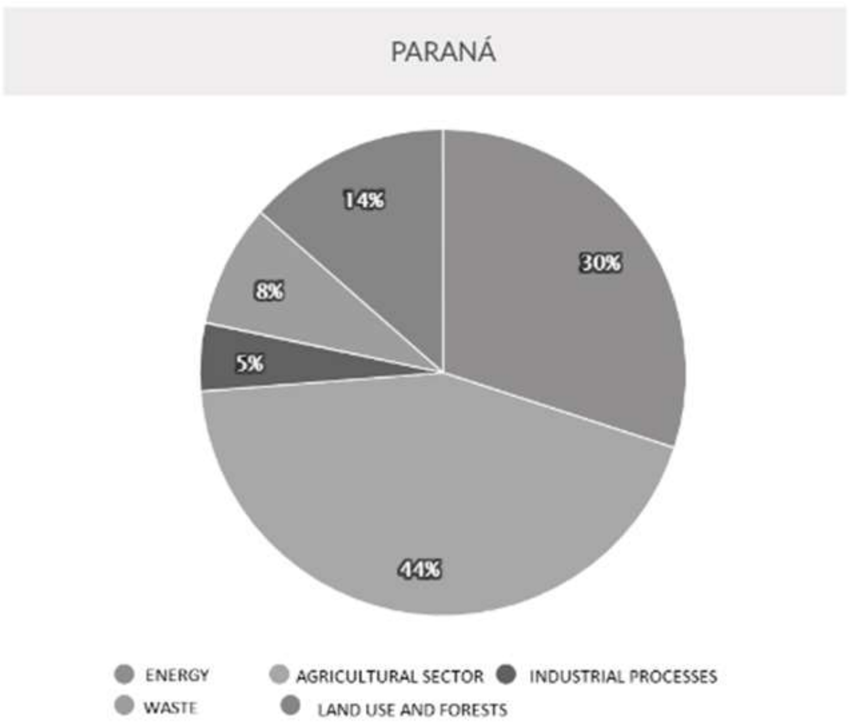

Figure 1. Gross emissions in Paraná State (Source: adapted by the authors from SEEG, 2020).

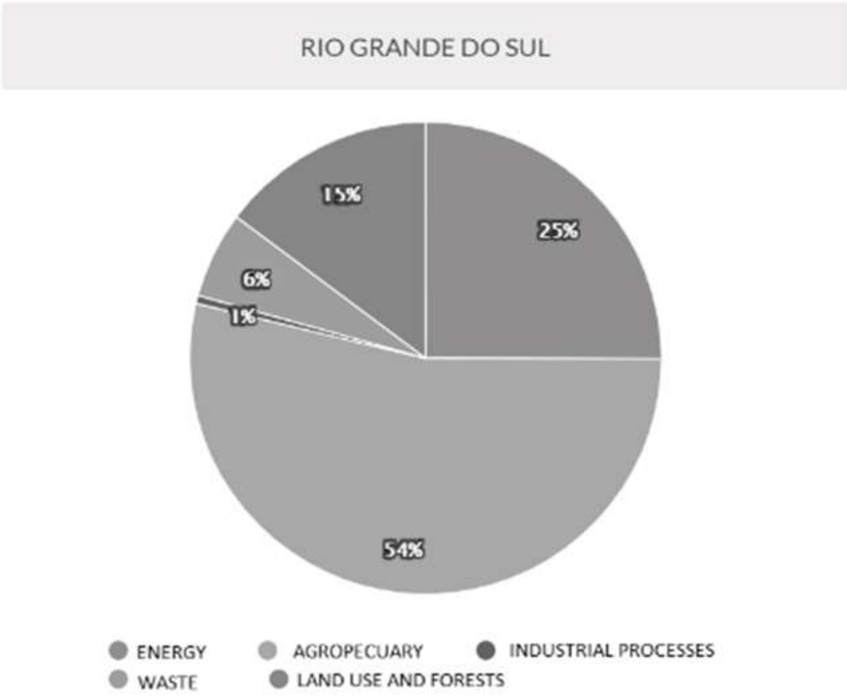

Figure 2. Gross Emissions in the Rio Grande do Sul State (Source: adapted by the authors from SEEG, 2020).

5.2. Energy sector in Southeast Brazil

In this Sector, all anthropic emissions from production, transformation, and energy consumption are estimated. It includes emissions resulting from the combustion of fuels and leakages in the production, transformation, distribution and consumption of energy (BRAZIL, 2010). The analysis of this sector requires special care because some of the subsectors involved are stationary and others are not (CETESB, 2011).

In Espírito Santo, the energy sector corresponds to only 3% of the emissions in CO_2eq, far behind other sectors such as industry (51%) and transport (30%) (LORENA et al., 2013). But we must consider that 99.98% of emissions are CO_2 in the energy sector and that fossil fuels are responsible for 98.97% of emissions.

In Minas Gerais, the inventory accounts for emissions due to the burning of fossil fuels and biomass in the production, transformation, and consumption of energy and emissions from the refining, transportation, and distribution of fossil fuels. CO_2 was the most emitted gas by the sector, with a 94.1% participation, followed by

CH_4, with 3.5% and N2O, with 2.5% (FEAM, 2008). In Rio de Janeiro, excluding transport, final energy consumption emitted 18728.8 Gg CO_2 in 2015 (INEA, 2015).

In São Paulo, the estimate of the CO_2 emissions from the burning of fossil fuels in 2008 stood at 79,690 $GgCO_2$. These emissions grew about 47% from 1990 to 2008, i. e., an annual average increase of almost 2.15% (CETESB, 2011). The fuel that had the most significant participation in CO_2 emissions was diesel oil (33% in 2005), presenting an increase of 54% from 1990 to 2005. The second in the rank of fuel that contributed the most was gasoline (16%), with a growth rate of 65%. Natural gas with 12% ranked third in the contribution of CO_2 emissions. The fuel presented the highest growth in the period analysed (1,870%) (CETESB, 2011).

Fossil Fuel Power Plants by Southeastern State					
State	The amount	Installed Power (MW)	Generated energy (MWh*10^3)(1)	Calculated Emissions (tCO2/year)(2)	CO2e emissions (tCO2e/year)(3)
São Paulo	482	6,294	6,606	495,450	1,279,000
Rio de Janeiro	54	5,175	28,566	2,142,450	8,026,000
Minas Gerais	131	1,817	3,049	228,675	676,000
Espírito Santo	15	1,093	5,745	430,875	757,000
Total	**682**	**14,379**	43,966	3,297,450	10,738,000

Table 1. Fossil Fuel Power Plants by Southeastern State

Source: Table based on data from (MME, 2021).

5.3. Industrial processes in Southeast Brazil

Industrial activities can generate atmospheric emissions by burning fuels (generation of heat or electricity), the disposal of waste (treatment of industrial effluents and waste incineration) and processes of chemical and physical transformation of materials. For each of these three types of procedures, emissions occur under a wide variety of specificities: the product in production, the inputs that feed the processes, the type of technological route used in production, the equipment of the industrial plant and the efficiency levels (SEEG, 2020). Among the industrial activities of great relevance for CCS projects, cement production, iron and steel, oil refineries, and some other sectors stand out of the chemical industry. They are typically stationary sources of emission of large blocks of CO_2 into the atmosphere.

In Espirito Santo, the industrial processes sector was the leading emitter, with 40.1% of emissions (10,877.19 $GgCO_2eq$) IN 2006 (LORENA et al., 2013). The metallic minerals transformation industry was the most important, with 9,866.08 $GgCO_2eq$ (90.7%) of the sector's emissions. Next comes the production of coke, with 998.06 (9.18%). Lubricants and non-metallic minerals contributed only 0.1% and 0.02% of emissions, respectively (LORENA et al., 2013).

In Minas Gerais, the total emissions from the Industrial Processes and Product Use Sector reached the value of 7,086 Gg CO_2eq, being CO_2 responsible for 89.8% of this total. Cement production was mainly responsible for the sector's emissions, with 43.9%, followed by lime, 38.2%, and the aluminium industry, with a 13.0% share (FEAM, 2008).

Concerning Rio de Janeiro, the total CO_2 emissions associated with the industrial process sector in Rio de Janeiro were 11,514.4 GgCO_2 (INEA, 2015). In São Paulo, the emissions associated with industrial processes are divided into the following production subsectors: cement, lime, chemicals, metallurgy, food and beverages, glass, paper and cellulose, solvents and other products (CETESB, 2011). In 1990, CO_2 emissions associated with the industrial processes sector in the state of São Paulo were around 3,396 Gg/year and reached 12,218 Gg/year in 2008 (CETESB, 2011).

5.4. Agricultural sector

Emissions in this sector involve rice cultivation, enteric fermentation, animal waste management, burning of agricultural waste and soil management. In 2019, emissions from the agricultural sector totalled 598.7 million tons of CO_2 equivalent, an increase of 1.1% over 2018. (SEEG, 2020).

In Espírito Santo, the agriculture and livestock sector is sensitive to address in terms of CO_2 equivalent because most of the associated emissions are of CH_4. In Minas Gerais, the Agriculture, Forestry and Other Land Use Sector were responsible for the emission of 63.221 Gg CO_2eq. The main gas emitted was CH_4 (42.4%), followed by CO_2 (39.9%) and N2O (17.7%) (FEAM, 2008). In São Paulo, the CO_2 emissions associated with the agriculture and cattle raising sector in the state of São Paulo varied from 931 Gg/year to 1,462 Gg/year in 2006. The sector has its most significant emissions expressed in CH_4.

5.4.1. BECCS

Bioenergies have an important role to play in the face of the need for substantial cuts in greenhouse gas emissions and even to achieve negative emissions of these gases, which can partially offset emissions from fossil sources.

According to Pelissari et al. (2020), the use of bioenergy (whose net emission is considered neutral due to the sequestration of atmospheric CO_2 that occurs during photosynthesis), associated with the capture and geological storage of CO_2, known as BECCS, has the potential to reduce net CO_2 emissions to levels below zero.

Considering the production chain of ethanol in Brazil, CO_2 capture can be done in two stages: 1) in the process of fermentation of sugarcane must for the production of ethyl alcohol, used as fuel in automobiles, and 2) in the process from burning sugarcane bagasse to produce process heat and electricity (DAVID, 2016).

Moreira, J. R. et al. (2016) affirm that BECCS could reduce Brazil's emissions from energy production by roughly 5% because it is currently possible to eliminate 27.7 $MtCO_2$ per year through capture and storage of CO_2 released during the fermentation process of sugar cane-based ethanol production.

5.5. Land use

Changes in land use accounted for 363 million tons of CO_2 and national net emissions and 968 million tons of gross emissions in 2019. Most of the gross emissions (93%) are from changes in land use, most of which consist of the deforestation of the Amazon biome, which concentrates 87% (841 $MtCO_2e$) of the sector's gross emissions (SEEG, 2020).

In Espírito Santo, the planted forests remove more CO_2 (246.5 $GgCO_2eq$) than emissions (199.3$GgCO_2eq$). It is verified, therefore, that the removals exceeded emissions by 47.2 $GgCO_2eq$. The process of deforestation or burning of natural forest cover in the initial, medium and advanced stages of regeneration in 3,200 hectares generated the emission of 139.93 $GgCO_2eq$ in 2006 (LORENA et al., 2013).

The Minas Gerais and Rio de Janeiro's inventory dealt with land use issues alongside the agriculture sector. Finally, in São Paulo, anthropic nature's average annual net anthropic emissions totalise -10,663.29 $GgCO_2$, -11,753.35 $GgCO_2$ and -9,846.08 $GgCO_2$ in the first, second and third periods, respectively. The negative number indicates that there was a net removal of CO_2 (CETESB, 2011).

5.6. Waste

Total emissions calculated for the waste sector were 1669.68 $GgCO_2$ eq (6.2% of total). The percentage distribution was 50% from municipal solid waste, 32.15% from industrial effluents, 17.83% from domestic and 0.01% from industrial solid waste (LORENA et al., 2013).

In Minas Gerais, the Waste Sector emitted 7,294 Gg CO_2eq, 65.0% from solid waste and 35.0% from industrial, domestic, and commercial effluents. Urban solid waste was the one that most contributed to the emission of greenhouse gases, with a participation of 40.9% of the total, and CH_4 was the main gas emitted, with a share of 82.9% (FEAM, 2008). Total CO_2 emissions from the waste and effluent sector in the state of São Paulo varied from 0.01Gg/year in 1990 to 19.69 Gg/year in 2008 (CETESB, 2011).

6. POLICIES IMPLICATIONS

Law No. 12,187 of 2009 institutes the National Policy on Climate Change-PNMC, which foresees mitigation via lay down principles, objectives, guidelines and instruments. It involves technological changes and substitutions that reduce resources that contribute to CO_2 emissions to serve as the basis for the production unit. It implements measures that reduce the GHG effect's and increase sinks, including CCS (Carbon Capture and Storage) technologies. Currently, decree no 9578/2018 regulates the policy that provides the action plans for prevention, mitigation and adaptation to climate change. Article 18 says that the projection of national greenhouse gas emissions for the year 2020, referred to in the sole paragraph of art. 12 of Law No. 12,187 of 2009, will amount to 3,236 million ton CO_2eq composing of projections for the following sectors: I - land-use change - 1,404 million tonCO_2eq; II - energy - 868 million tonCO_2eq; III - agriculture - 730 million ton CO_2eq; and IV - industrial processes and waste treatment - 234 million ton CO_2eq.

An essential ally of industries and organisations regarding the voluntary responsibility and verification of the studied effect of gases is the norm ISO 14064. It supports the industry and the government with tools to develop programs focused on reducing GHG conditions. The ISO 14064 standard consists of three parts: Part 1 - specifies the requirements for designing and developing inventories for organisations or GHG agencies; Part 2 - detailed requirements for quantifying, monitoring and reporting on emission reductions and improvements in reducing GHG projects; and Part 3 - provides the requirements and guidelines for conducting the validation and verification of GHG information. In Brazil, the standard is provided with the name "Greenhouse Gases - Principles and requirements for the quantification and reporting of emissions and removals of greenhouse gases (GHG) - ABNT NBR ISO 14064: 2007". Despite that, it is essential to note that Brazil reached 2020 without complying with the PNMC, including regressing in the treatment Against emissions established in the NDC because there are no active implementation plans. It was not enough to classify it as "insufficient" to fulfil the Paris Agreement's goal of stabilising global warming to well below 2ºC in this century concerning the pre-industrial era, with efforts to limit it to 1.5ºC (SEEG, 2020).

CONCLUSIONS

Espirito Santo's inventory does not discriminate between the gases involved (e. g., CH_4, N2O, HFC, SF6), showing all values in terms of CO_2eq. Therefore, CO_2 emissions are likely to be overestimated, but they are the safest information available. The total emissions of Espírito Santo are well below the average of the other states that make up the Southeast region of Brazil, which is the most developed region of the country.

In Minas Gerais, the Agriculture, Forestry and Other Land Use sector was the largest emitter of greenhouse gases, with 51.4%, mainly due to agriculture and cattle-raising. In second place is the Energy Sector, with 36.9%, due to the burning of fossil fuels in industry and transport. CO_2 contributed 60.6%, CH_4 28.0%, and N2O 10.8% in terms of greenhouse gases.

The weight of the energy sector in greenhouse gas emissions is closely associated with the use of transport and, therefore, loses considerable relevance when only stationary sources are considered. The efforts to survey bibliographic data on CO_2 emissions in Brazil, made available by government agencies and other national and international institutions, reveal a gap to be filled when the intention is to build proposals for the implementation of projects of CCS. The data provided are mostly aggregated by large sectors of activity or by units of the federation and presented in different patterns, making it challenging to locate and quantify.

The implementation of CCS projects requires systematised and georeferenced data considering the CO_2 emitting sources. Therefore, there is an urgent need to collect data from a bottom-up perspective from this study specifically. It will allow us to identify the sectors where and how CO_2 emissions occur, at the most disaggregated level possible, enabling the identification of the sectors of most significant interest for carbon dioxide storage, with an emission amount of CO_2 in southern and south-eastern regions around 420 Mt/year (SEEG, 2020).

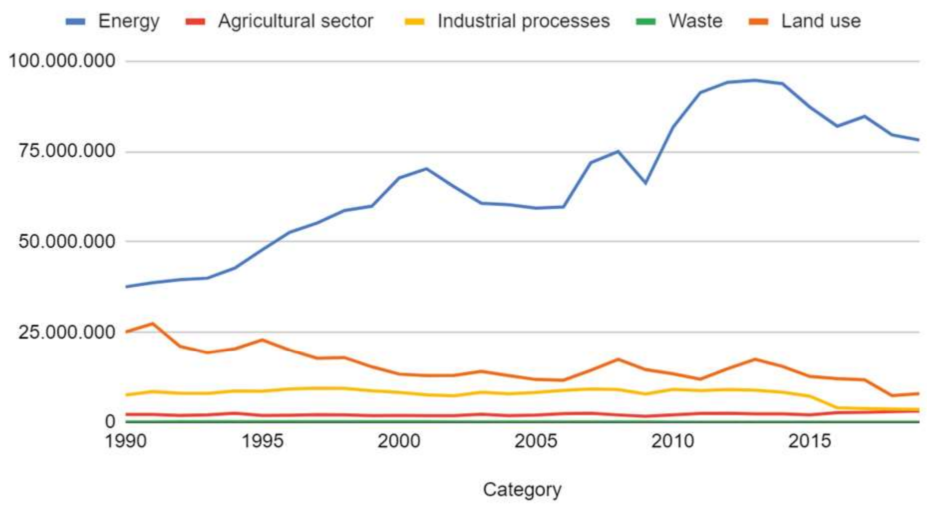

Figure 3. Total emissions in São Paulo (tCO_2). Source: SEEG, 2020.

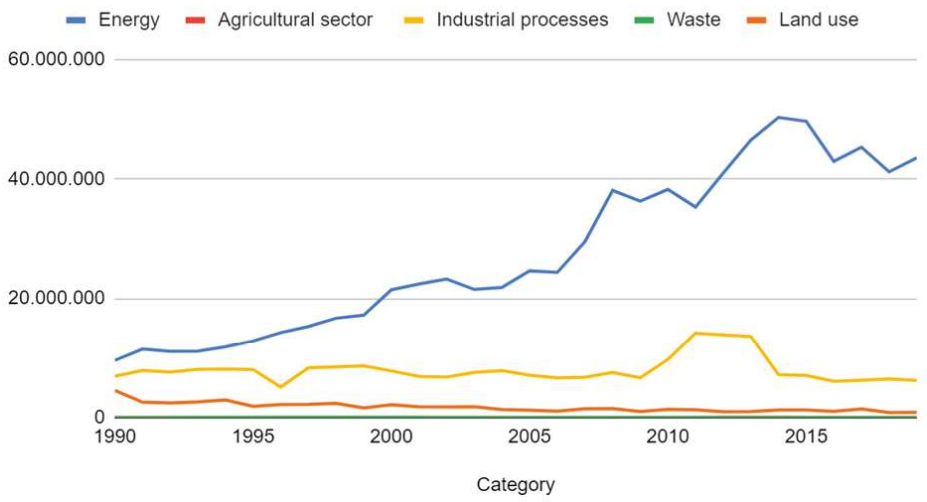

Figure 4. Total emissions in Rio de Janeiro (tCO2). Source: SEEG, 2020

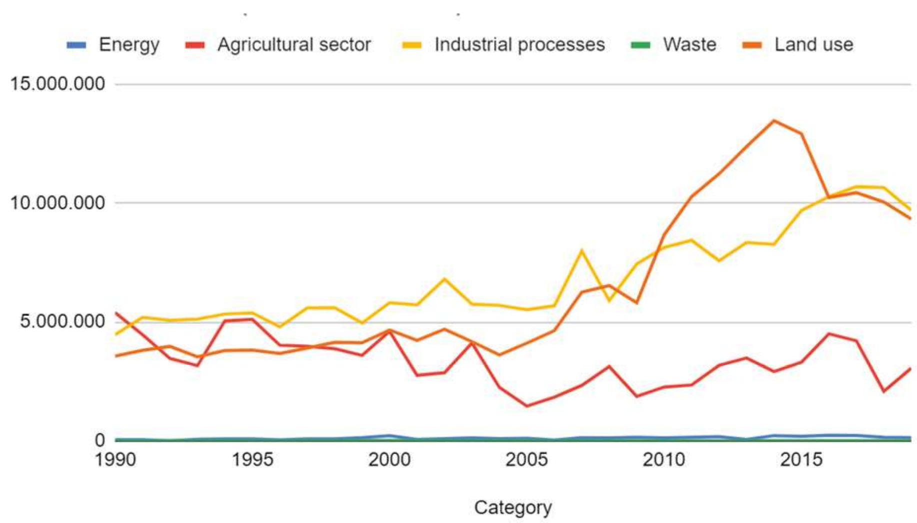

Figure 5. Total emissions in Espirito Santo (tCO_2). Source: SEEG, 2020.

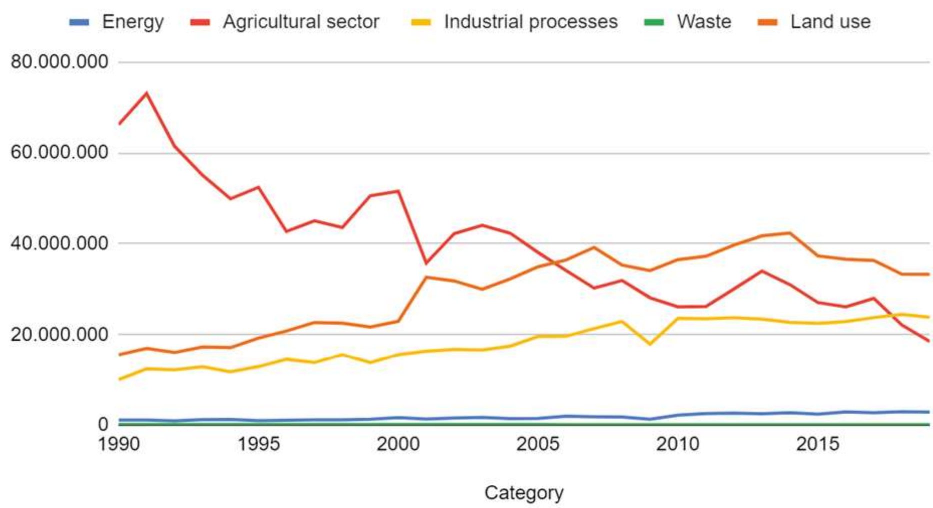

Figure 6. Total emissions in Minas Gerais (tCO2). Source: SEEG, 2020

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CHAPTER 2

CO_2 GEOLOGICAL STORAGE IN SANTOS BASIN: POTENTIAL AND BEST SUITABLE SITES

Mariana Ciotta

ABSTRACT

The search for reservoirs is a relevant part of CCS projects, and in the Brazilian context, it is crucial to think about strategic locations associated with stationary CO_2 sources. Thus, the Santos Basin is a region of interest since it contains essential oil and gas reserves like those in the subsalt area. Depleted oil and gas fields appear to be more favourable reservoir options due to local technical studies, infrastructure availability, connections with emission centres by pipelines or ship routes, and fewer environmental risks. This chapter explores the potential and best suitable sites, focusing on the case of the Merluza Field. The presence of infrastructure is another favourable point for choosing the Merluza Field as a location for the geological storage of CO_2. Economically, adaptation to the existing activity tends to be much cheaper than construction with no initial infrastructure available. In the case of Merluza Field, the reservoir structure is open for use. The existing pipeline is also an advantage if the field is selected as the continental CO_2 storage site. The two reservoir possibilities (rocks from the Juréia Formation and Itajaí-Açu, Ilhabela Member) have characteristics favourable to be CO_2 geological reservoirs.

The high porosities, mainly for the Ilhabela Member, indicate that large amounts of gas can be injected.

Keywords: CO_2 geological storage; Depleted hydrocarbon fields; Santos Basin.

1. INTRODUCTION

The global community has authorised the choice of an ambitious greenhouse gas (GHG) reduction target from the Paris Agreement (UNFCCC, 2015; IEA, 2016). The global energy sector has a significant role in this paradigm shift since it accounts for 72% of global GHG emissions (WRI, 2019). Among the various options for mitigating emissions, carbon capture and storage (CCS) has emerged as a relevant tool, especially concerning energy transition (IEA, 2007). The search for geological reservoirs is an integral part of a CO_2 capture and storage project because it corresponds to the final destination of the gas. Thus, it is necessary to find regions that adequately meet the criteria established for a reservoir to retain CO_2 in the long term. Making this analysis depends on compiling various geological data and information associated with infrastructure and local regulation. The Santos Basin (figure 1) has a total area of about 35,2260 km² spreading across Rio de Janeiro, Santa Catarina, São Paulo and Paraná states (FREITAS et al., 2006).

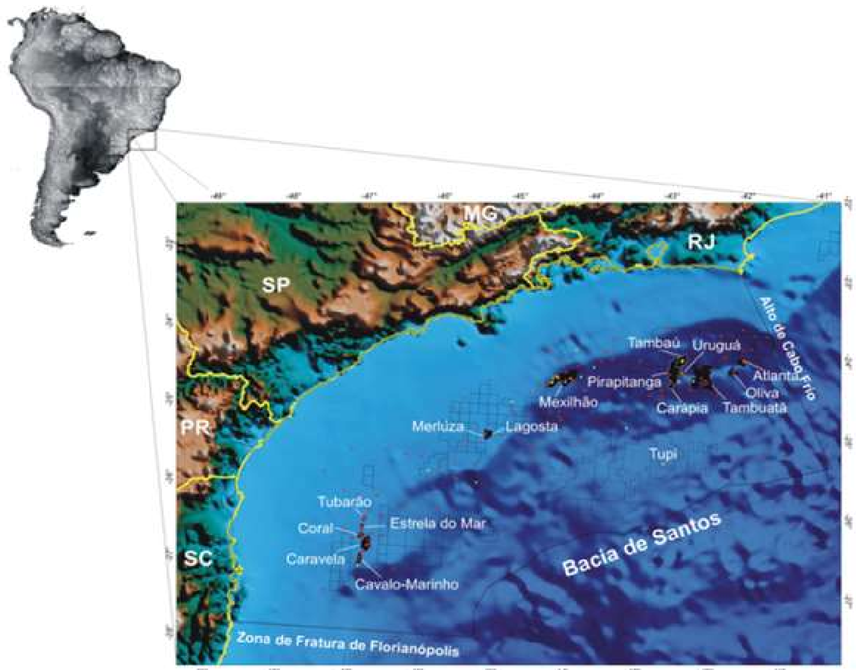

Figure 1. Location of the Santos Basin. Source: Chang (2008).

This work is set in a world scenario of the search for global solutions to climate issues. In this sense, CO_2 capture and geological storage technologies work as possible tools to reduce greenhouse gas (GHG) emissions to achieve the goals proposed in the 2015 Paris Agreement (UNFCCC, 2015). For the national energy planning to consider the geological storage of CO_2 as a GHG abatement tool, studies about the geological feasibility of the Brazilian territory are necessary. The search for regions in the national environment must also consider infrastructure and economic feasibility and cost optimisation. In this sense, the search for reservoirs in the Santos Basin arises naturally due to the Basin's strategic position geographically (located near relevant economic-emitting hubs) and the arrangement of oil fields distributed throughout its area.

Therefore, the scope of this work is to investigate the potential use of the Santos Basin for CO_2 storage. Looking for reservoirs in the Santos Basin means looking at rock formations with suitable geological conditions for CO_2 storage. The site selection criteria are separated into geological, physical and economic-social factors (BACHU, 2000; TOMIĆ et al., 2018). The previous selection of depleted fields is based on their proven higher economics and advantages concerning technical expertise, available infrastructure for adaptation, and lower environmental risks (HANNIS et al., 2017). The Santos Basin has also stood out in activities related to supply infrastructure (figure 2). : There are five refineries installed in its vicinity (REDUC, RPDM, RECAP, REVAP and RPBC) within a distance of up to 80 km from the Basin's limits, with a total daily refining capacity of 119,200 m3 of oil representing approximately 32% of the current national capacity (EPE, 2019).

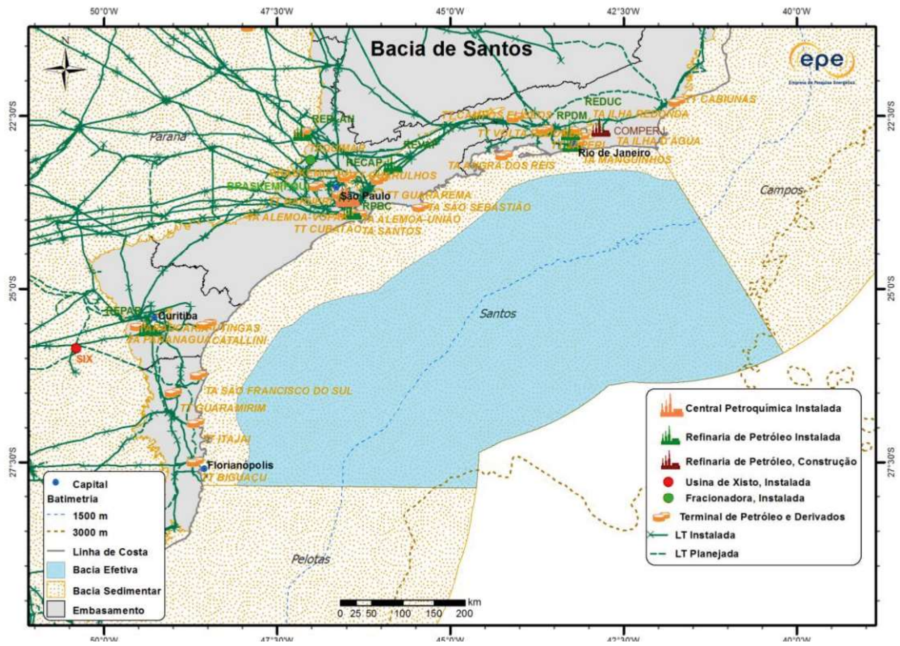

Figure 2. Santos Basin supply infrastructure: refineries, terminals and transmission lines.
Source: EPE (2019).

Therefore, this paper presents a general overview of the characteristics of the Santos Basin, which favour its use for carbon storage, considering the Merluza Field as a case study. It hopes to establish the state-of-the-art knowledge of the Santos Basin from the perspective of the geological storage of CO_2.

2. METHODOLOGY

The methodology (figure 3) of this work consists of a critical literature review and the indication of the most appropriate units to store CO_2 in the Santos Basin based on the selected data. The outline of the methodology is as follow; i: data collection, a bibliographic survey on the Santos Basin geology and infrastructure, ii. Data analysis based on the bibliographic survey on CCS and selection criteria for CO_2 storage, and iii) Mapping of results: definition of the desirable characteristics for a rock to act as a reservoir.

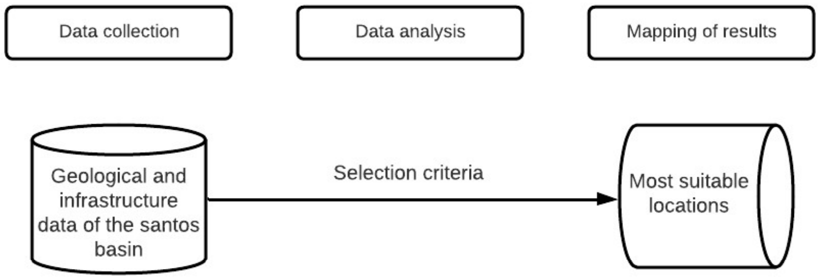

Figure 3. Methodology layout.

3. RESULTS AND DISCUSSION

The results of this work aided to define the storage site selection criteria, CO_2 storage possibilities in the Santos Basin in general terms, and finally, presenting the Merluza Field case study.

3.1. Criteria

Before developing storage technologies, it is necessary to identify critical selection criteria to tell whether the chosen reservoir is environmentally safe, economically suitable and geologically feasible (AMINU et al., 2017). The requirements that should be considered when geological reservoirs for CO_2 storage are diverse and are divided into three main categories (BACHU, 2000; LLAMAS, 2014; TOMIĆ, 2018):

i) geological;

ii) physical, thermodynamic and hydrodynamic;

iii) techno-economic, social and regulatory. When dealing with geological criteria, one must pay attention to porosity, permeability, tectonic stability, reservoir characteristics, CO_2 sorption (clay minerals and organic matter) and the degree of exploitation of the Basin. The physical, thermodynamic and hydrodynamic criteria consider gas behaviour in the reservoir and its relationship with nearby water bodies. Finally, the techno-economic, social and regulatory criteria range from project costs to impacts on human life and regulatory possibilities.

Therefore, the results expressed in this work do not start from a single perspective but the combination of several views for the same problem in the search for the most appropriate regions in the Santos Basin for CO_2 storage.

3.2. Best locations for CO_2 storage in Santos Basin

The offshore location of the Santos basin presents both challenges and benefits for a CCS project. While there is no need to worry about human populations in nearby cities, the marine fauna and flora require attention, and more difficulties in addressing the environment are needed.

Before going into the criteria previously mentioned, it is necessary to look at the entire Basin. The Santos Basin has approximately 352 260 km2 and faces the states of Rio de Janeiro, Santa Catarina, São Paulo and Paraná. It is limited to the north by Alto do Cabo Frio (Campos Basin), to the south by Alto de Florianópolis (Pelotas Basin). The Basin extends to roughly the limit between the continental crust and the oceanic crust to the east, and the Santos Fault limits it to the west (FREITAS et al., 2006).

The origin of the Santos Basin is associated with the opening of the South Atlantic Ocean. There are several possible interpretations for this event, with three main approaches standing out: (1) thermal doming caused by crustal thinning (ASMUS, BAISCH, 1983); (2) lithospheric stretching preceding the opening and placing thermal anomalies as secondary (CHANG et al., 1992); (3) mixed processes depending on the absence or presence of mantle plumes and different stretching rates along the proto-edge (GLADCZENKO et al., 1997). The Santos Basin is due to an anomalous stretching caused by the excessive heat in the area of the São Paulo Plateau by the Tristão da Cunha plume (MACEDO, 1990). The anomaly caused by the Tristan plume may have resulted in a regional uplift associated with the Basin's mechanical subsidence, explaining a rift section with less thickness (ANP, 2003). The rift phase of the Basin would be represented by a mosaic of NS to NE/SW synthetic faults, with antithetic secondary systems, resulting in a series of half-grabens with internal highs (CAINELLI, MOHRIAK, 1998).

The primary geological information and main characteristics of the stratigraphic units are summarised in tables 1 and 2.

Geographical Situation		Sea
Sedimentary Area		308057 km²
Effective Basin Area		240901 km²
Exploratory Maturity		High potential
Main Oil System		Guaratiba - Guaratiba (!)
Exploratory Plays	**Play**	**Main Reservoir**
1	Marambaia (Neogene)	Neogenous turbiditic sandstones - Marambaia Formati
2	Marambaia (Paleogene)	Paleogenous turbiditic sandstones - Marambaia Formation
3	Santos - Jureia	Campanian-Maastrichtian sandstones - Santos Juréia Formation
4	Ilhabela	Lower Coniacian-Santonian turbiditic sandstones - Itajaí-Açu Formation (Ilhabela Member)
5	Camburi	Albo-Cenomanian carbonates - Guarujá Formation
6	Pré Sal Microbialites	Aptian microbialites - Barra Velha Formation
7	Pré Sal Coquinas	Barremian-Aptian coquinas - Itapema Formation
8	Fractured basement	Neocomian fractured basalts - Camboriú Formation

Table 1. Geological information of Santos Basin. Source: adapted from EPE, 2019.

Geological unit	Main features
Camboriú Formation	Basaltic spills below the sedimentary section for almost the entire length of the Basin.
Guaratiba Formation	Pack of clastic and carbonate rocks located above the Camboriú Formation and below the evaporites of the Ariri Formation, with both discordant contacts.
Ariri Formation	They are composed of thick packages of halite and white anhydrite, calcilutites, shales and marl.
Florianópolis Formation	Fine to coarse, red sandstones with clayey matrix, shale and micromicaceous red siltstones
Guarujá Formation	Bioclastic oolitic calcarenites that appear, varying laterally for cream-greyish / brownish-grey calcilutites and grey marl.
Itanhaém Formation	Pelitic package occurs between the clastics of the Itajaí-Açu Formation and the carbonates of the Guarujá Formation.
Santos Formation	Clusters and reddish lithic sandstones occur interspersed with grey shales and red clays.
Itajaí-Açú Formation	Pelitic package sotoposto and interdigitated with the clastics of the Jureia and Santos formations. It is composed of a thick section of fine clastics and the predominant lithology is dark grey shale.
Jureia Formation	Dark grey to greenish and reddish-brown shales, dark grey siltstones, fine and very fine sandstones and light cream calcilutites.
Iguape Formation	Bioclastic calcarenites and calcirruditesthat occur interspersed with greenish-grey clay, siltstone, marl and conglomerates.
Marambaia Formation	A thick section of shale and light grey marl intersecting with fine turbiditic sandstones.

Table 2. Geological units at Santos Basin and its main features. Source: Ciotta and Tassinari, 2020.

The choice of the most appropriate formations for CO_2 storage goes through two main criteria: initially, those that meet the suitable geological criteria are selected; secondarily, the depleted oil and gas fields, a situation considered most appropriate for application in the Santos Basin. When considering the use of depleted hydrocarbon fields, it is essential to note that the exploratory use of the

Santos Basin is recent, and only the Merluza Field currently fits into this scenario. It is possible to explore other areas thinking about a future situation, but for the scope of this work, the focus was on the Merluza Field. In this sense, the chosen units include the sandstones of the Juréia and Itajaí-Açu Formations corresponding to the Ilhabela Member. The subsequent subsection presents the criteria of choice based on the Merluza Field. It is evident that other possibilities exist, requiring a more detailed investigation of each particular case. However, for the scope of this work, the following topics seek to comment on the selection made.

3.3. Merluza Field study case

The Merluza platform (PMLZ-1) (figure 2) has been in operation since 1993 and produces the Merluza and Lagosta natural gas fields. It is located about 180 km off the coast of Praia Grande (SP), a fixed platform on a water sheet of about 131 m (PETROBRAS, 2019). The Merluza Field is equivalent to the first commercial gas discovery in risk contract drilling on the Brazilian continental shelf, carried out by Pecten Brazil Exploratory Company. Due to mechanical problems, the first well drilled in this field (1-SPS-11) was not adequately assessed. The second well (1-SPS-21), in turn, reached reservoirs at the base of the Juréia Formation, saturated with gas. In 1984, the drilling of well 1-SPS-20 in the bathymetric quota of 122 m allowed the evaluation of gas-saturated reservoirs in reservoirs of the Itajaí Formation, Ilhabela Member (SOMBRA et al., 1990).

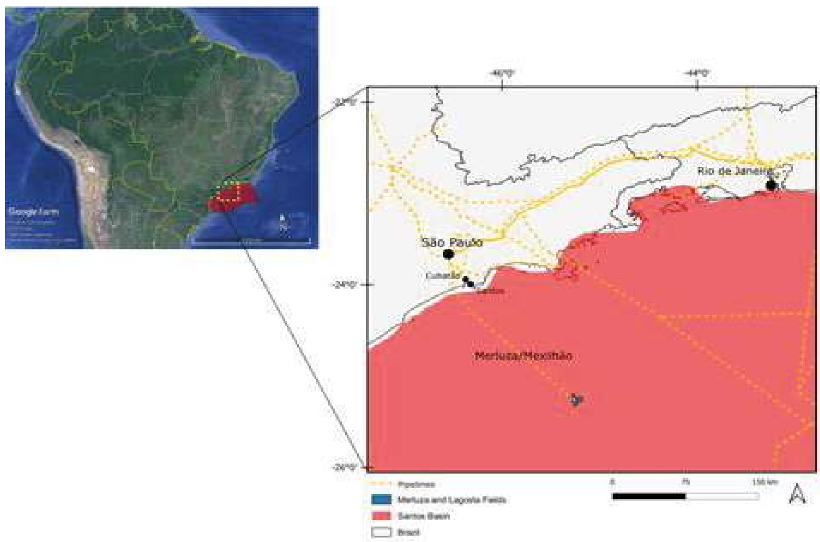

Figure 2. Merluza Field location. Source: Ciotta and Tassinari (2020).

The Merluza Field has two reservoirs of the Santonian age (Upper Cretaceous between 86.3 million and 83.6 million years ago). There are the sandstones of the Juréia Formation, whose deposition took place in the shallow platform. There is also the sandstones of the Itajaí-Açu-Member Ilhabela Formation, beds and channels in neritic slope (region of the oceans that corresponds to the relief of the continental platform and the water layer without tidal influence), presenting average porosity of 16% and permeability of 12 mD (SOMBRA et al., 1990).

The presence of usable infrastructures for CCS is another criterion favouring the choice of the Merluza Field as a location for the geological storage of CO_2. Engaging existing infrastructures is relatively cheaper than constructing new ones (HANNIS et al., 2017). In the Merluza Field, depleted hydrocarbon reservoirs are available, and the existing pipelines are favourable for transporting the captured CO_2 to the storage site to curb continental emissions.

Criteria	Note
Average porosity	Ilhabela Member - 21% a 4 700 m Ilhabela Member - 16% a 4 900 m Jureia Formation - 12% a 4 450 m
Porosity (qualitative comments)	In both reservoirs, the macroporosity is almost entirely intergranular, of primary origin. Volcanic feldspars and lithoclasts appear poorly dissolved. Higher levels of calcite in the Ilhabela Member occur close to the shales, indicating that the acidic fluids that originated in the shales were ineffective in dissolving the reservoir constituents.
Permeability	Ilhabela Member (1-SPS-20) - 10 a 100 mD Ilhabela Member (1-SPS-25) - 1 a 5 mD Jureia Formation (1-SPS-25) - 10 a 100 mD
Tectonic stability	The tectonically stable environment in general.
Reservoir characteristics	Lithic arcosios/arcosios constitute both reservoirs without significant variations in their detrital compositions—predominant lithoclasts: intermediate and acidic volcanic rocks, and in lesser basic volcanic quantities.
Clay minerals	Ilhabela Member - presence of chlorite fringes.
Degree of exploitation	High exploratory knowledge.
Infrastructure	Fixed platform; exclusive pipeline.

Table 2. Favourable criteria for the use of the Merluza Field for geological CO_2 storage.
Source: Ciotta and Tassinari, 2020.

The estimated CO_2 storage capacity of Merluza Field is 49,9 $MtCO_2$[1] (CIOTTA, 2020). The capacity estimation encourages the current study and planning of a viable CO_2 storage project. It is possible, for example, to consider the emissions of a given plant located in the Santos Basin coastline and examine if the chosen field can store the emissions emitted in the industrial processes.

4. CONCLUSIONS

The search for geological reservoirs is a relevant part of CO_2 capture and geological storage undertaking. The Santos Basin is strategically located due to its proximity to centres that emit greenhouse gases and the availability of oil-producing fields throughout its extension. The search for suitable regions for storage seems a logical path for the portfolio of CO_2 capture and geological storage in the Basin.

The use of the future depleted fields of the Santos Basin seems promising, both because it is an alternative to simple decommissioning in a world that is seeking solutions for its greenhouse gas emissions and because it takes advantage of the advanced geological knowledge and available infrastructure. The proximity of the Merluza Field to its decommissioning period suggests that it can be used as a CCS pilot project in the Santos Basin.

Finally, the search for geological reservoirs for CO_2 storage, even though incipient, is a process that makes sense within the dynamics in which the oil market and any enterprise that results in greenhouse gas emissions (Brazilian and worldwide) are inserted. As structured in this work, the analysis of local possibilities requires obtaining accurate data, but estimates and indications can be made.

It is worth noting that the study of potential results from an interconnection of factors: studying the feasibility of these developments requires the analysis of different parameters acting together. Therefore, an investigation that considers various factors involving economic and geological analysis is pertinent. With this type of information at hand, it is possible to zone areas of greater interest to be investigated with greater precision.

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1 New methodologies show more accurate data but they are still being published in peer-reviewed journals.

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CHAPTER 3

PARANA SEDIMENTARY BASIN'S POTENTIAL FOR CO_2 GEOLOGICAL STORAGE

Maria Rogieri Pelissari

ABSTRACT

Techniques of Carbon Capture and Storage (CCS) are important alternatives for decarbonisation, based on the world scenario aiming at net-zero emissions and energy transition. In Brazil, there is a vast potential for these technologies. The Parana Sedimentary Basin presents one of the best alternatives for CO_2 storage, considering the proximity to stationary sources of CO_2 and potential geological reservoir units, such as the significant variability of lithologies and total depth of the volcano-sedimentary succession. Also, the region comprising the basin includes the main areas of national production of biofuels. Therefore, locating CCS plants within the area can contribute to significant reductions in carbon emissions. This chapter presents an overview of the geological aspects of the Parana Sedimentary Basin, focusing on an assessment of its theoretical potential for CO_2 geological storage. This evaluation is based on data available in the literature involving geological investigations, considering saline aquifers, black shales, coal and basalts as the main potential reservoirs for CO_2 storage. The Rio Bonito, Itararé, Irati,

Ponta Grossa and the Serra Geral Formations present potential geological reservoirs for CCS.

Keywords: CO_2 Geological Storage; Parana Sedimentary Basin; BECCS; Decarbonization.

1. INTRODUCTION

Brazil's southern and south-eastern regions are associated with the highest CO_2 emissions from stationary sources in the country, with local emission rates up to 14,000 kt/year (Rockett et al., 2011). According to SEEG (2018, 2019), CO_2 total emissions in these regions would sum up to 420 Mt/year. More than half of these emissions would come from power plants, together with a large share of the steel and cement production industries, which contribute to over 3,000 ktCO_2/year (SEEG, 2018, 2019).

In a global scenario looking for a reduction in emissions and striving to tackle and prevent the impacts of climate change, Carbon Capture and Storage (CCS) technologies are considered one of the most important paths to achieve the proposed goals based on the Paris Agreement. According to the International Energy Agency (IEA), these techniques could reduce a cumulative amount of around 100 GtCO_2 by 2050, representing 14% of the total reduction in CO_2 emissions by 2050 (IEA, 2019). Also, limiting the availability of CO_2 storage would increase the cost and complexity of the energy transition once this technology is part of a least-cost portfolio needed to achieve climate and energy goals (IEA, 2019).

In summary, CCS technologies allow the final disposal of CO_2 captured from sources such as combustion of fossil fuels for power generation on thermoelectric complexes and cement industries. The CO_2 produced must then be separated from other gases, dehydrated, compressed and transported to the recommended site for permanent storage. Some of the main reservoirs described in the literature for CO_2 storage are depleted oil and gas reservoirs, coal layers, saline aquifers, black shales and mafic and ultramafic rocks, such as basalts (IPCC, 2005; Busch, 2008). Geological reservoirs for CO_2 storage must meet specific criteria (Table 1) to guarantee safe and permanent storage, including: minimum depth and thickness of the layer, presence of effective seal, good porosities, and trapping mechanisms. Sedimentary basins are good prospects considering CO_2 reservoirs. They generally contain a combination of various rocks that can be combined to provide suitable potential reservoirs for CO_2 storage.

Reservoir type	Depth (m)	Thickness (m)	Permo Porosity	Main trapping mechanism	Critical factors
Oil/Gas Reservoir	> 800	> 10	Porosity >10 % Permeability	Stratigraphic and structural	Retrofit
Saline Aquifer	> 800	> 10	2Md	Sealant layer	Potability
Coal layer	> 300 < 1.000	>2	Microporosity	Sorption in organic content	Low permeability
Black-shale	> 800	> 10	Microfractures	Sorption in clay	Distance > 600m from aquifers
Basalts	> 400	-	Vesicles and fractures	Mineralisation and sealant layer	Hydro availability

Table 1. Summary of requirements for CO_2 storage of each potential reservoir type.

Source: Pelissari (2021).

According to IPCC (2005), basins suitable for CO_2 storage have structural simplicity, thick sediment accumulations, permeable rock formations and low porosity formations acting as seals. The Possible geological units with potential for CO_2 storage within the Paraná Sedimentary Basin are predictable based on the data collected from the available literature.

The Paraná Sedimentary Basin extends through the states of Mato Grosso, Goiás, São Paulo, Paraná, Santa Catarina, and the Rio Grande do Sul in Brazil. It presents potentials to store the CO_2 emitted in its region considering the proximity to source sinks and reservoir rock units with the required geological configurations to serve as CO_2 repositories. According to Lima et al. (2011), this basin presents geological formations favourable for CO_2 injection, but it has no record carbon storage activity yet.

Also, Brazil's Southern and South-Eastern regions have great potential for geological storage because they have significant CO_2 emitting sources, principally from the Energy and Industrial Sectors (Figure 1) close to the Parana Basin (Carneiro et al., 2013). Therefore, there is a demand for reducing emissions, and there are geological reservoirs available for CO_2 storage within the Paraná Sedimentary Basin. According to Ketzer et al. (2007), there is a storage capacity of 462,000 $MtCO_2$ in saline aquifers and around 200 $MtCO_2$ in coal layers of the basin.

There are also significant potentials for CO_2 storage in basalts. Pelissari (2021) also indicates a potential for carbon sequestration in the basin's coal, black shales and basalts.

This chapter aims to present a brief discussion on the potential of the Paraná Sedimentary Basin for CO_2 geological storage, considering the main aspects of emissions, geological settings of the units and a summary on the legal and economic topics.

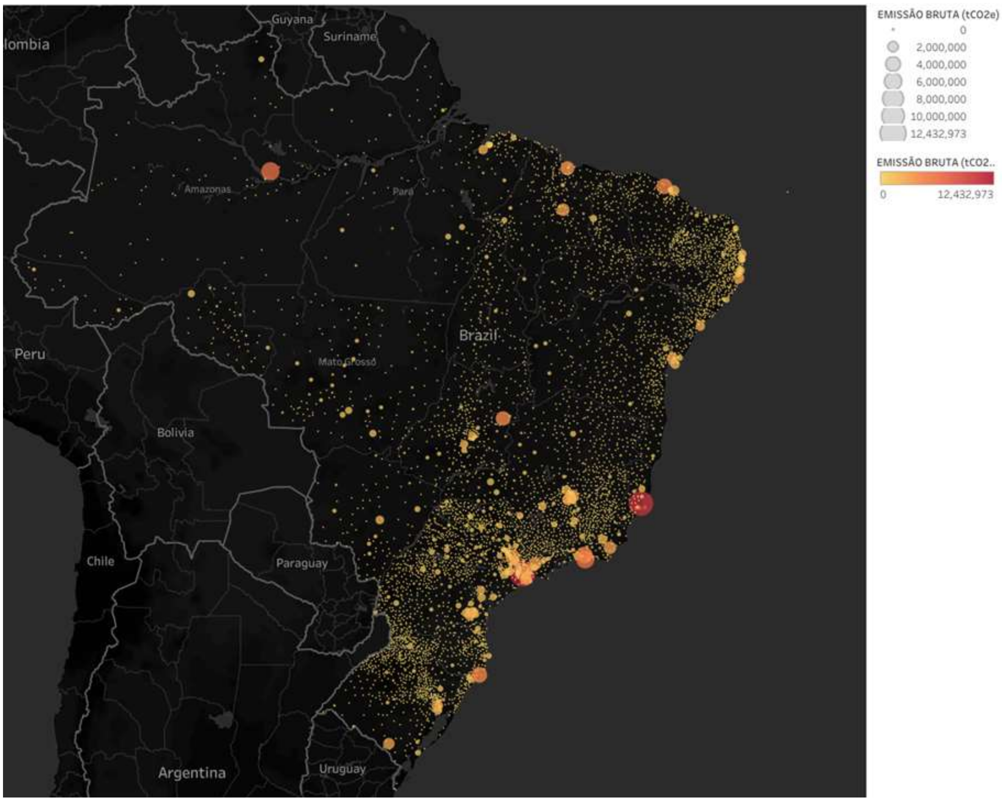

Figure 1. Brazilian gross emissions (tco2eq) by the city from the Energy and Industrial Sectors. Source: SEEG (2020)

2. GEOLOGICAL SETTINGS

As compiled in Milani et al. (1994, 2007), the Paraná Sedimentary Basin is filled by a sequence of volcano-sedimentary rocks from Ordovician to Cretaceous, with a depocenter of about seven kilometres thick, occupying an area of over one million square kilometres in the South-Central region of the Brazilian territory (Figure 2). The stratigraphic sequence includes rocks described in the literature as potential reservoirs for carbon geological storage, such as coal layers, oil and gas reservoirs, saline aquifers, black shales and basalts (IPCC, 2005).

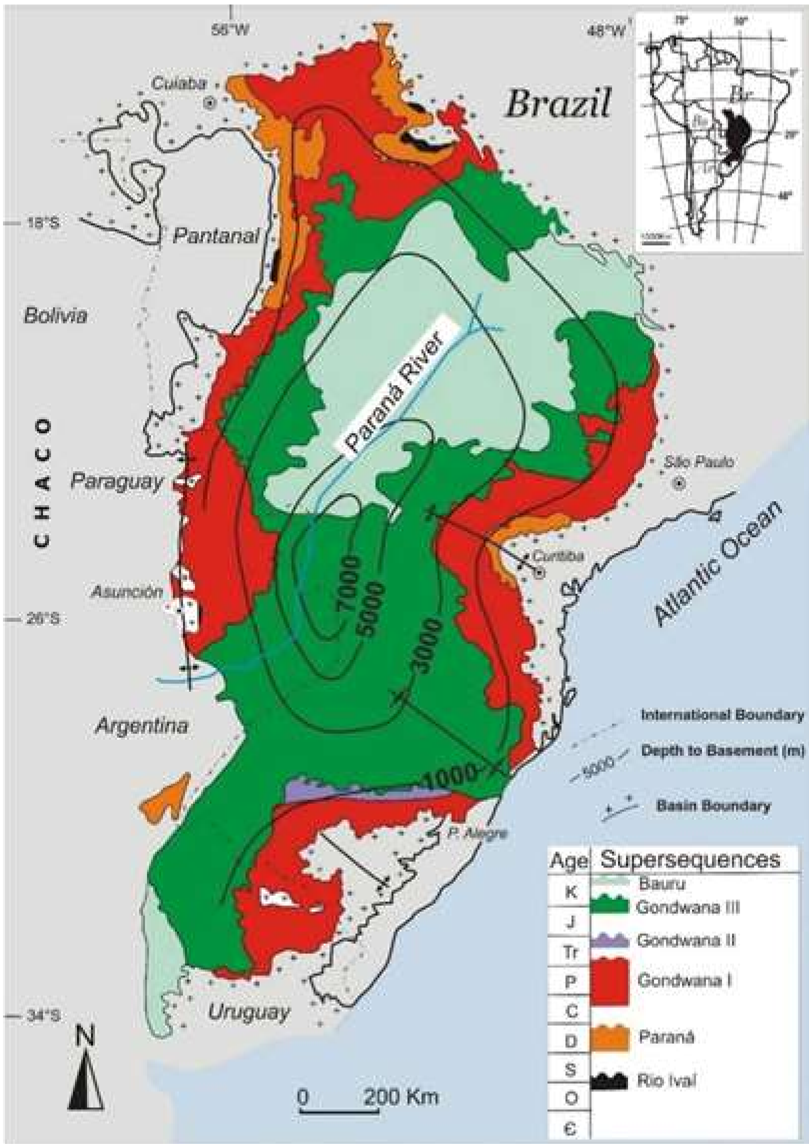

Figure 2. Geological map of the Brazilian portion of the Paraná Basin . Source: Milani et al. (1997, 2004).

The basin's stratigraphic column consists of six super-sequences correspon-ding to the Paleozoic and Mesozoic eras, including volcanic and sedimentary rocks—the Precambrian basement is composed of granite-gneiss complexes. The accommodation space for the Rio Ivaí Supersequence was created by reactivating basement weaknesses. The super-sequences include the basal sandstones of the Alto Garças Formation, diamictite layers of the Iapó Formation and Vila Maria Formation's fossiliferous shales and siltstones (Milani, 1997). Above and separated by erosive discordance is the Paraná super-sequence, which is deposited with Eodevonian sandy sediments of the Furnas Formation, gradually transitioning to marine sediments of the Ponta Grossa Formation composed of shales, siltstones and sandstones (Milani et al., 2007).

The Gondwana I super-sequence, separated by an unconformity, including the occurrence of the constituent formations of the Itararé Group, representing different environments of a fluvio-lacustrine and marine depositional systems under the influence of glaciers (Schneider et al., 1974). Covering the rocks of the Itararé Group are the rocks of the Rio Bonito and Palermo formations, which constitute the Guatá Group, with sandstones, siltstones and pelites of different depositional systems, and coal layers in the Rio Bonito formation.

The Irati, Serra Alta, Teresina, and Rio do Rastro formations constitute the Passa Dois Group, covering the Guatá Group. The rocks of the Irati Formation represent deposition in the marine environment of calm waters consisting mainly of shales and limestones (Schneider et al., 1974). The shales and siltstones of the Serra Alta Formation represent deposits of the marine environment, and the Teresina Formation comprises shallow and rough water marine silt and sandstone deposits (Schneider et al., 1974).

The Rio do Rastro Formation is at the top of the Passa Dois Group, composed of intercalations of sandstones and siltstones. The deposition of this formation is initially attributed to a shallow marine environment (supra-tidal) that transitions to coastal lowland deposits and subsequently to the establishment of fluvio-deltaic sedimentation (Schneider et al., 1974).

Above are the eolian deposits of the Botucatu Formation and the volcanic rocks of the Serra Geral Formation, from the Supersequence Gondwana III (Milani et al., 2007). The Botucatu Formation predominantly comprises sandstone facies deposited in a desert environment (Milani et al., 2007). The volcanic rocks of the Serra Geral Formation emerged from a Mesozoic fissural magmatic event and consist of a thick pile of basaltic lava and an intricate network of dikes and sills that cut through the entire sedimentary section of the Paraná Basin (Milani et al., 2007).

3. POTENTIAL RESERVOIRS FOR CARBON GEOLOGICAL STORAGE

Large urban and industrial centres are located in the area of occurrence of the Paraná Sedimentary Basin. It has significant stationary sources of CO_2, with a considerable variety of lithologic units in the stratigraphic sequence of the Basin, presenting great potentials for the application of CCS technologies. Studies such as Lima (2010), Rockett et al. (2011), Kalkreuth et al. (2013), Ketzer (2014), Diakakis (2019), San Martín Cañas (2020) and Pelissari (2020a, 2021) indicate prospective formations for CO_2 geological storage within the Basin.

Considering the potential CO_2 geological reservoirs described in the literature, at least five significant units in the Paraná Basin can be related to high regional potential for CO_2 storage: organic shales of the Irati and Ponta Grossa formations, basalts of the Serra Geral Formation, sandstones of the Itararé Group and sandstones, and coal of the Rio Bonito Formation. Each formation has its specific characteristics and requirements to fit as safe reservoirs and guarantees an effective abatement of CO_2 along the time, as summarised in Table 1. In this way, the five mentioned potential reservoirs should fit the minimum requirements for carbon sequestration on a local scale.

3.1. Coal Layers

The occurrences of coal in the Parana Sedimentary Basin are related to the bottom portion of the Rio Bonito Formation, the Barro Branco and Bonito Members, with depths varying up to 4,000m and average thicknesses up to 100m (Vilela & Cardoso, 2018). The Rio Bonito formation is also composed of cyclic Permian successions of sandstones and conglomerates, shales, clayey and carbonate siltstones, with the main structures consisting of parallel and cross stratifications (Schneider et al., 1974). The coal layers have an average cumulative thickness of 10 m and 40 km of horizontal continuity (Holz et al., 2000).

The coals are volatile bituminous coal with major maturation in areas close to the basic igneous intrusions, where they get up to anthracites (Kalkreuth et al., 2008, 2010). Almeida (2019) categorised the coals according to the ISO 111760:2005 classification as Bituminous C, with variable Vitrinite and high ashes content. Once the coal presents great affinity to CO_2, with preferential adsorption of CO_2 on the macerals, carbon storage has a huge capacity, mainly on its micro porosities (Rodrigues et al., 2015). Besides, the stratigraphically superior formation is the Palermo Formation, which contains shales, siltstones and claystone, with low permeabilities, which presents potential for capping rocks, guaranteeing safety for the CO_2 storage.

According to Weniger et al. (2010), the volumetric ratios of adsorption of CO_2 versus CH_4 are around 2:1 to 7:1, indicating a great potential for CO_2 enhanced-coalbed methane. In this way, considering that the coals of the formation achieved the generation window of gas, mainly CH_4 (Costa et al., 2014; Kalkreuth et al., 2020), it becomes an attractive aspect for the CO_2 injection and storage in the formation, with associated CH_4 production.

Considering that the main coal deposits occur in the southern portion of the Basin, within the State of Rio Grande do Sul, there would be a significant potential for carbon storage in this region, as already assessed by studies like Kalkreuth et al. (2013). However, there would also be a considerable potential on the south-eastern portion of the State of Santa Catarina, where there is a considerable thermoelectric activity, and the coal occurrences also satisfy the minimum criteria for carbon geological storage, as studied by Pelissari (2021).

Thus, coal layers of the Rio Bonito Formation, occurring under 300m of depth, present significant potential for carbon storage in the Parana Basin. The potential of these coal layers for carbon storage was also assessed and confirmed by Rockett et al. (2010), Ketzer et al. (2014), Holz (2010) and Kalkreuth, et al., (2013) and Pelissari (2021).

3.2. Saline aquifers

Saline aquifers are one of the most used reservoirs for carbon storage around the world. Considering the minimal criteria for CO_2 storage, such as capping rocks, depths higher than 800m and minimum porosities and permeabilities, at least two possible formations within the Parana basin present significant potentials; the sandstones of the Rio Bonito Formation and Itararé Group. The sandstones of the Rio Bonito Formation occur at depths up to 4,000m, being typically coarse and associated with porosities of around 20 % (Milani et al., 2007). Above the Rio Bonito Formation are the Palermo and Irati formations, composed of low permeability rocks such as claystones, siltstones and shales, serving as capping rocks (Lima et al., 2011).

In this way, these rocks present significant potentials for CO_2 storage, which is even major due to their associations with the coals of the Rio Bonito Formation, which offers excellent potential for carbon adsorption, increasing the storage capacity of the formation. Thus, in places with depths higher than 800 m, it would be possible to store CO_2 on the saline aquifers of this unit if the other minimum safety criteria are fit.

The Itararé Group is the bottom unit of the Parana Basin, and it is divided into four Formations: Lagoa Azul, Aquidauana, Campo Mourão and Taciba. It consists of rocks related to glacial marine and fluvio-lacustrine environments (Schneider et al., 1974), which hosts the Ponta Grossa-Itarare Oil System reservoirs. The total thickness of the formation is up to 1,500m, mainly composed of coarse sandstones interbedded with diamictites, conglomerates and claystones (Milani, 1997).

The porosities vary from 1 to 20% on the sandstones (França & Potter, 1991), favourable for CO_2 storage. The unit is covered by rocks of the Guatá Group, including sandstones, claystones, siltstones, coal and conglomerates, which do not guarantee a satisfactory capping aspect due to relatively high permeabilities and porosities. Although both the Rio Bonito and the Itararé units host hydrocarbon reservoirs, presenting better potentials for carbon sequestration.

Hence, above the depths of 800 m, if the capping units present suitable thickness, continuity and integrity, besides low permeabilities, these units can be potential saline aquifer reservoirs for carbon sequestration once they meet the theoretical and geological minimum criteria.

3.3. Black Shales

The basin has two main geological formations that contain black shales: the Irati and the Ponta Grossa Formations. The Ponta Grossa formation comprises Devonian shales, with total organic carbon contents ranging from 1.5 to 2.5% of organic matter type II (Zalán et al., 1990). These are the source rocks of the Ponta Grossa-Itararé Oil System (Zalan et al., 1990).

The rocks of the formation occur at depths up to 4,500 m and with thicknesses up to 600m along the basin (Zalán et al., 1990; Candido, 2007), sealed by low permeability rocks, such as the Itararé Group's clayey and siltstones and the formation shale layers themselves, serving as internal sealants (Zalán et al., 1990; Milani, 2007). The black shales have considerable contents of phyllosilicates in their composition, reaching about 60% of the total components (Weniger et al., 2010), which is favourable for carbon storage, once CO_2 is adsorbed by clay minerals and organic matter (IPCC, 2005; Bush et al., 2008).

In this way, the Ponta Grossa Formation presents a considerable potential for CO_2 storage, just as concluded by Ketzer et al. (2007). According to the depths and thickness maps by Zalan et al. (1990) and Ferreira et al. (2010), considering that for CO_2 storage in shales, the reservoirs should have minimum depths of 800m, the most prospective areas for carbon storage on the unit would be in the western-central region of the Paraná Basin.

The Irati Formation consists mainly of black shales and Permian carbonates (Hachiro, 1996), with 8 to 13% organic content, peaks up to 24%, and type I-II organic matter (Zalán et al. al., 1990). These black shales are source rocks of the Irati-Pirambóia Oil System, with potential for generating hydrocarbons due to thermal activities from the basic igneous intrusions in the basin (Milani et al., 1990, Milani & Zalán, 1999; Milani et al., 2007; Rocha, 2021).

Their thickness varies along the basin, up to 150 m, with depths of up to 3,500 m (Zalan et al., 1990), being sealed by internal sealing rocks (shales and carbonates with low permeabilities), as well as shales from the overlying Serra Alta Formation and carbonates from the Teresina Formation (Rohn, 1994). Also, the clay content reaches up to 70 % of the total components (Holanda et al., 2018; Abreu, 2004), favourable for carbon storage once CO_2 is adsorbed by clay minerals and organic matter (IPCC, 2005; Bush et al., 2008). In this way, the Irati Formation presents a potential for CO_2 storage, accordingly to San Martín Cañas (2020). The areas of the formation with higher prospects for CO_2 storage are the western part of the state of São Paulo, where the depths are > 800m.

The portion also has favourable thickness and logistics conditions considering the proximity to stationary sources of CO_2, hence, reducing costs of transportation (San-Martin Cañas, 2020). Besides, according to Weniger et al. (2010), the volumetric sorption capacity ratios are between CO_2 / CH_4 for shales of Irati, and Ponta Grossa formations range from 1.5: 1 to 4.5: 1, with maximum CO_2 sorption capacities of 3.2 to 12.2 m^3/t, varying mainly with mineralogical composition. Preferential sorption of CO_2 in shales leads to CH_4 desorption, presenting an attractive aspect for CCS projects once the injection of CO_2 could be coupled to shale gas production.

3.4. Basalts

Another potential unit for CO_2 storage is the Serra Geral Formation, associated with successive Cretaceous volcanic spills, consisting essentially of tholeiitic affiliation basalts (Melfi et al., 1988), with thicknesses up to 1,700m (Milani et al., 2007). The high degree of fracture of the unit described by Lastoria (2002) defines the unit as a fissured aquifer with calcic waters (Machado e Freitas, 2005; Lisboa, 1996; Reginato et al., 2013).

Basalts are good prospects for carbon storage due to their susceptibility to react with CO_2 in the presence of water and to form carbonate minerals from a continued reaction, which guarantees permanent and effective imprisonment of the gas (Bachu, 2007; Matter et al., 2016). The calcic waters of the Serra Geral

Aquifer also favour this process, helping with the availability of ions for mineralisation reactions. Thus, the Serra Geral Formation presents good potential for CO_2 storage, according to Carneiro et al. (2013), which indicates potential storage of about 270 $MtCO_2$ / year in this formation. However, the author stresses that large-scale CO_2 storage in volcanic rocks is still in the demonstration phase, as in Matter et al. (2016) and Von Strandmann et al. (2019).

4. BECCUS

Coupled with biofuels facilities, such as bioethanol or biodiesel production, CCS can lead to negative emissions, considering BECCS (Bio-Energy Carbon Capture and Storage). Once biomass captures CO_2 through photosynthesis, it leads to a net-negative carbon cycle if the generated CO_2 from biomass fermentation is captured and stored. Or it can be related to a carbon neutral cycle (i. e. when CO_2 is captured from the atmosphere by biomass and then returned to the atmosphere after biofuel combustion) (IEA Bioenergy, 2020). In this way, BECCS technologies should be strongly encouraged and implemented to achieve more significant reductions in carbon emissions.

The production of biofuels is divided into four different generations, according to the feedstock type: saccharine and starch (first generation); lignocellulosic biomass (second generation); micro/macroalgae biomass (third generation) and genetically modified cyanobacteria (fourth generation) (De Souza Abud & Silva, 2019). The primary industrial route for bioethanol production is the microbiological process from alcoholic or ethanolic fermentation (Silva et al., 2005). Sugars from different feedstocks, such as sugarcane and corn, are converted into ethanol, CO_2 and other byproducts by yeast cells (Monceaux, 2009). Brazil is the second biggest world producer of bioethanol, mainly from first-generation production from sugarcane fermentation, with a production increase of around 5% in 2019, achieving 33 billion litres (Conab, 2019) and emissions of approximately 24 million tons of CO_2/year (Garcia and Sperling, 2010). The sugarcane culture is concentrated mainly in the Northeast and South-Center regions (Vieira, 2008; novaCana, 2020).

Considering that the South-Center region of Brazil contains the Paraná Sedimentary Basin, the bioethanol-CCS combination may present a good possibility for BECCS projects (Pelissari et al., 2020b). The gas effluent from sugar fermentation for ethanol production is 99% pure CO_2, which is much more concentrated than the gas effluents from thermoelectric plants and refineries, giving it a very competitive character among others on the capture aspect (Smeets and Faaij 2010).

5. INFRASTRUCTURE

Some of the essential requisites for CCS projects are: satisfy geological conditions to guarantee safe and permanent storage; innovative technologies to capture and separate CO_2 at minimum costs; the proximity of the emitting source of CO_2 to the reservoir to reduce expenses with transportation; the existence of robust legislation to regulate all the steps of the CCS process and to guarantee continuous monitoring of the reservoir units, mainly after the end of the injection. Other factors include financial and economic incentives from both the governmental and private sectors, coupled with a consolidated carbon credit market to make CCS projects feasible, and the public acceptance of the technology (Kheshgi et al., 2012).

The necessary infrastructure for CCS projects consists mainly of the CO_2 capture and compression plant, transportation and injection facilities. The transportation can be done by different possibilities, according to the distances and conditions involved. Pipelines are generally the most economical and safe way to deliver CO_2 to storage sites, but ships and roads are alternatives for longer and shorter distances.

On the economic side, according to literature, the carbon capture phase is the most expensive one, representing up to 75% of CCS costs (Plasynski et al., 2009). Besides, new technologies are being developed with time and may bring down these elevated costs. It is crucial to consider the importance of incentives for developing CCS technologies and their implementation from both governmental and private sectors. Thus, fiscal incentives, a carbon market and carbon taxes are alternatives to be used for that.

On the legal aspect, the regimentation of CCS activities is essential to guarantee its correct implementation, safety, and efficiency. It includes monitoring CO_2 behaviour in the underground reservoir after the end of the injection phase. In this way, defining the correct procedures, pointing out the responsibilities and presenting a robust regulatory framework that foresees the obligations and penalties for all the phases of the CCS project is of extreme importance.

In Brazil, there is still no such regulatory framework, but some academic and governmental institutions are working on this topic to provide possibilities for the development of CCS activities. In this scenario, the European framework for CCS could be used, the 2009/31/CE Directive from the European Parliament on carbon geological storage, from 23/04/2009, once it is currently the world reference on the topic. This directive is adaptable to the Brazilian reality to define correct management for CCS activities.

At last, the public acceptance of CCS technologies is also of great relevance, considering that the projects are to be implemented offshore and onshore and may impact the local populations. In this way, it is recommended that marketing and social consciousness be developed so that the community understands the possible benefits and impacts of the project to be implemented and accepts its consequences, if any (Abreu Netto et al., 2020).

6. FINAL REMARKS

The Paraná Sedimentary Basin can develop Carbon Capture and Storage facilities due to its geological favourability and proximity to stationary emitting sources of CO_2. There is currently no operating CCS plant in the area of occurrence of the basin, and regulatory and economic developments are crucial to bringing commercial feasibility for such.

On the geological aspect, considering the main reservoir types for carbon sequestration described in the literature, there are at least five main geological formations that present the potential for CO_2 storage on the basin:

- Coal and saline aquifers on sandstones of the Rio Bonito Formation and Itarare Group
- Black shales of the Irati and Ponta Grossa Formations
- Basalts of the Serra Geral Formation

Other units could also present the potential for CO_2 storage, mainly considering local occurrences and possible structural and stratigraphic traps that could guarantee permanent and safe carbon abatement.

Since there is an essential activity of the biofuels sector in the occurrence area of the Paraná Sedimentary Basin, there is also a potential for the installation of CCS plants coupled with the generation of biofuels like bioethanol, creating BECCS facilities that could deliver neutral or negative emissions.

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CHAPTER 4

PROSPECTIVITY MAPPING OF THE IRATI FORMATION FOR CO_2 GEOLOGICAL STORAGE IN THE PARANÁ BASIN

Stephanie San Martín Cañas

ABSTRACT

The Paraná Basin represents an enormous potential for Brazil concerning implementing carbon dioxide capture, utilization and storage (CCUS), a critical technology to ensure a global clean transition. The relevance of the Paraná Basin relies not only on its stratigraphic sequence with a thickness of over 7 km but also because this basin happens to hold most of the CO_2 stationary sources of the entire country. Thus, CCUS can offer a feasible CO_2 mitigation solution for the south-eastern region of Brazil. Furthermore, the Irati Formation is one of the lithologic units within the Paraná Basin that exhibit a high prospect for CO_2 geological storage. The purpose of this chapter is to conduct a prospectivity mapping looking to identify the most favourable areas. The methodology consists of a geological mapping for site selection using the inverse distance weighting (IDW) interpolation method, using as inputs the ANP's wireline logs information and spatial data generated by our IEE-CCS research group. The resulting map validates the high prospectivity of the black shales of the Irati Formation as reservoirs for CO_2 geological storage that comply with both the technical and environmental

requirements in the central region of the Paraná Basin, specifically in the states of São Paulo, Paraná, and Mato Grosso do Sul.

Keywords: CO_2 geological storage, prospect assessment, Irati Formation, Paraná Basin.

1. INTRODUCTION

The future of the global energy sector relies on complying with the climate agreements of decarbonizing its operations to mitigate the effects of climate change. Decarbonization may come through a global clean transition from fossil energy sources into renewable energy sources. According to the IPCC (2018), decarbonization could be through a combination of electrification, the use of hydrogen, sustainable bio-based feedstocks, product substitution, and carbon dioxide capture, utilization and storage (CCUS). In this context, CCUS has been considered as one of the critical technologies to ensure the global clean transition. Also, an essential part of the lowest-cost path to effectively meet the climate targets (Global CCS Institute, 2019).

The relevance of CCUS relies on its ease and flexibility to be retrofitted to many existing fossil energy facilities, especially into the natural gas operations, and its ability to be integrated during the processes of design and construction of new facilities (Global CCS Institute, 2016). Considering the crucial role of CCUS in achieving climate targets and readiness of Brazil for its wide-scale deployment according to the Global CCS Institute (2015), since 2014, lots of efforts have been made to identify the regions with the best rock formations for CO_2 geological storage. Ketzer et al. (2014), in the 'Brazilian Atlas of CO_2 Capture Geological Storage', classified the Campos, Potiguar, Recôncavo, Santos, and Paraná sedimentary basins with a high prospect for CO_2 geological storage. From these five basins, the Paraná Basin represents an enormous potential due to its 7 km of thickness and its strategic position where most of the CO_2 stationary sources the entire country is located.

Although the Brazilian Atlas is one of the most relevant bibliographical sources on the potential for CO_2 geological storage in Brazil, the classification presented by Ketzer et al. (2014) on this atlas was rather general. It did not offer the most favourable areas within the prospective locations in the basin, as it was previously proposed by Caporale (2007) in a map that Rockett (2010) reported.

Therefore, considering the minimum requirements for implementing CO_2 geological storage, Brazil's two existing CO_2 storage prospect maps should exhibit significant reductions of the proposed areas with high prospectivity. Additionally, to implement industrial CO_2 geological storage projects in the Paraná Basin, the Brazilian energy sector must face the barrier of the lack of nearby storage sites and connectivity to transport and storage infrastructure (NAPP et al., 2014). Based on these concerns, this chapter evaluates the most prospective areas for CO_2 geological storage via detailed mapping of the Irati Formation. Looking to contribute to mitigating CO_2 emissions within the south-eastern region of Brazil, associated with prospective natural gas production, and may help reduce the overall costs of the CCUS project in the Paraná Basin .

2. CO_2 GEOLOGICAL STORAGE PROSPECTIVITY MAPPING OF THE IRATI FORMATION IN THE PARANÁ BASIN

Many authors agree that the selection process of suitable CO_2 geological storage sites is the most crucial step towards successful deployments of CCUS projects (IPCC, 2005; WRI, 2008; ROSNES et al., 2011; THRONICKER et al., 2016; NETL, 2017; SELOSSE & RICCI, 2017; MIDDLETON & YAW, 2018).

According to the NETL (2017), the site selection process consists of four stages: extensive regional evaluations, subregional assessments, detailed characterization of prospective areas, and selection of suitable storage sites ready for permitting under all regulations. This chapter focused on the first stage by identifying the best subregional locations where the Irati Formation offers suitable geological characteristics optimal for detailed reservoir assessments.

A suitable storage site for CO_2 geological storage must comply with three general requirements – capacity, integrity and injectivity (Table 1). The capacity requirement refers to the availability of sufficient CO_2 geological storage volume, the integrity refers to secure sites that do not present a significant risk of leakages, and the injectivity refers to the suitable reservoir properties for continuous CO_2 injections at industrial supply levels (IPCC, 2005; WRI, 2008; and European Communities, 2011). Also, the suitable storage sites must follow all regulations concerning the environmental and societal impacts, as well as the local HSQE risks and economic constraints (RØSNES et al., 2011; JAKOBSEN et al., 2013; and SENIOR, 2014).

Capacity	High CO_2 sorption
	Porous rock
	Good thickness
	Areal continuity
Integrity	Reservoir depth >800 m
	Effective seal
	Simple structural complexity
	Reservoir pressure >73. 9 bar (CO_2 critical pressure)
Injectivity	Good permeability
	Appropriate salinity levels

Table 1. Parameters for suitable CO_2 geological storage sites

Source: San Martín Cañas, 2020.

2.1. The Irati Formation as a suitable storage site for CO_2 geological storage

The previous studies involving prospectivity of CO_2 geological storage in the Paraná basin by Ketzer et al. (2014) and Caporale (2007) did not consider the organic-rich shales formations as prospective reservoirs. According to San Martín Cañas (2020), the shale formations are considered unique exploratory assets that enable the co-development of the reservoirs for natural gas production and CO_2 geological storage in the Paraná Basin.

The relevance of the shales formations relies on the high potential to store CO_2 on their principal constituents: organic matter and smectites, especially montmorillonite (KROOS et al., 2003; BUSH et al., 2008; CHALMERS & BUSTIN, 2008; ROSS & Bustin, 2009; WENIGER et al., 2010; ESTUBLIER et al., 2014; BACON et al., 2015). Therefore, the Irati Formation represents an essential option for the development of CO_2 geological storage in Brazil considering the characteristics of its black bituminous shales: excellent organic matter content that reaches values over 20% (MILANI et al., 2007) and predominance of smectites (SOUZA, 2018; SAN MARTÍN CÃNAS, 2020).

Furthermore, considering the cost-effectiveness of co-developing natural gas with CO_2 geological storage, the Irati Formation has been considered a potential source rock for hydrocarbon generation in the Paraná Basin (MILANI et al., 2007; ANP, 2013; ANP, 2017; LÓPEZ et al. 2019).

The high prospectivity of co-development of the reservoirs of the Irati Formation for natural gas production and CO_2 geological storage has been presented by San Martín Cañas (2020) through an investigation based on the data mining of the organic geochemical data. The organic geochemical data consist of 484 rock samples retrieved from literature and 19 rock samples produced by our IEE-CCS research group. Considering the potential reservoir requirements for CO_2 storage, the black shales of the Irati Formation have a high CO_2 sorption capacity. The shales have a high content of smectites, high TOC values (mainly of type I and II kerogens), high secondary porosity volume from thermal maturation and magmatic influence of the Serra Geral Formation and good areal continuity. On the potential reservoirs integrity and security requirements, the Irati Formation appears to be safe due to the simple structural complexity within the central region of the Paraná Basin. At these regions, the potential reservoir's unit reaches higher depths (>800 m), confined by effective seals such as the organic-lean shales of the Serra Alta formation and the intrusions of the Serra Geral Formation.

Although San Martín Cañas (2020) verified the capacity and integrity requirements, the author did not validate the injectivity requirement since investigations involving reservoir pressure, permeability and salinity levels are absent because the Irati Formation is not associated with hydrocarbon production.

2.2. Methodology

To identify areas with high prospectivity for CO_2 geological storage within the Irati Formation of the Paraná Basin, a dataset with the information of 125 wells reported in the BDEP well technical data provided by the ANP for the RCGI project 36 were engaged. It involves a collection of shapefiles from San Martín Cañas (2020) corresponding to the minimum CO_2 injection depth, the Guaraní aquifer maximum depth, and the safe distance between the aquifer and the CO_2 injection. Other shapefiles engaged include those from the GASBOL pipeline (GISMAPS, 2016) with the Brazilian administrative boundaries, Paraná Basin's geological settings with the outcrops of the Irati Formation, and regional geological structures (Serviço Geológico do Brasil - CPRM, 2020). The methodology for the CO_2 geological storage prospectivity mapping of the Irati Formation in the Paraná Basin involves a numerical encoding of the well information regarding hydrocarbon shows and interpolation using the inverse distance weighting (IDW) tool software QGIS 3.12.1.

Understanding that there is a relationship between the hydrocarbon potential and the CO_2 geological storage potential due to the characteristics of the black shales of the Irati Formation discussed in the previous section, from the well information records it was encoded into two numerical values the hydrocarbon show attribute. Such numerical encoding designated values of 0 (zero) in the case of no presence of hydrocarbon shows, and values of 1 (one) for the presence of hydrocarbon shows within the Irati Formation.

Using the values from the numerical encoding and the IDW tool, a map of interpolations of the hydrocarbon occurrences was generated. The yellow colour indicates areas with the best chance for hydrocarbon occurrences. The IDW interpolation map was contrasted against the minimum depth limits for technical and environmental compliance based on CO_2 geological storage. The areas that resulted from the intersection between the IDW interpolation within the safe distance between the aquifer and the CO_2 injection have a high prospectivity for storage and then converted into a separated polygon in red colour. The areas that resulted from the intersection between the IWD interpolation and the Guaraní Aquifer maximum depth, the safe distance between the aquifer and the CO_2 injection, are considered portions with intermediate prospectivity for CO_2 geological storage and separated into an orange-coloured area polygon. The areas that resulted in no chance for hydrocarbon occurrences and outside the minimum CO_2 injection depth were not split into individual polygons and maintained a grey colour as an indicator of no likelihood of hydrocarbon; therefore, indicated as poor prospectivity areas for CO_2 geological storage.

2.3. Results and discussions

As a result, the CO_2 geological storage prospect map of the Irati Formation is presented in Figure 1. The map shows that the areas with high prospects are in the southwestern region of São Paulo, the northwestern region of Paraná, and the central part of the eastern region of Mato Grosso do Sul. Furthermore, the central part of the southern region of São Paulo, the central region of Paraná, and the southern region of Mato Grosso do Sul are considered areas with intermediate prospectivity for CO_2 geological storage.

The areas with high prospects for CO_2 storage comply with the technical constrain of a depth below -800m. The environmental constraints involving the distance between the CO_2 injection and the maximum aquifer depth of approximately -1000 m are consider safe. Based on capacity and integrity requirements, the Guaraní Aquifer is secure from any possible contamination related to the future CO_2 injection in reservoirs of the Irati Formation. In these high prospect areas, the CO_2 geological storage reservoirs are expected to reach depths between -1600 m and -3000 m. The intermediate prospects areas for CO_2 storage comply only with the technical constraints. Still, considering the uncertainties and variabilities related to the actual maximum depth of the Guaraní Aquifer, it is expected that many of these areas are suitable for CO_2 injections if further research validates accurate depths for these limits. In this regard, the proposed reservoirs may reach depths between -1000 m and -1600 m. Such reservoir units can offer a better cost-benefit option than those in the high prospects area, considering the less drilling depth, reservoir pressures, and temperatures that impact the storage infrastructure costs. However, the IDW interpolation of the hydrocarbon occurrences shows a high potential towards the southern part of the Paraná Basin in Santa Catarina and the Rio Grande do Sul. It is essential to address that this region has fewer control points; therefore, the performance of the IDW tool is not accurate. Contrasting with IDW interpolation results presented in Figure 1, San Martín Cañas (2020) proposed a prospectivity map using an interpolation generated by a Support Vector Machine algorithm where the Irati Formation has poor-to-no potential for CO_2 geological storage in this part of the Paraná Basin. This last fact reinforces the poor performance of the IDW tool in this southern region.

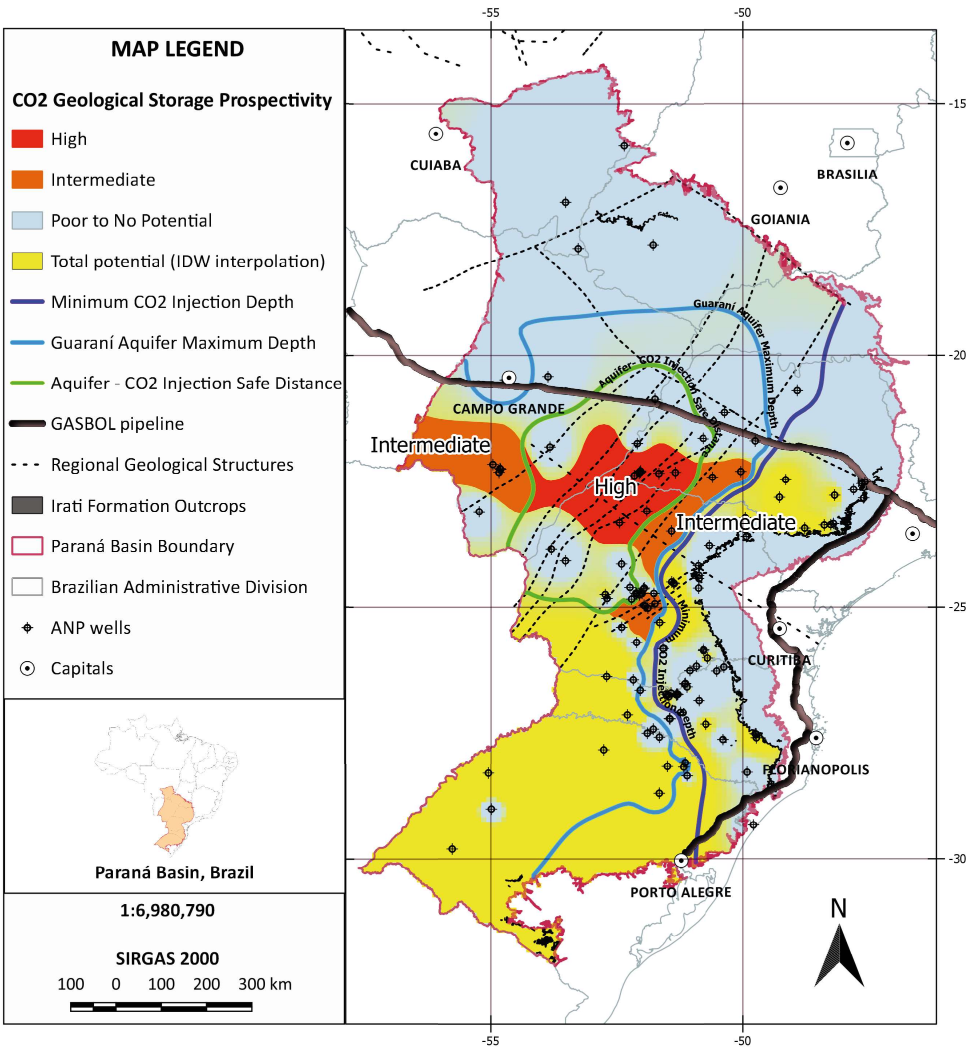

Figure 1. CO_2 geological storage prospectivity map of the Irati Formation in the Paraná Basin.

3. FINAL REMARKS

From mapping the prospective CO_2 storage sites, we can conclude that the most suitable areas of the Irati Formation for CO_2 geological storage within the Paraná Basin are in the states of São Paulo, Paraná and Mato Grosso. Areas with high to intermediate prospectivity for CO_2 storage only comply with the technical and environmental constraints. But also contain most of the CO_2 stationary sources of the whole country.

Addressing the need for connectivity between the storage and transport infrastructure, the proximity of the GASBOL pipeline to the proposed high to intermediate prospectivity areas offers an optimal scenario for the development of CCUS industrial projects in the south-eastern region of Brazil, the most carbon-intensive of the country. Furthermore, the proposed CO_2 geological storage prospectivity map of the Irati Formation offers a more detailed overview of suitable areas than the maps previously presented by Ketzer et al. (2014) and Caporale (2007).

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CHAPTER 5

CO_2 GEOLOGICAL STORAGE THROUGH ADSORPTION IN ORGANIC-RICH SHALES: A CASE STUDY OF IRATI FORMATION SHALES FROM THE PARANÁ BASIN, BRAZIL

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ABSTRACT

Geological sequestration of carbon dioxide (CO_2) can represent an efficient and safe long-term storage of this greenhouse-contributing gas. When applied to shales, CO_2 injection can enhance shale gas recovery (CO_2-ESG) and contribute to CO_2 abatement through geological storage. Shale is considered an unconventional reservoir due to its reduced permeability, consequently CO_2 storage in shales has peculiar characteristics: storage through adsorption into the microporosity of organic particles and clay minerals. The efficacy of CO_2 adsorption and CH_4 desorption processes drive CO_2 storage capacity and hydrocarbon production of organic-rich shale. Therefore, understanding gas sorption patterns in shale and how these are affected by its organic and inorganic composition is essential to evaluate shale's CO_2 storage capacity.organic matter quantity, type and maturation are vital parameters considering CO_2 adsorption in shale because it controls organic porosity, pore size, and internal surface area within this lithology. Besides the organic component, clay mineralogy also affects CO_2 storage capacity in shale. Expandable clay minerals, such as smectites, contribute as CO_2 adsorption sites and add to shale's overall CO_2 storage capacity. Thus, such organic and mineralogical characterisation should be the first step towards CO_2 storage capacity assessment in shale. This chapter investigates the complexity of the interaction between the organic and inorganic components in shale with CO_2. Due to the heterogeneity regarding the organic content and maturation stage of shales from Irati Formation, Paraná Basin, Brazil, these were selected as a case study in this research. Selected Irati Formation organic-rich shale samples went through the following experimental procedures: total organic carbon and Rock-Eval pyrolysis screening, paired with palynofacies, vitrinite reflectance and spore fluorescence to characterise the organic component; followed by x-ray diffraction and scanning electron microscopy to determine mineralogical composition; together with gas sorption isotherms (BET and Langmuir methods) to characterise the porous media and CO_2 storage capacity. The relation between shale's composition and sequestration was analysed and demonstrated in this study to improve the knowledge on CO_2 geological storage into organic-rich rock formations and scientifically communicate how these unconventional reservoirs can significantly contribute to CO_2 abatement.

Keywords: CO_2 geological storage; organic-rich shales; shale gas, sorption isotherms; CO_2 adsorption Irati Formation, Paraná Basin, Brazil.

1. INTRODUCTION

Carbon capture, utilization, and storage (CCUS) refer to a suite of technological processes to reduce carbon dioxide emissions. These technologies include: (i) CO_2 capture and separation from gaseous effluents; (ii) CO_2 transport through pipelines or ships from the capture facility to a storage site or industrial facility; (iii) CO_2 utilization via service or product with economic value and(iv) CO_2 storage in suitable geological formations (Bachu, 2002; Bachu et al., 2007; GCCSI, 2019; Lal, 2005).

CCUS technologies stand out among a diverse portfolio of CO_2 mitigation strategies due to their potential to decarbonize the carbon-intensive power and industrial sectors worldwide (IPCC, 2005; 2014). Additionally, CCUS is required as a component for other essential CO_2 abatement technologies, such as bioenergy with CCS (BECCS) and direct air capture (DAC), which are vital to reaching net-zero by providing negative emissions (Budinis et al., 2018; Daggash, Fajardy, & Mac Dowell, 2020; Leeson, Ramirez, & Mac Dowell, 2020).

CO_2 geological storage is the segment within the CCUS chain that plays a significant role in mitigating the worst impacts of climate change and meeting net-zero emission targets (IPCC, 2005, 2014). This role arises from the capacity of injecting large volumes of CO_2 into adequate geologic formations. For instance, global targets are estimated at 10 Gt CO_2 emission abatement per year by 2050 (IPCC, 2014), and this could only be achieved with geological CO_2 storage (Zahasky & Krevor, 2020), which despite the yet few large-scale facilities, the already reached 97.5 million tonnes of CO_2 been stored annually (GCCSI, 2019).

CO_2 geological storage consists of CO_2 injection and storage into adequate reservoirs for a geologically significant period (Bachu, 2002). Suitable reservoirs must present (i) sufficient capacity to store large volumes of CO_2; (ii) adequate “injectivity” to allow the injection and flow of CO_2 into the geological formation; and (iii) confinement or integrity of the reservoir (e. g., geological configuration with traps and sealing that retain the upward CO_2 buoyancy and prevent leakage for the desired period) (Bachu et al., 2007; Krevor, Blunt, Trusler, & Simone, 2019). Additionally, reservoirs should be permanently monitored to ensure that the CO_2 remains stored within the geological formation (EC, 2009).

Such a combination of geological features is common in both conventional (e. g., sandstones and carbonates) and unconventional reservoirs (e. g., coal seams and organic-rich shales) (Rodrigues, 2002). However, it is essential to highlight that CO_2 storage sites are not simply associated with a sedimentary basin and a suitable geological formation. It relies on geological, geochemical and petrophysical processes and properties such as porosity, permeability, caprock integrity, injectivity and fluid dynamics (Haszeldine, 2019; Krevor et al., 2019)

This chapter raises the hypothesis that organic-rich shales can store substantial volumes of CO_2 due to rock-fluid properties that attribute a remarkably high CO_2 storage capacity to these unconventional reservoirs. The hypothesis was tested by Rocha (2021) on Irati Formation organic-rich shales to discuss if the Irati Formation can be a feasible target for both CO_2 reduction and shale gas production under small-scale CO_2 emitting-sinking/closed-cycle systems in southern Brazil, where the CO_2 emitting sources are close to the geological reservoir. Moreover, the chapter aims to project the understanding of the geological requirements for CO_2 storage in shale reservoirs and further assess storage capacity in organic-rich shales.

2. CO2 STORAGE IN SHALE RESERVOIRS

Shales are considered unconventional reservoirs, and the CO_2 storage in shales has peculiar characteristics: storage through adsorption in pore internal surface areas (Bemani et al., 2020; Chen & Xiao, 2014; Yu et al., 2019; Zhou et al., 2019, 2020). As shown in Figure 1 and in contrast to the conventional reservoir, smaller pores in organic-rich shale imply a higher internal surface area. Thus, smaller pores in organic-rich shale suggest a higher internal surface area; therefore, a higher storage capacity due to the adsorption trapping mechanism.

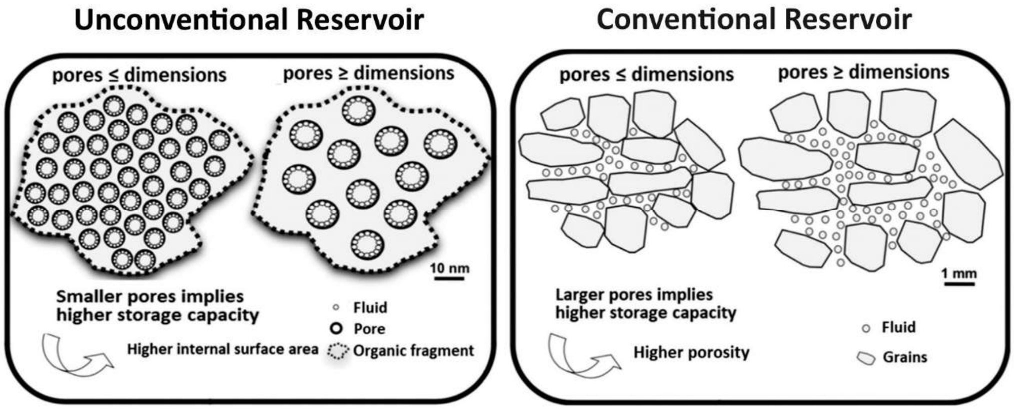

Figure 1. Porous media, CO_2 trapping mechanism and storage capacity illustration scheme for unconventional (on the left) and conventional reservoirs (on the right side of the image), focusing on the role of organic porosity and pore-size distribution. Adapted from de Rodrigues & Lemos de Sousa (2008)

The co-existence of organic and intergranular porosity in shales results in a wide range of pore volumes and pore size distribution, affecting gas flow patterns within this lithology. According to Mastarlez et al. (2013), gas flow in shales occurs through Knudsen diffusion and slip flow in nanometre-size pores, and through Darcy-like flow, in larger pores. It differs from the gas flow pattern in conventional reservoirs, such as sandstones, which is Darcy-like flow in the micrometre to larger pore sizes (Chen & Xiao, 2014; Curtis et al., 2011; Han et al., 2017; Mastalerz et al., 2013). Therefore, understanding shale's organic porous systems and the CO_2 adsorption process is essential to evaluate the potential for CO_2 storage into this geological formation.

Shale composition determines its porosity, therefore, its CO_2 sorption capacity and storage potential. In organic-rich shale, gas storage capacity mainly relies on organic porosity and clay mineralogy, where the CO_2 gets stored through adsorption.

Additionally, part of the CO_2 is held in a `free` way into larger pores and fractures (Al-Mutarreb et al., 2018; Klewiah et al., 2020).

Shale's porous system (e. g., primary and secondary porosities) result from a complex interaction of physical and chemical processes before and after deposition (Al-Mutarreb et al., 2018; Fatah et al., 2020; Romero-Sarmiento et al., 2012). In this sense, shale's pore size/type, interconnectivity, and distribution, rely on the inorganic matrix and the organic matter content. It can be divided into clay matrix porosity, non-clayey matrix porosity, and organic porosity (kerogen) – which hosts most of the porosity fraction in organic-rich shales.organic parameters to be considered include kerogen quantity (TOC wt. %), type and maturity level, while inorganic aspects rely on mineralogy, such as ratios of silica/quartz, carbonates, and predominant clay minerals (Goodman et al., 2020; Schaef et al., 2014; Weniger et al., 2010).

2.1. The Role of the Organic Matter

CO_2 sequestration in organic-rich shales is mainly driven by its organic porosity (Boruah et al., 2019; J. Chen & Xiao, 2014; Chen et al., 2020; Hackley & Cardott, 2016; Han et al., 2017; Pan et al., 2015; Sihra & Head, 2010). Moreover, the storage capacity of shales relies on kerogen evolution, more specifically to its thermal cracking during catagenesis and to hydrocarbon generation and migration (Romero-Sarmiento et al., 2012).

Organic maturation is crucial for organic porosity and CO_2 geological storage and hydrocarbon recovery processes in shale reservoirs. It controls organic porosity, pore size and surface area within these lithologies; therefore, the efficacy of CO_2 adsorption and CH_4 desorption processes, which drive CO_2 sequestration in shales and enhanced shale gas and oil recovery associated processes.

During the early stages of thermal maturation, the total organic content (TOC) controls fluid adsorption in organic-rich shales (Han et al., 2017) due to the kerogen swelling and shrinkage effect and the associated organic porosity generation. Kerogen swelling reaches its maximum at the transitioning oil to the gas window, at a Tmax of approximately 445°C and vitrinite reflectance of 0.8% Rr. After 0.8% Rr, organic nanopores are formed by the shrinkage of kerogen and by the release of hydrocarbons, leading to an increase in internal surface area and organic porosity. The continued cracking of the kerogen results in a more rigid kerogen residue, and subsequently, the swelling and retention ability of the kerogen network is decreased. Therefore, fluid sorption in shales tends to increase with maturity until a maximum sorption capacity is reached (Chen & Xiao, 2014;

Han et al., 2017). In this sense, organic-rich shales with vitrinite reflectance above 0.8% Rr and below 3.5% Rr are more suitable for CO_2 storage through adsorption.

According to Chen & Xiao (2014), the evolution of organic porosity in shales is divided into three stages. The first stage of nanopores formation, with vitrinite reflectance measurements between 0.6% and 2.0% Rr. In this stage, there is an initial decrease in nanopores during oil generation (0.6% < Rr < 0.8%), followed by a nanoporosity increase during oil cracking to gaseous hydrocarbons, (0.8% < Rr < 2.0%). There is a second stage of nanoporosity development, with Rr between 2.0% and 3.5%. In this stage, further methane generation and kerogen cracking result in an even more matured solid, graphitic-like structure and nano and microporous kerogen residue. In the third and last stage of organic porosity development, with the Rr > 3.5%, high temperature and pressure decomposes the organic matter and transforms the nano and micropores to mesopores and macropores. At this stage, the shale has no longer sufficient sorption capacity to CO_2 adsorption.

2.2. The Role of Mineralogy

Clay minerals are genuinely relevant to CO_2 geological storage and affect the gas sorption capacity in shales. For instance, high surface area clay mineral-rich shale formations (e. g., clays of the smectite group) tend to have higher CO_2 storage capacity (BERTIER & ROTHER, 2016; BUSCH et al., 2008, 2017). Regarding sorption capacity, Ca-exchanged smectite can adsorb the most significant amounts, followed by Na-exchanged smectite, illite and kaolinite, and negligible amounts of CO_2 adsorbed on chlorite (BUSCH et al., 2008, 2020).

For smectites, which are expandable clays, CO_2 adsorption can lead to volumetric expansion followed by the generation of swelling pressures (BUSCH et al., 2008). Such volumetric expansion leads to dehydration cracks that work as pathways for CO_2 flow rates into the formation, possibly accelerating the CO_2 storage process. However, consequent swelling pressures can close the generated fractured path and result in reduced permeability overtime after a CO_2 saturation breakthrough point is reached (BUSCH et al., 2008). In summary, CO_2 sorption on clay minerals in shale formations will increase flux rates after CO_2 breakthrough, while times scales for a breakthrough are still far above the critical time scale of 10,000 years requested by most regulators. At the same time, depending on the details of the CO_2 concentration gradients across the seal, significant amounts of CO_2 will be temporarily immobilized, contributing to storage safety and reducing reservoir pressure (BUSCH et al. 2020).

3. RESEARCH METHODS

To evaluate the potential of shale gas reservoirs for CO_2 sequestration, the research methodological must comprise a general characterization of the geological formation, followed by a detailed analysis of its organic and mineralogical content. Additionally, gas sorption isotherms measurements and reservoir properties must be considered.

Besides bibliographical research and sampling the studied formation, it is essential to apply further analytical procedures, including organic geochemistry, petrography, mineralogy, and gas sorption isotherms. These analytical procedures must include: (i) organic geochemistry analysis, such as TOC and Rock-Eval pyrolysis; (ii) organic petrography techniques, such palynofacies and kerogen typing, vitrinite reflectance measurements and spore colour and fluorescence identification; (iii) mineral characterization through x-ray spectrometry, and (iv) gas sorption isotherms, such as low-pressure (BET method) and high-pressure (Langmuir method) adsorption and desorption measurements, for petrophysics data acquirement and storage capacity estimates, respectively. This combination of analysis and experimental procedures provides the overall geological feasibility of organic-rich shales for CO_2 storage.

3.1. TOC and Rock-Eval screening

Total organic carbon (TOC) analysis is essential to source-rocks evaluation. It is usually the first analytical procedure to be carried out to determine hydrocarbon generation potential since it quantifies the preserved organic matter within the rock, expressed as a percentage. The measured organic content includes the insoluble fraction (kerogen) and the soluble in organic solvents fraction (bitumen). TOC classifies the shale into four categories: (i) shale containing less than 0.5% TOC is considered as poor source rock, (ii) shales containing a TOC between 0.5% and 1% indicate fair source rocks, (iii) shales containing TOC values between 1% and 2% indicate good source rocks, and (iv) shales containing TOC values above 2% often indicate a highly reducing environment and preserved organic content and indicate excellent source-rock potential (BOSTICK & DAWS, 1994; HUTTON, 1987; MUSTAFA et al., 2015). After determining the TOC levels, samples with significant TOC values (usually greater than 1%) proceeded to the pyrolysis Rock-Eval analysis.

Rock-Eval pyrolysis is a rapid screening technique for source-rock evaluation. Under laboratory conditions, it simulates the catagenesis and metagenesis processes by which the rock was exposed, determining the stage of maturation in which the preserved organic matter is found. It consists of the volatilization of the sample's hydrocarbons by a controlled temperature increase and wavelength reading via an infrared cell – in a similar process for determining TOC, there is no combustion. Overall, Rock-Eval pyrolysis can be used to identify the type and maturity stage of the organic matter and determine the hydrocarbon potential of source rocks (ESPITALIÉ et al. 1977).

Besides organic geochemistry, organic petrography techniques are essential to characterise and classify the organic content of organic-rich shales, such as organic matter quantity, type, and maturation.

Petrographic Composition and Palynofacies

The petrographic composition of organic-rich shales should be carried out for palynostratigraphy and geological age determinations, depositional environment interpretations, and stratigraphic correlations with other sedimentary basins. Additionally, organic petrography techniques are applicable to determine the kerogen type and origin through palynofacies associations based on maceral group classification and its relative frequency among the analysed sample`s organic compounds.

Maceral classification should be in accordance with the International Committee for Coal and Organic Petrology (ICCP). It should follow the ISO 7404-3 (2009), which classifies organic compounds based on morphological constituents: amorphous organic matter, palynomorphs, and phytoclasts divided between non-opaque/translucent and opaque phytoclasts, and opaque organic matter (ICCP, 1998, 2001).

Vitrinite reflectance, Spore Fluorescence and Colour

Vitrinite reflectance (Rr%) measurements constitute an optical petrographic methodology for determining organic maturity based on reflected light microscopy. It estimates the degree of thermal maturation of the organic content by measuring the percentage of incident light reflected from the surface of vitrinite particles in the rock sample (TAYLOR et al., 1998). This analytical method was developed to classify the coals' rank, also applied to other organic-enriched lithologies, such as shales. Vitrinite particles identification and reflectance measurements should follow the guidelines recommended by the ASTM D7708-14 (2014), ISO 7404-5 (2009) and ICCP (1998).

Qualitative spore fluorescence and spore colour are two optical parameters of thermal maturity of organic maturation, helpful in evaluating maturation levels of low-rank rocks until the end of the oil window (RODRIGUES, 2002). When correlated with the quantitative Rr% method, spore fluorescence and colour parameters can provide additional support for the thermal maturity of the rocks.

Spore exine colour is a method to assess the thermal maturity of sedimentary rocks. With increasing burial depth, spore colour changes from light to dark, and it is irreversible. Moreover, maturation causes a gradual shift in organic matter fluorescence colours (redshift) from the shorter to the longer wavelengths: blue and green to yellow, orange and finally red. According to the scale, colours vary from blue and green for an immature sample to orange to red for more mature rocks, following the ICCP Standard (ICCP, 1998).

Whole-rock and Clay-fraction Mineralogy

Mineralogy plays an essential role in CO_2 geological storage reservoirs. Mineralogical content, especially clay minerals, contributes to shale's total porosity (AL-MUTARREB et al., 2018; BUSCH et al., 2020; KLEWIAH et al., 2020). Therefore, it contributes to its adsorption capacity and gas storage potential. Analysing the mineralogical content helps determine the depositional paleoenvironment and paleoclimate and identify post-depositional processes and thermal history of a sedimentary basin (SANT'ANNA et al., 2006). X-ray diffraction (XRD) technique, a scanning electron microscope (SEM) should be applied for mineral content characterization and identification of clay minerals.

Gas Sorption Isotherms

Gas sorption isotherms and models are efficient methods to evaluate the CO_2 storage potential in a geological reservoir, especially in coals and organic-rich shales, where the adsorption drives CO_2 storage that is accumulating in minerals and organic surfaces (KALKREUTH et al., 2013; KLEWIAH et al., 2020; WENIGER et al., 2010; RODRIGUES, 2002). Sorption of CO_2 or CH_4 onto shales are determined in laboratory experiments through isotherms. Sorption isotherms quantify gas storage within the studied sample by measuring gas adsorption and desorption processes at different pressure gradients – from atmospheric pressure to above the reservoir pressure and under constant temperature – analogous to the reservoir temperature. Sorption models quantify the relation between the absorbed/free gas and the adsorbed (stored) gas within the studied sample.

The Langmuir sorption model is the most adequate to explain the behaviour of gas storage in the coal and shale organic porosity, based on experimental analysis

(RODRIGUES, 2002; RODRIGUES et al., 2013, 2016; WENIGER et al., 2010; YU et al., 2016; ZHOU et al., 2019). It provides a good description of adsorption into microporous sorbents and the existing equilibrium between stored/adsorbed gas and free gas by determining saturation limits (RODRIGUES, 2002). The Langmuir isotherm model is the following:

$$Gcs = V_L * P/(P+P_L)$$

Gcs is the gas content at saturation (scf/ton), P is the pressure, V_L and P_L are the Langmuir volume (scf/ton) and pressure (psi), respectively. The Langmuir volume (V_L) corresponds to the maximum gas adsorption capacity of the studied samples at a given temperature (Bachu et al., 2007). Langmuir sorption isotherms calculations depend on volumetric techniques or PVT (pressure–volume-temperature). The volumetric method considers gas expandability aspects for determining volume based on the Boyle-Mariotte principle. The Langmuir equation is mainly used for microporous material characterization, exhibiting Type I Isotherms. In the Langmuir model,, the adsorption is assumed to be limited to one monolayer (with pressure increase, gas molecules cover the sample surface to form a one molecule thick layer).

Besides the Langmuir model, the called Brunauer, Emmett and Teller (BET) sorption isotherms can be applied to analyse the porous media further. BET sorption isotherms can be used for porous material characterization, determining surface area, pore size distribution and pore volume of the studied sample through adsorption data. The isotherms are obtained by measuring the amount of gas adsorbed to the sample`s surface across a wide range of relative pressures at a constant temperature (typically referenced for liquid N2, at 77.4K). Desorption isotherms are determined by measuring the volume of gas removed as pressure is reduced at the same temperature as adsorption.

The BET sorption isotherm equation was developed in 1938. It is a well-known model for porous material characterization and a conventional method for specific surface area evaluation. The BET theory is derived from adsorption analysis. It is an extension of the Langmuir model, considering multi-layered gas molecule adsorption – the BET model is a derivation of adsorption isotherm equations for multimolecular adsorption (Brunauer et al., 1938). The BET equation is expressed below.

$$1/[V_a (P_0/P-1)] = (C-1)/(V_m C) \times P/P_0 + 1/(V_m C)$$

Va is the volume of adsorbed gas at standard temperature and pressure (STP), while Vm is the adsorbed gas volume at STP to generate an apparent monolayer on the sample`s surface. P0 is the saturated pressure of the adsorbate gas. P is the pressure of the adsorbate gas in equilibrium with the surface temperature at 77.4 K (temperature of liquid nitrogen). C refers to a dimensionless constant related to the enthalpy of adsorption of the adsorbate gas on the powder sample (BET constant). Total pore volume is derived from the amount of vapour adsorbed at a relative temperature close to unity (assuming pores are filled with liquid adsorbate). The average pore size is estimated from the pore volume.

Sorption isotherms and gas storage capacity are affected by numerous variables that can either be related to the reservoir sample or the sorption gas (individual or mixture). The main variables attributed to the samples are mineralogy, petrographic composition, and organic maturity. Variables in the experimental procedure are moisture, temperature, pressure, and gas composition, which affect the gas compressibility factor, which, together with gas molecule size, has a significant effect on the sorption process (Rodrigues, 2002; Fatah et al., 2020; Klewiah et al., 2020; Rodrigues et al., 2016).

Overall, gas sorption isotherms applied to geological CO_2 storage in shales and coals can provide the following data: (i) maximum storage capacity in reservoir conditions, (ii) gas saturation estimates by calculating the difference between the maximum storage capacity and the actual gas volume content, (iii) diffusion rate of gas flow, (iv) composition and behaviour of the stored gas, (v) released gas volume from the system due to pressure drop, and (vi) critical desorption pressure, which is the required pressure to gas desorption start at the reservoir (RODRIGUES, 2002).

4. IRATI FORMATION CASE STUDY

Organic-rich shales of the Irati Formation are among Brazil's most studied geological formations worldwide due to its recognized potential for hydrocarbons. They are considered one of the largest shale oil deposits in the world (EIA, 2013). Additionally, these shales are a recognized source rock unit for various accumulations within the Paraná Basin (Hachiro, 1996; Araújo et al., 2000; Milani et al., 2007), such as the oil accumulations in carbonate levels at São Paulo State (ARAÚJO et al., 2000; ARAÚJO 2001; ARAÚJO et al., 2001; MATEUS et al., 2014; FERREIRA, 2017), and in oil shales at Paraná State (CORRÊA DA SILVA & CORNFORD 1985; SANTOS et al., 2006).

The Irati Formation is part of the Gondwana I sedimentation of the Passa Dois Group, corresponding to the Lower Permian section of the Paraná Basin (ZÁLAN et al., 1990; MILANI & ZALÁN, 1999; MILANI et al., 2007). It presents a heterogeneous lithologic distribution, consisting of carbonates and evaporites in the northern region and bituminous shales in the southern portion of Paraná Basin (MILANI et al., 2007). It has an overly broad geographical occurrence, covering most of the Paraná Basin in an area of approximately 700,000 km2 (MILANI et al., 2007), where it outcrops in a narrow range, resembling an "S" shape, on its northern and south-eastern borders (HACHIRO, 1996). Concerning its thickness, the Irati Formation presents an average thickness of 40m (MENDES et al., 1966), with a typical thickness of 10 m at the margins of the Paraná Basin, reaching up to 70 m in the depocenter (HACHIRO, 1996).

Two distinctive members were identified within the Irati Formation: Taquaral and Assistência (HACHIRO, 1996). The Taquaral Member comprises silty-clayey, non-bituminous, greyish shales with lenticular carbonate interleaves and silex nodules. It varies from 5 to 10 meters of thickness in the marginal areas of the basin and reaches 30 meters in central portions (Hachiro, 1996). The Taquaral Member was deposited under low to moderate oxygenation conditions, below the storm wave base (ARAÚJO, 2001; GOLDBERG & HUMAYUN, 2016). The Assistência Member consists of clayey, bituminous shales, grey-dark to black, locally interbedded with carbonate beds. Its depositional environment ranged from shallow-water and subaerially exposed to stratified and anoxic conditions (ARAÚJO, 2001; GOLDBERG & HUMAYUN, 2016). The thickness of this package varies between 10 and 20 meters in the margins and reaches approximately 40 meters in the basin depocenter (Hachiro, 1996; MILANI et al., 2007) (Figure 2)

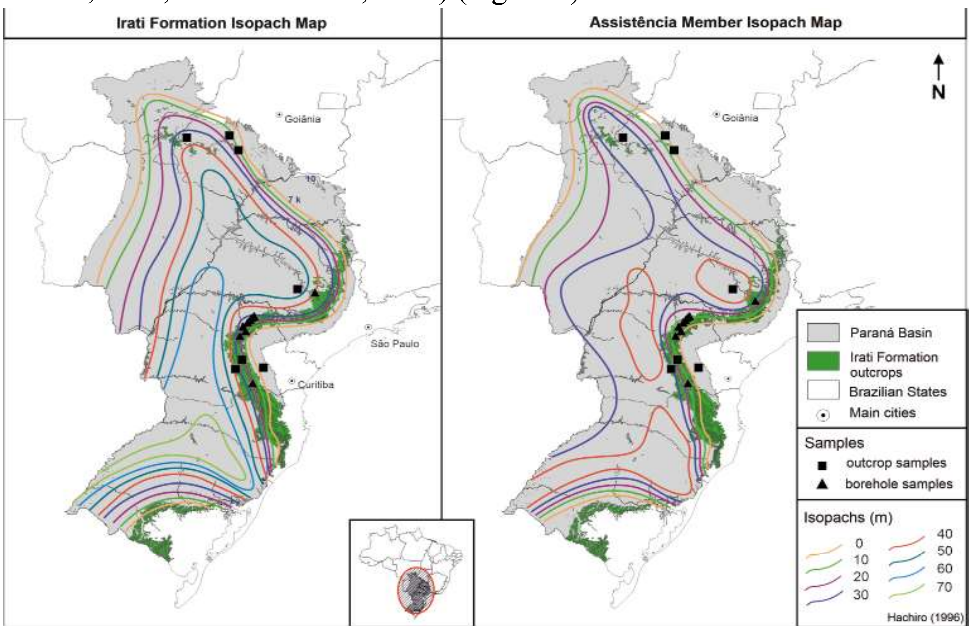

Figure 2. Paraná Basin with outcrops and isopach of the Irati Formation adapted from Hachiro (1996). A: Isopach map of the Irati Formation. B: Isopach map of the Assistência Member. The Irati Formation outcrops along the Paraná Basin are represented in green

The black shales of the Assistência Member are rhythmically intercalated with limestones and dolomites. These vary from the millimetre scale (laminae) to meter-thick beds (HACHIRO, 1996). The intercalation between dolomite and shale beds has higher rhythmicity in the northern and eastern parts of the Paraná Basin but is less predominant in the southern part of the Ponta Grossa Arch (HACHIRO, 1996; ARAÚJO, 2001). Hachiro (1996) attributes the intercalation of shales and carbonates to paleoclimate variability, characterized by well-marked alternation between arid and humid seasons. According to the author, carbonate deposition is associated with periods of drier climate – and consequent high evaporation ratio and salinity. While shales were associated with more humid climates and lower salinity - a hypersaline environmental context in the Paraná Basin, due to water circulation restriction between the paleo-ocean Panthalassa and the syncline (AFONSO et al., 1994; HACHIRO, 1996). According to Holz et al. (2010), the Taquaral Member was deposited in a marine epicontinental in a restricted environment while the Assistência Member originated in a vast and shallow sea with an influx of continental waters in some marginal areas of the basin (e. g., presence of Botryococcus - brackish to freshwater algae) or hypersaline conditions in other sections (CORRÊA DA SILVA & CORNFORD, 1985; ROCHA et al., 2020).

4.1. Irati Formation Shales Components and Implications to CO_2 Storage

Based on the organic geochemical and petrographic assessments conducted by Rocha (2021), the organic-rich shales of the Irati Formation correspond to excellent hydrocarbon source rocks.

Regarding the role of shale components on CO_2 storage capacity, Rocha (2021) also confirmed the effect of kerogen type and maturity on CO_2 adsorption and storage capacity in organic-rich shales. Experiments conducted on Irati Formation organic-rich shales indicate a positive correlation between total organic carbon (TOC wt. %), vitrinite content (Type III kerogen), organic maturity, and CO_2 storage capacity. Such correlation follows previous studies (CHEN & XIAO, 2014; HAN et al., 2017) attributed to nano and micro-porosity development within the organic particles, associated with kerogen cracking and gaseous hydrocarbon release (ZHOU et al., 2020).

The impact of mineral constituents on CO_2 sorption capacity in shales was also observed. Mineralogical parameters, such as clay content, proportion and type, drive gas adsorption in low-TOC shales (BUSCH et al., 2008; 2020). Additionally, much clay content and the prevalence of expandable clay minerals of the smectite group contribute to the CO_2 storage capacity of Irati Formation shales. Based on obtained mineralogical and sorption data, a positive correlation is established between samples with a high content of clay minerals from the smectite group and CO_2 storage capacity (ROCHA, 2021).

5. FINAL REMARKS AND CONCLUSIONS

Considering the current scenario of an increasing share of fossil fuels in the Brazilian energy mix and consequently CO_2 emissions upwards, CCUS technologies have become a clear strategy for decarbonising the Brazilian energy and industrial sectors. In this sense, CCUS can enable the continuous participation of fossil fuels in the Brazilian energy mix and still meet national (and international) climate change targets. However, to meet the Paris Agreements and 2050 net-zero goals, a regulatory regime supportive of CCUS is necessary and assesses Brazilian geological storage capacity. Such CO_2 storage capacity assessments must target extensive geological formations with significant rock volume, occurrence, and laterality. It should prioritise storage sites that are geographically close to CO_2 emitting sources and storage infrastructure, such as the Paraná Basin, Irati Formation case study.

CO_2 geological storage and the injection of fluids into the subsurface, such as to enhance oil recovery (EOR), is generally a mature technology already extensively deployed in Brazil. CO_2 injection can lead to enhanced shale gas recovery (CO_2-ESG) and CO_2 sequestration into shale's organic and clay content if applied to shale reservoirs.

Experimental analysis indicates that organic matter maturity is a controlling variant for total porosity and pore volumes, affecting pore size distribution and the relative proportions of micropores, mesopores, and macropores in shales. However, thermal maturity is not the only controlling factor of porosity-related variances in organic-rich rocks. Other contributing factors include quantity and quality of organic content (TOC and kerogen type) and mineralogical composition (clay minerals). These, together with organic maturity, are the pivotal causes of CO_2 adsorption patterns in shales and determine shale reservoirs storage capacity (ROCHA, 2021).

The characteristics of the analysed shale samples from the Irati Formation indicate the geologic potential for unconventional hydrocarbons and CO_2 geological storage. The Irati shales can be targeted for both shale oil and shale gas, according to the local geology of the Paraná Basin. However, the high level of heterogeneity requires local estimates if the potential is for shale oil or shale gas, besides CCUS.

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CHAPTER 6

USE OF 3D MODELLING IN THE CO_2 GEOLOGICAL STORAGE, POSSIBLE APPLICATIONS FOR PARANÁ AND SANTOS BASINS

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ABSTRACT

The use of 3D modelling in geosciences has become increasingly present in its various applied areas nowadays. This chapter presents a compilation of the international CO_2 storage resource assessment methodologies and their correlation with the use of computational 3D geological modelling techniques currently available through commercial software and open-source alternatives. The applications of these techniques are then discussed concerning the existing spatial data available in the Paraná and Santos sedimentary basins, aiming at assessing possible reservoirs for CO_2 geological storage. The steps from site selection to initial characterization are addressed, including determining storage capacity according to international standards.

Keywords: 3D geological modelling, CO_2 geological storage, Paraná Basin, Santos Basin, CO_2 storage capacity, CCS

1. INTRODUCTION

In the current world climate change scenario where we are experiencing global warming driven by anthropic emissions of greenhouse gases, there is an increasing search for technologies that reduce the planet's average temperature. Many alternatives have been proposed (Lawrence et al., 2018). They include the injection of sulfur dioxide into the atmosphere (Visioni et al. 2017), space-based solar reflectors (Salazar et al. 2016), the covering of deserts, oceans, or grasslands with mirrors that reflect the solar radiation (Salter et al. 2008), ocean iron fertilization (Williamson et al. 2012), and sea spray (Partanen et al. 2012). Among all these alternative technologies, the one that has proven most plausible for implementation in the last few decades is the CO_2 geological storage, including 27 initiatives already in operation presently and more than 62 under development (Global-CCS-Institute 2021). The technology of CO_2 storage integrates a chain of activities that involves trapping the carbon dioxide at its emission source, transporting it to a storage location, and isolating it, named Carbon Capture and Storage (CCS).

The present chapter discusses the use of 3D geological modelling to evaluate potential sites for CO_2 storage, briefly addressing the geological environments currently considered for storage, working scales, and evaluation stages of a given location. The types and techniques of 3D geological modelling presently available are presented and illustrated with some existing examples when possible or with similar applications.

2.3D GEOLOGICAL MODELLING IN GEOSCIENCES

3D geological modelling comprises a group of methods used for computerized representations of any geological body or surface in three dimensions via specialized software, whose final product is generally known as the geological model. 3D geological modelling has a wide range of applications, including but not limited to oil and gas reservoirs, mineral deposits, contamination plumes, groundwater aquifers, nuclear waste underground storage and tunnels, and other underground engineering works. Some examples of application in the oil and gas sector include Bueno et al. (2011); Bigi et al. (2013); Durand-Riard et al. (2013); Aadil and Sohail (2014); Altameemi and Alzaidy (2018); Alhakeem et al. (2019); Trentin et al. (2019); Ali et al. (2020); Palci et al. (2020); Islam et al. (2021). Tectonic approaches through 3D modelling are seen in Brun et al. (2001); Courrioux et al. (2001); Do Couto et al. (2015); de Kemp et al. (2016); Thornton et al. (2018); dos Santos et al. (2019); Lesage et al. (2019); Molezzi et al. (2019).

Some examples of 3D geological modelling supporting mineral exploration are seen in Fallara et al. (2006); de Kemp (2007); Wang et al. (2011); Yuan et al. (2014); Wang et al. (2015); de Kemp et al. (2016); Li et al. (2019); Mao et al. (2019); Wang et al. (2019). 3D modelling applications in a wide range of ore deposits types and geometries can be found in Gumiel et al. (2010); Hill et al. (2014); Vollgger et al. (2015); Basson et al. (2016); Liu et al. (2016); Schetselaar et al. (2016); Pavičić et al. (2018); Stoch et al. (2018); Braga et al. (2019); Xiang et al. (2019); de Oliveira and Sant'Agostino (2020); Arias et al. (2021); de Oliveira et al. (2021a). Applications of 3D modelling on hydrogeology include Artimo et al. (2003); Cox et al. (2013); Hassen et al. (2016); Magnabosco et al. (2020); D'Affonseca et al. (2020). The use of 3D modelling in geothermal reservoirs is presented in Milicich et al. (2010), Milicich et al. (2014), Alcaraz et al. (2015); Poux et al. (2018); Calcagno et al. (2020). Other examples of 3D geological modelling use include the urban and infrastructure areas like Breunig and Zlatanova (2011) and He et al. (2020) and in the differentiation of soils (Queiroz et al. 2017). From this extensive list of references, it is noticed that the application of 3D geological models in several areas of geosciences started to appear more often from the 2000s and grew in recent years. As it is a knowledge area of geosciences in constant expansion due to the recent advances in computer graphics and software technology, there are no limits for new and innovative applications.

A reference book with terms definitions in 3D geological modelling and richly illustrated examples of diverse geological applications is "3D geoscience modelling: computer techniques for geological characterization" (Houlding, 1994). A more recent review of the state-of-the-art geological modelling methods includes Wellmann and Caumon (2018). Other books that also address 3D modelling but are already in some specific geoscience fields are Merriam and Davis (2001) in sedimentary systems, Groshong Jr (2006) in structural geology, Rossi and Deutsch (2013) in mineral resources, and Pyrcz and Deutsch (2014) in oil and gas reservoirs modelling. Perrin et al. (2005) presented a geo-ontology proposal, defining a set of terms for using, sharing, revising, and updating 3D geological models by different users over time. Three special issues of Minerals journal were devoted to the 3D geological modelling theme, "Geological Modelling" (2018); "Geological Modelling, Volume II" (2020); "3D-Modelling of Crustal Structures and Mineral Deposit Systems" (2021). Some specific events and conferences on 3D geological modelling include the workshops held in GSA Annual Meetings, United States (2001, 2002, 2004, 2007, 2009, 2011, 2013, 2015), and in the Resources for Future Generations (RFG), Canada (2018), the European Meetings on 3D Geological Modelling (2013, 2014, 2016, 2018, 2019), and the Visual 3D Conference 2019.

The advantages of 3D geological modelling include expanding the analysis of conventional geological data by visualizing continuities, clusters and spatial trends, geometries of geological bodies or units, structural geological framework, and variation of geochemical contents or any other numerical parameters in geosciences. CO_2 storage models are applied the same way as in oil and gas reservoirs evaluations. They are also used to define suitable reservoir-seal pairs for the trapping of CO_2. It aims to better understand the spatial variability and continuity of the reservoir and seals facies interpretations. The 3D analysis also allowed the ranking of more favourable and unfavourable facies. The main variables from petrophysical wireline logs that can be visualized and estimated in 3D are usually porosity, permeability, and water saturation, considering saline aquifers and depleted reservoirs. In coal seams and shales, the adsorption capacity and total organic carbon (TOC) are important variables of interest.

Some case studies with the specific application of 3D modelling in CO_2 geological storage are present in the literature (Kaufmann and Martin 2008; Douglass and Kelly 2010; Gunnarsson 2011; Monaghan et al. 2012; Alcalde et al. 2014; Lech et al. 2016; Mediato et al. 2017; Shogenov et al. 2017; Vo Thanh et al. 2019; Zhong and Carr 2019). These examples focus mainly on defining the volume capacity to support resource assessment (discussed in the following sections). A different application is the 3D geomechanical model presented by Vidal-Gilbert et al. (2009), which evaluates the changing of in situ stress caused by increased pore pressure during CO_2 injection.

The term geological modelling discussed in this text is not synonymous with numeric modelling, a widely applied technique in geosciences that uses computational simulation to describe the physical conditions of geological scenarios through numbers and equations (Ismail-Zadeh and Tackley 2010). A numeric model could be performed on a grid or a block model with previous domains defined by geological modelling, but this interrelation is not mandatory. The use of numeric models in the CO_2 geological storage is better discussed and exemplified in Chapter 8.

3.3D MODELLING TECHNIQUES

3D geological models may consist of 3D solid surfaces or 3D block models, or both, depending on what features or geological bodies one wants to represent in the three-dimensional space. Generally, the block models are used when the objective is to know some variable in more detail or resolution in a more significant number of points in the space when then estimation, interpolation, or assignments of values are applied to a given block. On the other hand, 3D surfaces are helpful in defining spatial domains, geometries or volumes, and understanding interactions between geological planes. The surfaces or solids generation techniques could be classified as explicit, traditional and implicit modelling (Cowan et al., 2003).

In explicit modelling, the geological interpretation usually comes from polylines drawn directly in 2D projections or digitalized from paper sections with drill holes, wells, geophysical, or any other source of geological data. Generating 3D solids or surfaces requires the polylines to be linked individually and triangulated through tie lines (Fig. 1A). In the implicit modelling, the surfaces to be generated are therefore not constructed directly, as done in the explicit method, but instead are created now from selected points, which could be geological contacts in a well (Fig. 1B). A function is defined throughout space by specifying the function values at selected points and interpolating them through the rest of the space (Cowan et al., 2003). Manual polyline digitization and triangulation in explicit modelling are more labour intensive. These polylines are generated semi-automatically with implicit modelling, allowing automatic updates as new data is available. It is not possible in models consisting of explicit surface triangulations. In some complex cases, the implicit modelling could not be applied as a stand-alone technique, and both of them need to be integrated to get a better result. More in-depth descriptions of these techniques and comparatives can be found in Savchenko et al. (1995), Carr et al. (2001), Cowan et al. (2002); (Cowan et al. 2003; Cowan et al. 2004), Turner (2006), Knight et al. (2007), Birch (2014), Jessell et al. (2014).

Geological contacts and domains could also be defined directly on a block model or grid generating a probabilistic model. In the probabilistic approach, the domains of interest are not defined by surfaces, called meshes or wireframes, representing the geological contacts or faults. Instead, a block model is generated for the studied region. Then, the probability of each block being or not being of a certain lithology or a particular fault side is determined. The probability estimation in each block is performed by geostatistical techniques, commonly indicator kriging, and then by applying threshold values, portions or domains of interest are defined inside the model (Fig. 1C). Geostatistical methods used on categorical variables are better presented, discussed, and exemplified in Journel (1983), Rivoirard (1994), Olea (1999), Lloyd and Atkinson (2001), de Oliveira and Rocha (2011), Pyrcz and Deutsch (2014), Rivoirard et al. (2014).

Several commercial software packages are available nowadays with explicit and implicit 3D modelling engines, as well as geostatistical modules that allow generating probabilistic models, citing: Surpac, Gems, Minesight, Vulcan, Isatis, EarthVision, GeoModeller, Datamine, GoCAD, Leapfrog, Move, Petrel, Micromine, among others. Open-source packages for 3D geological modelling are also available, citing: GemPy (de la Varga et al. 2019; Schaaf et al. 2020); and Loop 3D (Grose et al. 2020; Jessell et al. 2021).

The modelling of the five main geological environments (saline aquifers, oil and gas reservoirs, coal seams, shale, and basalts) where the CO_2 storage has been studied is related to sedimentary basins. The proper characteristics required for CO_2 storage include non-location in the fold and thrust belts and limited to moderate structures (Chadwick et al. 2008; IEA-GHG 2009; Smith et al. 2011). The 3D geological models tend to be more straightforward in these environments. The sedimentary contacts are represented commonly by flat smooth, stacked surfaces. Points generate these surfaces or polylines interpreted from seismic data and the contact points from wells in the subsurface (Fig. 2). The interpretation of distinguished facies with sharped erosional contact could be a challenge for the three-dimension representation due to the complexities involved in the interaction of inter-cutting surfaces. A little bit of complexity may emerge when trying to represent possible fault sets. The most common types are steeply deep normal faults, characteristic of extensional regimes (Etheridge et al. 1985). The fault planes are generated by surface traces interpreted from radar data or satellite images and seismic interpretation.

4. UNCERTAINTY IN GEOLOGICAL MODELLING

Modelling the subsurface geometry is known to be uncertain. Modelling uncertainty is not a goal on its own; usually, it is needed to answer a particular question raised. The subsurface medium's heterogeneity (fluids and soils/rocks) is a critical parameter influencing the decision. Rarely, we have perfect information to model the geological variability of the subsurface deterministically. Hence, there is a need to model all aspects of uncertainty related to subsurface heterogeneity. Several sources of data are available to constrain the models of uncertainty built. These data sources can be remarkably diverse, from wells (driller's logs, well-log, cores, etc.) to geophysical or remote sensing measurements. Tying all this data into a single uncertainty model without making too many assumptions about the relationships between various data sources is quite challenging (Caers 2011).

The traditional geostatistical approach for purposes of uncertainty calculation in geological modelling is carried out, generally, through the sequential simulation of categorical variables, of which stand out truncated Gaussian simulation (Journel and Isaaks 1984; Matheron et al. 1987; Xu and Journel 1993) and the sequential stimulation of the indicators (Journal and Alabert 1989; Alabert and Massonnat 1990). As initially proposed, the sequential simulation's goal is the reproduction of the histogram and the covariance model of the properties to be simulated through the sequential drawing of conditional distributions. Each grid node is randomly visited sequentially, and simulated values are taken from the conditional distribution of value on that node, based on the data neighbourhood and previously simulated nodes. Other examples of simulation techniques used in geological modelling are object-based algorithms or Booleans (Haldorsen and Lake 1984; Stoyan et al. 1987), process-based algorithms (Bridge and Leeder 1979; Lopez et al. 2001), surface-based modelling methods (Xie et al. 2001; Pyrcz and Deutsch 2014) and multi-point simulation algorithms based on pixels (pixel-based) (Guardiano and Srivastava 1993; Strebelle 2002).

5. CO2 STORAGE RESOURCE ASSESSMENT METHODOLOGIES

The classification systems for the assessment stages of a given site for CO_2 geologic storage (Goodman et al. 2011; Rodosta et al. 2011) follow the same processes developed by the petroleum industry (Etherington and Ritter 2008) in a bottom-up progression based on analyses conducted to reduce the project development risk (Fig. 3). Here the application of 3D geological modelling is approached in the Exploration phase, which comprises three stages in increasing order of geological knowledge: Site Screening, Site Selection, and Initial Characterization corresponding to each resource class: Potential Sub-Regions, Selected Areas, and Qualified Site (Goodman et al. 2011; Rodosta et al. 2011). The main technical site selection criteria for geological CO_2 storage (Chadwick et al. 2008; IEA-GHG 2009; Smith et al. 2011) are compiled in Table 1.

6. EXPLORATION PHASE

One of the first parameters to evaluate in any subsurface units suitable for CO_2 geologic storage is a depth of approximately 800 m or more (Chadwick et al., 2008; IEA-GHG, 2009; Smith et al., 2011; Miocic et al., 2016) regarding the CO_2 injected will be in the supercritical condition being in these temperatures and pressures. The CO_2 is stable as a supercritical fluid at a temperature and a pressure above a critical point: 31 ºC and 7.38 MPa, respectively. For these initial appraisals, 3D models of superimposed layers on the formation of interest can be generated on a basin or regional scale from seismic, exploration well, and outcrop data during the Site Screening or Site Selection stages, indicating more or less favourable regions. Similarly, areas with thickness with at least 20 m (Chadwick et al., 2008; IEA-GHG, 2009), caprock thickness with at least 10 to 20 m (Chadwick et al., 2008; IEA-GHG, 2009; Smith et al., 2011), and a safe distance to protected groundwater (IEA-GHG, 2009) could be determined using 3D models. However, in this case, this evaluation would probably occur during the site selection stage since wireline logs with seismic information are needed. A 3D structural model based on seismic data is generated during the site selection stage, indicating possible structural traps favourable for CO_2 reservoirs or areas of less incidence of faults avoiding potential gas leaks (Chadwick et al., 2008; IEA-GHG, 2009; Smith et al., 2011).

The evaluation of whether a basin or portion is located within a fold belt (IEA-GHG, 2009), reservoir-seal pairs, and a favourable stratigraphy (IEA-GHG, 2009; Smith et al., 2011; Miocic et al., 2016) is made at the Site Screening stage. Nevertheless, nothing prevents that with a 3D geological model developed during the assessment advance with new data addition, already in the Initial Characterization stage, the local stratigraphy and structural context may prove more or less favourable, for example, with details of internal facies of a given formation. The addition of a small number of wells or new seismic surveys could dramatically change the interpretation and evaluation of a given area or site.

So we can see that the volumetric evaluation of the CO_2 storage site, where modelling has been applied more frequently (Gunnarsson, 2011; Alcalde et al., 2014; Lech et al., 2016; Mediato et al., 2017; Shogenov et al., 2017; Vo Thanh et al., 2019; Zhong and Carr, 2019), will only occur effectively and commonly in the Initial Characterization stage. Nevertheless, 3D modelling can also be applied in a basin-scale approach at an early stage of exploration (Douglass and Kelly, 2010). An example of 3D geological modelling used in both Site Selection and Initial Characterization stages could be seen in de Oliveira et al. (2021b).

7. SITE CHARACTERIZATION

The U. S. Department of Energy (DOE) methodologies for capacity calculations for the distinguished major geologic media: depleted oil and gas reservoirs, saline formations, unmineable coal seams (Goodman et al. 2011), and organic-rich shales (Goodman et al. 2014) are briefly described next. Other similar volumetric-based methodologies were also developed for CO_2 storage resource assessment (Bachu et al. 2007; Brennan et al. 2010; Bradshaw et al. 2011; Spencer et al. 2011) and were compared and discussed in detail by Popova et al. (2012).

The general equation to calculate the CO_2 storage resource mass estimate for geologic storage in oil and gas reservoirs is based on the standard industry method to calculate original gas or oil-in-place (Dake 1983) as follows:

$$G_{CO2} = Ah_n\Phi(1 - S_w)B\rho_{CO2std}E_{oil/gas} \quad (1)$$

where G_{CO2} is CO_2 mass, A is the area, h_N is the net thickness, Φ is the effective porosity, S_w is the water saturation, B is the initial oil (or gas) formation volume factor, ρ_{CO2std} is the standard CO_2 density, and $E_{oil/gas}$ is the storage efficiency factor, that reflects the volume of CO_2 stored in an oil or gas reservoir per unit volume of original oil or gas in place.

The equation to calculate the CO_2 storage resource mass estimate for geologic storage in saline formations is:

$$G_{CO2} = Ah_g\Phi\rho_{CO2}E_{saline} \quad (2)$$

where h_g is the gross thickness, ρ_{CO2} is the density of CO_2 evaluated at pressure and temperature that represents storage conditions anticipated for a specific geologic unit, and E_{saline} is the storage efficiency factor, reflecting the fraction of the total pore volume that the injected CO_2 will fill.

The equation to calculate the CO_2 storage resource mass estimate for geologic storage in unmineable coal seams:

$$G_{CO2} = Ah_gC_{s.max}\rho_{CO2std}E_{coal} \quad (3)$$

Where $C_{s.max}$ is the maximum CO_2 volume at standard conditions that can be sorbed per volume of coal, assumed to be on an in situ or "as is" basis, and E_{coal} is the storage efficiency factor, which reflects a fraction of the total coal bulk volume that CO_2 contacts.

The equation to calculate the CO_2 storage resource mass estimate for geologic storage in shales:

$$G_{CO2} = AE_Ah_gE_h[\rho_{CO2}\Phi E_\Phi + \rho_{sCO2}(1 - \Phi)E_s] \quad (4)$$

where ρs_{CO_2} is the mass of CO_2 sorbed per unit volume of solid rock, and E_A, E_h, E_Φ, and E_s are efficiency factors for the area, thickness, pore-volume, and sorbed volume, respectively (see Goodman et al. 2014 for more details).

Note that all of them use volumetric-based CO_2 storage estimates being computationally equivalent. The volume of a given geological layer *(A x h*), in (1) to (4) equations, can be obtained through the application of the 3D geological modelling techniques presented here with certain precision - depending on the data that support them.

In the present methodologies and the general approach discussed in this text, the 3D models are being considered to use static volumetric models based on commonly accepted assumptions about in-situ fluid distribution in porous media and fluid displacement processes. Currently, most studies are focused on evaluating possible new locations for CO_2 storage. However, 3D geological models can also be used jointly with numerical models, as already mentioned, in the management and monitoring of reservoirs during their injection life (see Chapter 8). A dynamic volume would be considered in this case because detailed site injectivity and pressure data are most commonly available only after CO_2 injection.

When production-based data are available, they should be preferred over a new volumetric-based model estimate in the specific case of an evaluation of depleted oil and gas reservoirs. Production data contain general detailed information collected from the formation.

Similarly to the mineral industry (CRIRSCO 2019) and the oil and gas industry (Etherington and Ritter 2008), for reporting of CO_2 storage capacity, a technical-economic classification system was proposed (Bachu et al. 2007) according to an increasing level of geological knowledge and confidence based on a pyramid (Fig. 4). Storage capacity in this pyramid is expressed in mass CO_2 (e. g., Mt or Gt CO_2) rather than volume because the volume of a given mass of stored CO_2 depends on the pressure and temperature at which it is stored (Bachu et al. 2007). Four technical and economic classes are considered: Theoretical, Effective, Practical, and Matched capacity. A Theoretical capacity assumes that the whole of reservoir formation is accessible to store CO_2, providing a maximum upper limit to a capacity estimate. The application of technical constraints as cut-off limits of porosity and permeability, and limiters as seal quality, depth of burial, pressure and stress regimes, the reservoir's pore volume, and trap determines the Effective capacity. The practical capacity considers economic, legal, and regulatory barriers to CO_2 geological storage beyond just geoscience and engineering aspects. It corresponds to the reserves used in the petroleum and mining industries.

The Matched capacity refers to the detailed matching of significant stationary CO_2 sources with adequate geological storage sites considering potential, injectivity, and supply rate. Other refinements and modifications of the initial pyramid have been proposed recently (Ackhurst et al. 2011; Bunch 2013; Anderson 2017; Vasilis et al. 2018; Mikhelkis and Govindarajan 2020), although all considering a decrease in the geological and economic uncertainty of the classes from the bottom to the top.

Most mineral resource and ore reserve classification systems adopted are based on sampling spacing, geological confidence, and economic viability. These systems define categories of resources based on a degree of uncertainty associated with parameters being estimated. Evaluation and classification are included in the mineral resource and CO_2 geological storage sites assessment. Drilling and sampling combined with quality assurance and quality control practices systematically update this process. New and sophisticated methods used for modelling and evaluation are worthless if sampling, preparation, and chemical assays are not adequately controlled and validated. The procedure selected for the CO_2 geological storage sites classification should have some required characteristics. The method used for classification should be able to define confidence either in geometry or petrophysical properties estimates. Classes of storage sites are determined based on the sample's spatial distribution and the uncertainty associated with tonnages calculated for a given deposit or part of it. Thus, the classification of a mineral resource requires the definition of the uncertainty associated with the estimate. However, what is not clearly stated in the main classification systems is how uncertainty should be assessed.

8. DATASETS FOR CO_2 STORAGE RESOURCE ASSESSMENT

Generating a model representing some geological form or body depends on previous georeferenced data in three dimensions. Georeferenced data is any geological data or information that has spatial coordinates X, Y and Z defined. These data can be of land surface topography, maps, drill holes or wells, geophysical surveys, location points of outcrops, structural measures, samples, among others. Therefore, the first step to evaluate before starting the geological modelling is to check what data is available for the area of interest and if it is possible to use them in a 3D environment. More details about data types and methodology for an integrated 3D model could be seen in Kaufmann and Martin (2008). All GIS data presented in the figures 5 and 6 is public data and come from Agência Nacional do Petróleo, Gás Natural e Biocombustíveis, Brazil (ANP) (http://geo. anp. gov.br/)

and from Companhia de Pesquisa de Recursos Minerais, Brazil (CPRM) (http:// geosgb. cprm. gov.br/).

9. AVAILABLE DATA FOR PARANÁ BASIN

The Paraná Basin presents CO_2 storage potential to be investigated in almost all types of CO_2 geological storage: saline aquifers and coal seams (Rio Bonito Formation), shales (Irati Formation), and basalts (Serra Geral Formation). Some of these geological environments already had some preliminary work. The saline aquifers hosted in Rio Bonito Formation were initially focused, and experimental studies suggested that CO_2 could be permanently stored as carbonates due to good reaction with host rocks (Ketzer et al. 2009; Lima et al. 2011). The Rio Bonito Formation also presents depth and thicknesses compatible with storage approximately CO_2 stationary sources (Rockett et al. 2011; Machado et al. 2013). The CO_2 sorption capacities were initially assessed on coals from the Rio Bonito Formation and oil shales from Irati Formation with potential for storage and coalbed methane production (Weniger et al. 2010; Kalkreuth et al. 2013; Santarosa et al. 2013). The Irati Formation shales were addressed on CO_2 storage investigations considering a possible shared production of methane (Mabecua et al. 2019; Richardson and Tassinari 2019; Rocha et al. 2020).

The Paraná Basin presents an extensive data set with 123 hydrocarbon exploration well data. Petrobras Company carried out this survey from the 1950s until the 2000s, with more than 61,100 line kilometres of 2D reflection seismic data covering most of its extension (Fig. 5), and local electromagnetic, magnetic, and gamma surveys, as well as geological maps in regional scale. These data allow the interpretation of the main layers of interest of Irati and Rio Bonito Formations, delimiting units and facies within these formations, and evaluating depths, thickness, distance from protected groundwater. These were used to interpret structures and traps for storage, allowing further capacity calculations and economic evaluations using 3D geological models.

10. AVAILABLE DATA FOR SANTOS BASIN

The potential for CO_2 storage in the Santos Basin is verified, especially from the study of the oil and gas fields in its extension, which is justified by the less accessible nature of offshore basins. The reuse of oilfield infrastructures and the geological knowledge associated with these enterprises favours that the optimal environment for storage is the natural structure of the oil reservoirs.

Therefore, the use of depleted fields for storage in the Santos Basin seems a natural path because it results in lower costs, less environmental damage, and more excellent local geological knowledge (Hannis et al., 2017). The Santos Basin has eight exploratory plays in its extension, and throughout its territory, there is robust coverage of seismic surveys. Therefore, when associated with oil reservoirs, the target formations for storage in the Santos Basin are those that correspond to the reservoir rocks: Marambaia Formation, Santos Formation, Juréia Formation, Itajaí-Açu Formation, Guarujá Formation, Florianópolis Formation, Itanhaém Formation (Freitas et al. 2006; Moreira et al. 2007; Chang et al. 2008). Turbiditic sandstones of the Upper Cretaceous are the focus for CO_2 storage. The pre-salt reservoir formations are not considered because their very high depths diverge from the optimum characteristics for CO_2 storage. An initial CO_2 storage evaluation on Santos Basin considered the Merluza zone indicating geological favorability and the presence of installed infrastructure that can be reused after adaptations (Ciotta and Tassinari 2020). Another potential that could be explored in Santos Basin is the anthropic excavation of salt caverns in ultra-deepwater (da Costa et al. 2019a; da Costa et al. 2019b; Goulart et al. 2020). The selection of a cluster of salt domes for the location of the first experimental and pilot caverns built-in ultra-deepwater was based on interpretation of 3D seismic and 2D seismic from one of the major pre-salt oil fields in Santos Basin (Goulart et al. 2020).

The basin has 27 oil fields, five non-associated gas fields, and eight fields under evaluation. The data collection resulting from the Santos basin's exploratory efforts includes 435 exploratory wells, a dense mesh of seismic data, and 3D seismic surveys that cover a large part of the basin (Fig. 6). The availability of this data allows an in-depth study of the viability of the Santos Basin fields for storage. Thus, it is possible to verify the essential characteristics of a CO_2 sink (e. g., depth, thickness, integrity) and the verification of the long-term permanence of the gas from the verification of the adjacent formations. The availability of these data also enables the production of reservoir models, favouring understanding the fluid dynamics at the sites of interest and a scale prediction of storage capacity.

11. FINAL CONSIDERATIONS

The chapter brings a brief review of some applied examples of 3D geological modelling in geosciences in the last years, focusing on CO_2 geological storage. International CO_2 storage resource assessment methodologies are presented and discussed, in the stages, when the 3D modelling could be useful and expected results. Since all assessment methodologies proposed to the current use volumetric-based

CO_2 storage estimates, the site characterization phase is when the 3D modelling is presented to be used for the volume and posterior capacity calculation. However, there are still few examples in the literature. Nevertheless, there is an excellent variety of 3D modelling applications in the Exploration phase, such as thickness models for the reservoir formation and the depth seal rock, favourable depth models, and distance models for protected aquifers. The 3D ambient could also help integrate distinguishing data from the surface, seismic and other geophysical surveys, wells, and derived data, helping select favourable areas or sites.

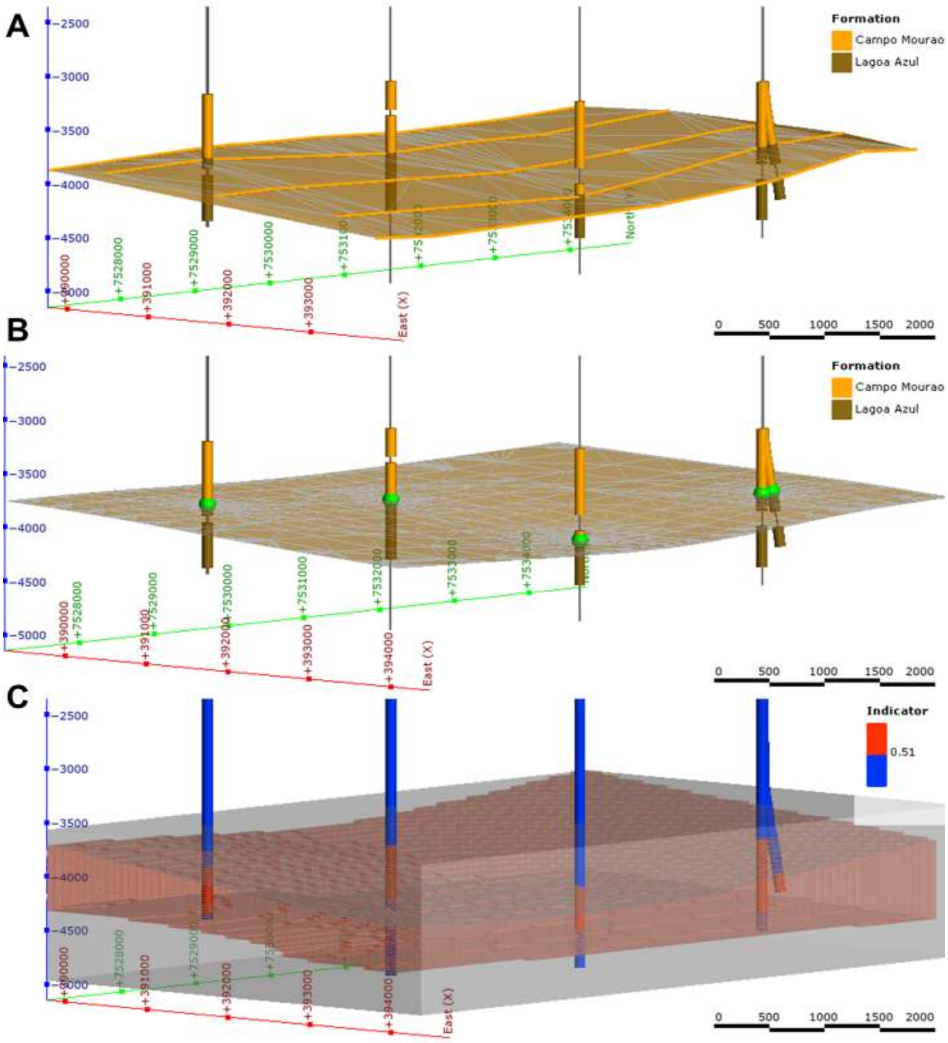

Fig. 1. Comparison between different 3D geological modelling techniques for an example of the contact between sedimentary layers. A) Explicit modelling, B) Implicit modelling, C) Probabilistic modelling

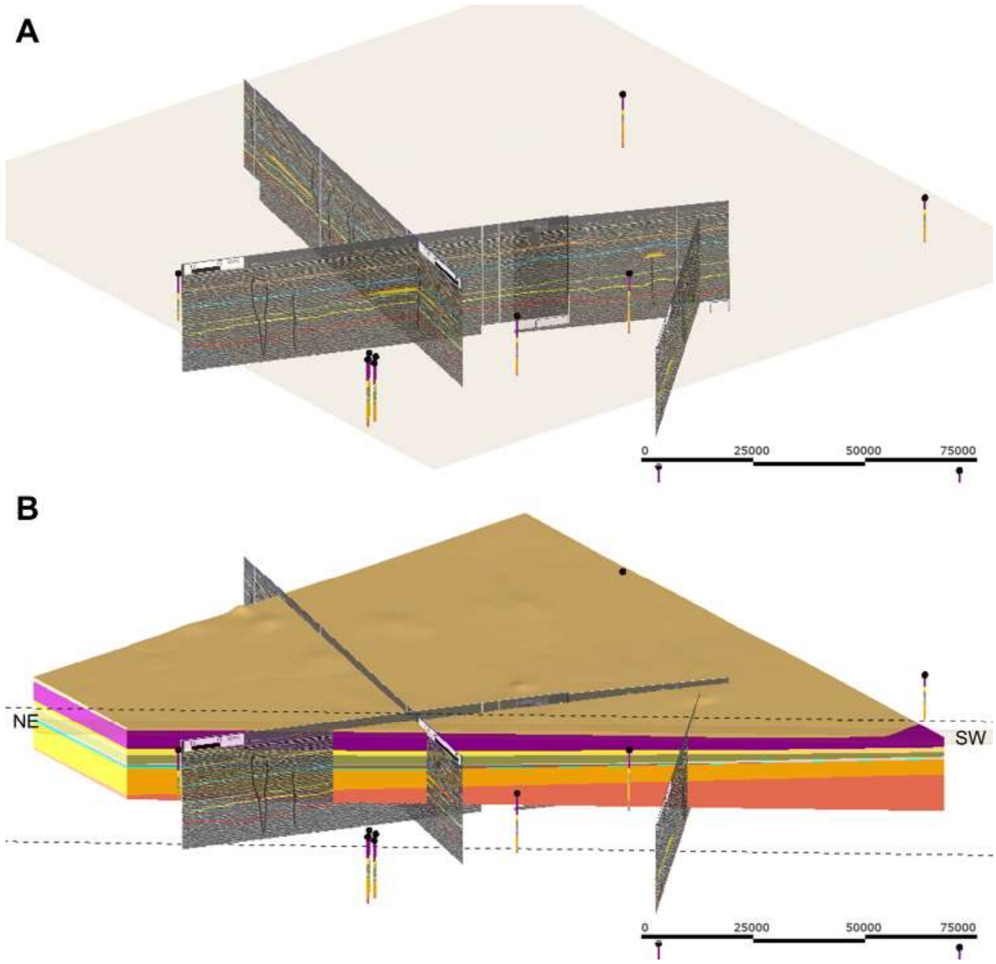

Fig. 2. A) Example of data integration of topography surface, interpreted seismic sections, and exploration well data in a 3D environment. B) 3D stratigraphic model generated from the data together.

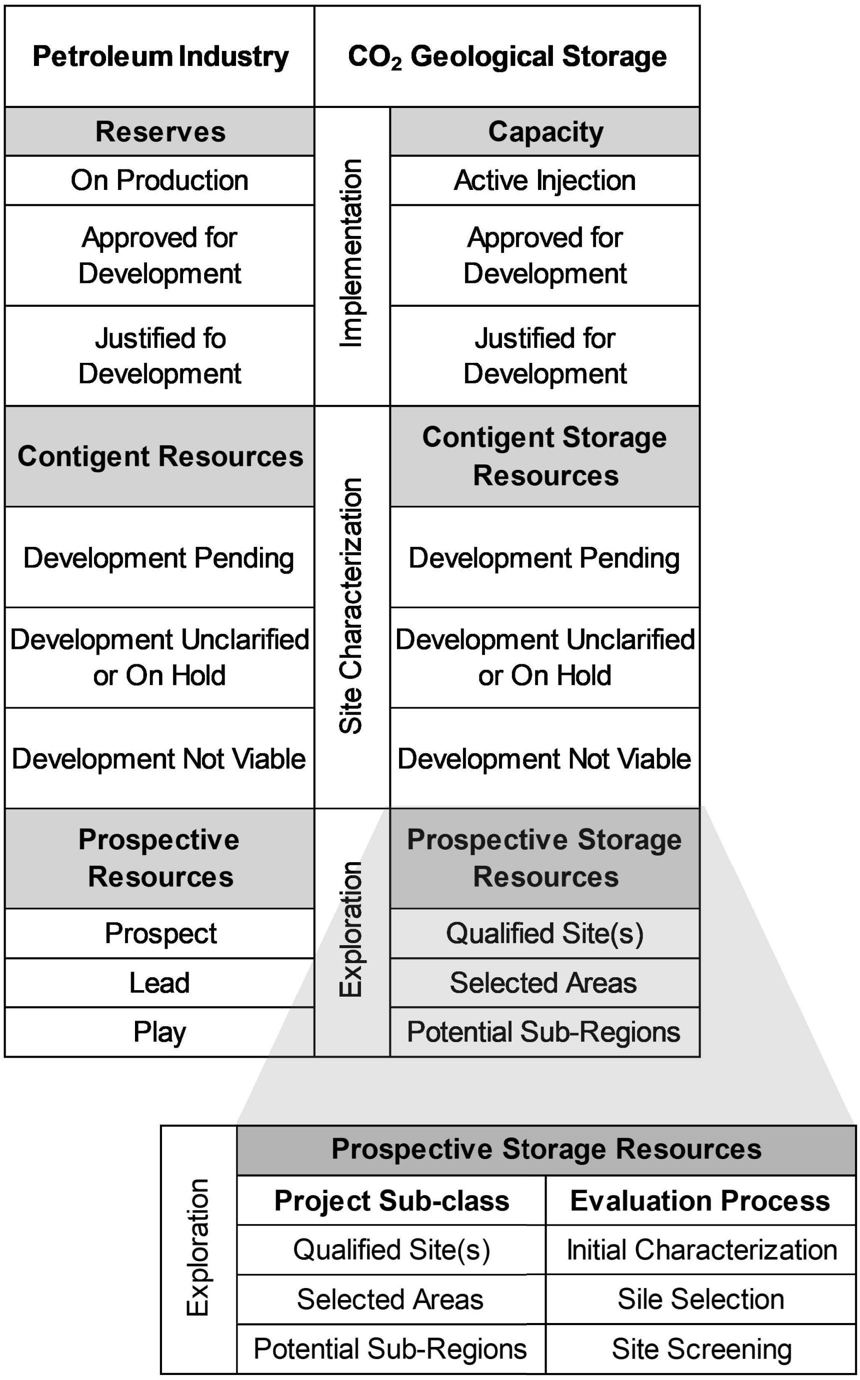

Fig. 3. CO_2 geologic storage classification system (after Goodman et al. 2011)

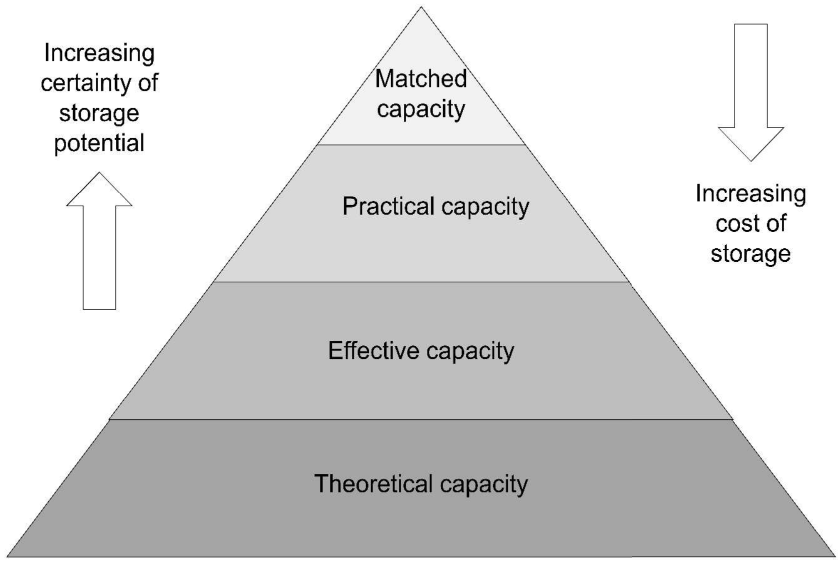

Fig. 4. Techno-economic resource pyramid for capacity for CO_2 geological storage (after Bachu et al. 2007).

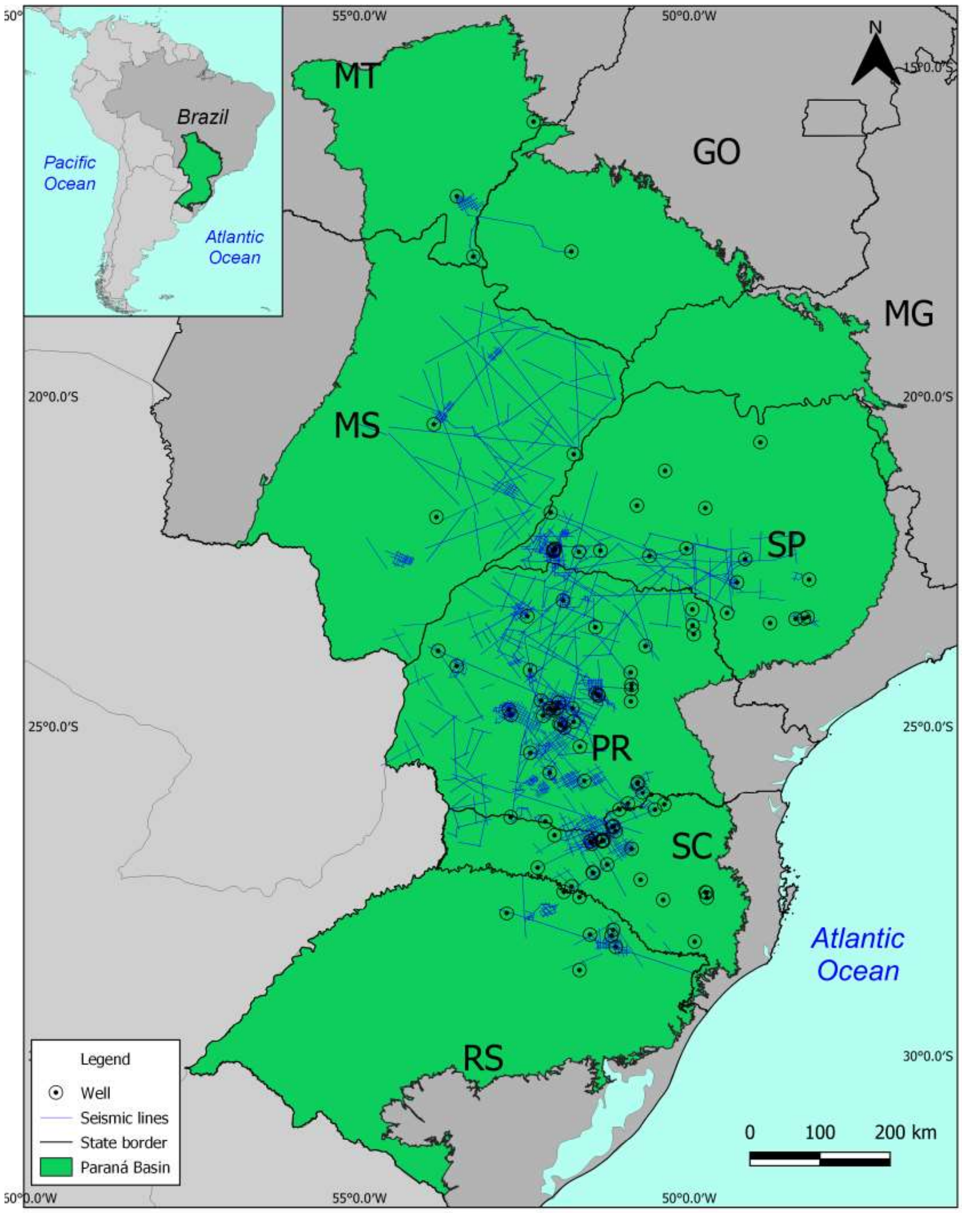

Fig. 5. Available data of seismic and exploration wells for Paraná Basin (data from ANP, 2021)

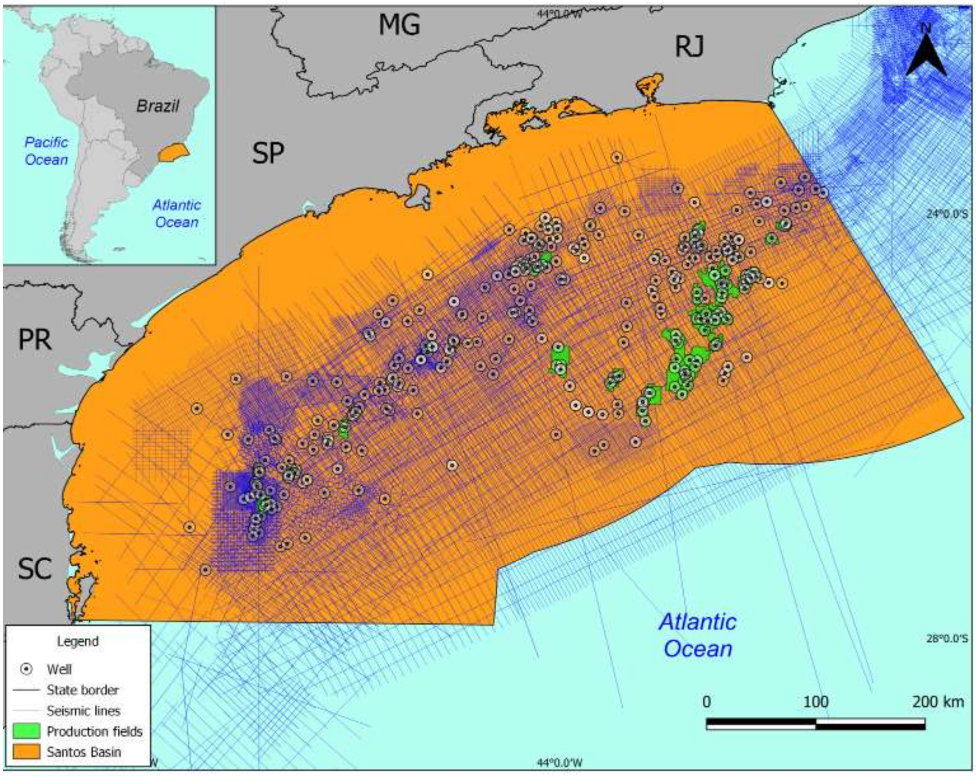

Fig. 6. Available data of seismic and exploration wells for Santos Basin (data from ANP, 2021)

Criterion	Eliminatory or unfavourable	Preferred or Favourable	References
Reservoir-seal pairs; an extensive and competent barrier to vertical flow	Poor, discontinuous, faulted and/or breached -	Intermediate and excellent; many pairs (multi-layered system) Vertically sealing faults, multi-layered systems	IEA-GHG, 2009 Miocic et al., 2016
Stratigraphy	Complex lateral variation and complex connectivity	Uniform	Smith et al., 2011
Located within fold belts	Yes	No	IEA-GHG, 2009
Depth	< 800 m or > 2,500 m < 750-800 m < 800 m > 2,500m -	Between 1,000 and 2,500 m > 800 m > 800 m < 2,500 m > 1,200 m	Chadwick et al. 2008 IEA-GHG, 2(IEA--GHG 2009)009 Smith et al., 2011 Miocic et al., 2016
Thickness	< 20 m < 20 m	> 50 m ≥ 20 m	Chadwick et al. 2008 IEA-GHG, 2009
Affecting protected groundwater quality	Yes	No	IEA-GHG, 2009
Faulting and fracturing intensity	Extensive	Small or no faults Limited to moderate Minimal faulting, with a trapping structure	Chadwick et al. 2008 IEA-GHG, 2009 Smith et al., 2011
Caprock thickness	< 20 m < 10 m < 20 m thick -	> 100 m ≥ 10 m > 100 m thick > 150m	Chadwick et al. 2008 IEA-GHG, 2009 Smith et al., 2011 Miocic et al., 2016
Lateral continuity of caprock	Lateral variations faulted	Unfaulted (uniform)	Chadwick et al. 2008
Total storage capacity	Total capacity is estimated to be similar to or less than the total amount produced from the CO_2 source	Total capacity is estimated to be much larger than the total amount produced from the CO_2	Chadwick et al. 2008

Table 1. Compilation of site selection criteria for geological CO2 storage where 3D geological modelling could be applied.

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CHAPTER 7

THE INFLUENCE OF FLOW UNITS ON CO_2 STORAGE WITHIN THE SHALE AND CARBONATE RESERVOIRS OF THE IRATI FORMATION, PARANA BASIN, SOUTHWEST OF SÃO PAULO

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ABSTRACT

CO_2 injection and storage within the potential reservoirs depend on the geological/geochemical trapping mechanisms and the reservoir quality involving porosity (Φ), permeability (K) and other flow unit factors. Core samples are not available for petrophysical evaluation of the rock units. Therefore, the reconceived expressions aided to predict the hydraulic unit in the shale and carbonate reservoirs concerning the CO_2 storage capacity of the Irati Formation. The study presents the average values of flow units in shale and carbonate units and their influences on the injection and storage of CO_2. Low flow units may restrict the CO_2 storage potential in shale, while water saturation (S_w)may affect the carbonate reservoirs. However, there are potentials for CO_2 storage in the shale and carbonate rocks based on the abundance of the rock units within the study location, higher reservoir depths and proximity to CO_2 emitting sources. The Irati Formation can also serve as a shale-carbonate hybrid geological reservoir for CO_2 storage. The presented parameters (Φ, K, reservoir quality index-RQI and flow zone indicator-FZI) may be applied in future studies involving hydrocarbon exploration, thereby expanding the CO_2 storage potentials of the targeted reservoirs.

Keywords: Atmospheric CO_2 Reduction; Petrophysical characterisation; Flow Units; Hybrid Reservoir; Irati Formation

1. INTRODUCTION

The need for carbon capture and storage (CCS) in São Paulo stems from global warming mitigation and the presence of CO_2 emission sources. São Paulo has CO_2 emission sources (mainly from the energy and biomass sectors) with capacities ranging from 20Kt/yr to 6400 Kt/yr (Ketzer et al., 2014). 25.8% of the domestic CO_2 production and 31.4% of CO_2 acquisition via importation activities in Brazil come from São Paulo (Imori and Guilhoto, 2016). References have been made to the geological reservoirs within the Parna Basin concerning CO_2 storage potentials (Ketzer et al., 2015; Richardson and Tassinari, 2019). The Irati Formation of the Parana basin consists of shale, carbonate and siltstone lithologies intruded by basalt sills at some intervals. The petrophysical characterisation based on the rock units is of pertinent interest in predicting the CO_2 storage potentials of the geological reservoirs. It aids to evaluate the storage efficiency factors such as reservoir thicknesses and porosity (Φ) for volume estimation. The shale and carbonate rock of the Irati Formation could provide the required efficiency to aid CO_2 repositioning within the Parana Basin. Depleted and already enhanced reservoirs for hydrocarbon recovery have been on the target for CO_2 storage (Steven et al., 2010; Pearce et al., 2011; Gabriela et al., 2013). This idea does not disregard the possibility of CO_2 storage in geological Formations without hydrocarbon production history. Wireline logs are engaged to estimate the flow units, reservoir thicknesses/depths and water saturation (S_w) in shale and carbonate reservoirs. The wireline logs consist of density and sonic logs to aid the estimation of the porosity (Φ), permeability (K), Reservoir Quality Index (RQI) and Flow zone indicator (FZI). These parameters (Φ, K, RQI and FZI) are essential to predict the reservoir characteristics such as pore-throats, pore sizes, distribution of pores, grain sizes, grain sorting, textures and structures of grains and pores in the reservoirs. The injection, movement, storage and security of fluid within geological structures depend on the above-stated parameters, geological/geochemical trapping mechanisms and overburden integrity.

Brazil has existing CO_2 injection wells and storage sites monitoring, measuring and verification (MMV) related projects (Moreira et al., 2014; Ketzer et al., 2014). The MMV project is an advantage for CCS in the country, and São Paulo via the collaboration of related institutions [e. g. Research Centre for Gas Innovation (RCGI) of the University of Sao Paulo (USP)] should be able to benefit from this programme to foster CO_2 storage within its environs. CCS is possible in São Paulo, considering the shale and carbonate units of the Irati Formation as potential repositories. However, the best reservoir option could be the shale-carbonate hybrid geological reservoir to minimise CO_2 storage uncertainties involving thin-bedded factors and overburden integrity.

2. SHALES

Shales are naturally fine-grained clastic sedimentary rocks consisting of mud/clay minerals with tiny particles of other materials (quartz, calcite and others) depending on the area's geology. Based on the depositional environment, there are different types of shales. There are calcareous shales, carbonaceous and black shales. There are also siliceous shales, ferruginous shales and sandy/silty shales. Black and carbonaceous shales exist within the Parana basin, and they could serve as a reservoir for CO_2 storage in the Formation of Irati. Free gas occurs in shales within dispersed organic matter, adsorbed by these organic matter or other related minerals. The organic matter rich lamina is also a factor related to the injection and storage of CO_2 in shales. K, in shales, is directly related to the degree of natural cracks/fractures that allow fluid passage. Therefore, K depends on fractured paths, fracture patterns, organic matter content and cementation. Other factors include relative configuration of the building grains of the rock, pore/grain sizes, thermal maturity, and volume of organic matter per unit area/organic matter distribution and mineral composition. In shales, the intra-particle of organic pores and inter-particle of organic and inorganic pores hold the gas (Loucks et al., 2009; Loucks et al., 2012; Yang et al., 2015). The abundance and the distribution of cracks and fractures aid the movement and positioning of fluid in shale reservoirs. It is uncertain at this point whether or not fracturing to increase the storage potential in shales will be an option because hydraulic units of the shale reservoir rock in situ may not encourage high CO_2 storage. Shale fracturing to increase permeability (K) enhances injection rate and transmissibility of fluid. Further exploration activities within the region may reveal significant gas in the shale units to call for fracturing for gas production and increase the CO_2 storage potential of the shale afterwards.

3. CARBONATES

Limestone and dolomite are found in the Irati Formation and could also offer units for CO2 storage. In the carbonate reservoirs category, dolomites will present better reservoirs in terms of porosity and permeability distribution. Dolomitisation is a process that involves the substitution of some Ca^{2+} ions in limestone $(CaCO_3)$ by Mg ions to form dolomite $[Ca.\ Mg\ (CO_3)_2]$. It includes the dissolution of pre-existing carbonate rocks with subsequent precipitation of dolomite. The balance between dissolution and precipitation rates brings about changes in porosity (Tucker and Wright, 1990; Purser et al., 1994; Warren, 2000; Wang et al., 2015). Dolomitisation produces new crystals due to the dissolution of the less stable parent rock (limestone). The repeated occurrence without complete pore cementation leads to inter-crystalline separations and porosity enhancement. Intercrystalline porosity is a highly interconnected porosity style that gives dolomite reservoirs significant fluid storage capacity and efficient drainage (Warren, 2000). Therefore, dolomitisation increases the crystal sizes; pore sizes and thus enhances porosity (Φ) and permeability (K) (David et al., 2008; Ritesh et al., 2014). Furthermore, dolomites are less reactive and less ductile compared to limestone, as such; they are less likely to lose porosity with depth due to dissolution or re-precipitation (Grammer & Harrison., 2003; Davis et al., 2008; Grammer and Harrison, 2013; Sharma et al., 2014; Chao et al., 2016). A dolomite bed can retain or create porosity and permeability to much greater burial depths and into higher temperature realms than a limestone counterpart (Warren, 2000). However, the injection of CO_2 into the geological structures activates physicochemical changes over time (Gaus, 2010; Ketzer et al., 2012; Siqueira et al., 2017). Injected carbon dioxide within the carbonate reservoir brings about geochemical alterations, imbalances in pore pressures, mineral dissolution, and alteration of porosity and permeability (Andreani et al., 2009; Bacci et al., 2011; Kampman et al., 2014). The presence of water in the reservoirs activates the CO_2-carbonate reaction. Therefore, the choice of carbonate reservoirs for CO_2 storage depends on the need for storage, geochemical composition of other surrounding rocks and water saturation (S_w).

4. THEORETICAL ESTIMATION OF HYDRAULIC UNITS

A couple of basic parameters are essential in the estimation of flow units. Cementation exponent (***m***) and factor of tortuosity (***a***) vary from one rock unit to another. A recapitulation of the use of these parameters reveals ranges of approximated values for shale and carbonate rocks. Such that, the tortuosity factor ranges from 0.59 to 1.00 in carbonates and up to 1.65 in shales. In the same vein, the cementation exponent could be up to 2 in carbonates and above 2.5 in clay minerals/shale depending on the type of clay minerals (Carothers, 1968; Asquith and Gibson, 1982; Schlumberger, 1989; Hilmi and George, 1999). The theoretical estimation of flow units based on wireline logs (Richardson and Taioli, 2017) shows the possibility of maximising porosity to estimate the reservoir quality and predict transmissibility. In the absence of core data, the interdependency among porosity (Φ), permeability (K), reservoir quality index [RQI] and flow zone indicator [FZI] is engaged in the prediction of the reservoirs flow units with the aid of wireline logs (Tiab and Donaldson 2012; Richardson and Tassinari, 2019). This study presents a combination of expressions based on reviewing the concerned intrinsic parameters (Φ, K, RQI and FZI) defined for the carbonate and shale reservoirs of the Irati Formation. Based on Equations (1) to (8), these parameters are engaged to predict the flow units and their implications on CO_2 storage.

$$\Phi_{S-D} = \frac{\Phi_S + \Phi_D}{2} \quad (1)$$

K may be expressed in carbonate as Equation (2) and in shales as Equation (3).

$$K = (4472\Phi_e^{3.25})^2 \quad (2)$$

$$K = \frac{(20000000\Phi_e^{6.7})}{1.65} \quad (3)$$

RQI is defined for carbonates by Equation (4) and shales by Equation (5).

$$RQI_{(e)} = \frac{140.4\Phi_e^{3.25}}{\Phi_e^{0.5}} \quad (4)$$

$$RQI_{(e)} = \frac{0.0314*\left(2\times10^7\Phi_e^{6.7}\right)^{0.5}}{1.65\Phi_e^{0.5}} \quad (5)$$

FZI is estimated based on Equations (6) in carbonates and Equation (7) in shales.

$$FZI = \frac{140.4\Phi_e^{3.25}}{\Phi_e^{0.5}*\Phi_R} \quad (6)$$

$$FZI = \frac{0.0314*\left(2\times10^7\Phi_e^{6.7}\right)^{0.5}}{1.65\Phi_e^{0.5}*\Phi_R} \quad (7)$$

Where Φ_R takes the form of Equation (8) (Tiab and Donaldson, 2012)

$$\Phi_R = \frac{\Phi_e}{1-\Phi_e} \quad (8)$$

5. CO_2 STORAGE EFFICIENCY FACTORS

In qualitative and quantitative reservoir evaluations, porosity (Φ) is a dependent factor used for the prediction of other parameters such as permeability (K), reservoir quality index (RQI) and flow zone indicator (FZI). RQI is a factor that describes the distribution of pore sizes, grain sizes and pore-throats, while FZI predicts the grain sizes, grain sorting, textures and structures of grains/pores (Tiab and Donaldson, 2012). Fluid mobility and storage within the reservoir depend on these parameters. During volumes estimations, among the considered factors are thickness (h) and Φ, which are derivable from wireline logs. Figures 1, 2, 3 and 4 show the delineated rock units and depths in the Irati Formation, southwest of São Paulo.

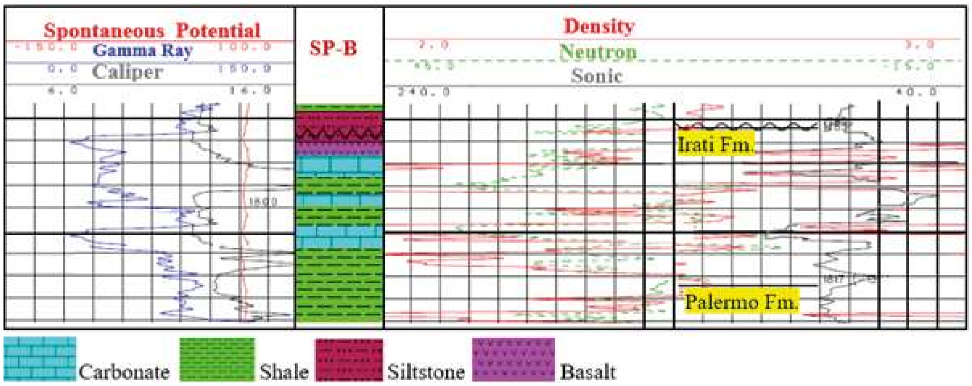

Figure 1: Showing the thicknesses of the rock units below 1780m

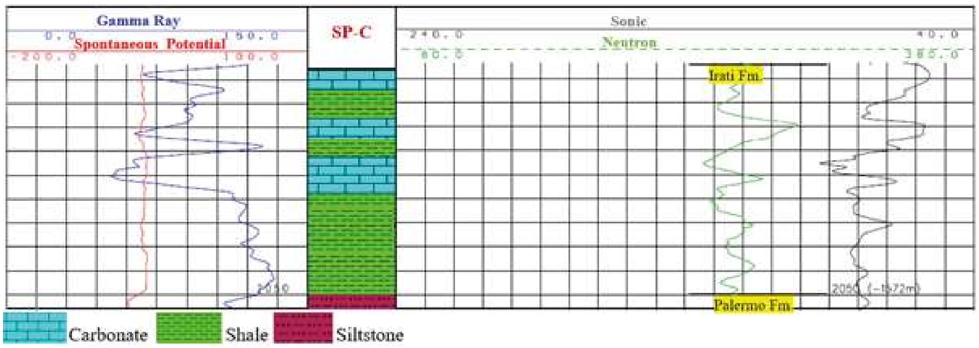

Figure 2: Showing the thicknesses of the rock units below 2000m.

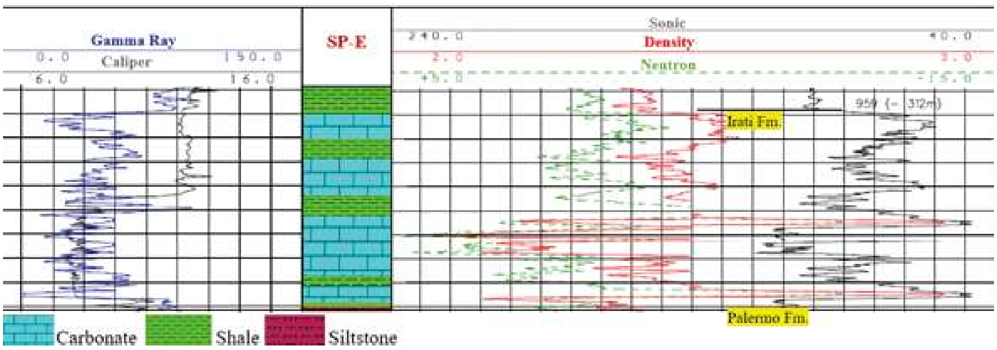

Figure 3: Showing the thicknesses of the rock units below 960m.

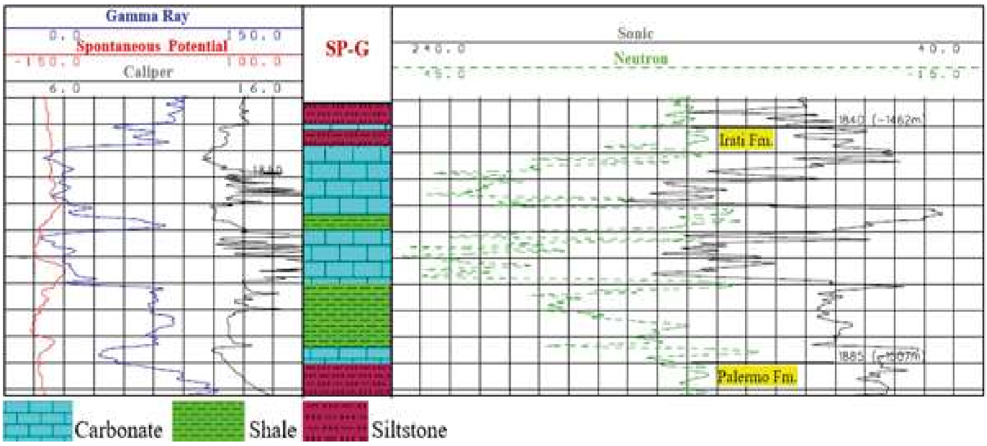

Figure 4: Showing the thicknesses of the rock units below 1840m.

The thicknesses of the rock units range from ≤2m to ≤33m, such that the average value for shale is about 17.1m and carbonate is about 17.5m. The shale and carbonate reservoirs consist of thin-bedded layers, and this factor may limit the CO_2 storage potentials within the Irati Formation. Other factors may include low permeability in shale units and overburden integrity. Therefore, the algorithm for volume estimation based on CO_2 storage for the Irati Formation will be affected by the fractional reductions in reservoir thickness, porosity and storage area. Hence, the associated volume efficiency factor (E_{av}) takes the form of Equation 9.

$$E_{av} = E_h \times E_a \times E_\Phi \qquad (9)$$

Where; E_h = fractional reduction in reservoir thickness, E_a = fractional reduction in the storage area, and E_Φ = fractional reduction in reservoir porosity.

The combination of seismic images with the wireline logs for further study is imperative. This way, the storage area (A) and the area-based efficiency factor (E_a) are predicted. Relevant seismic interpretations are required to confirm the seal and trap mechanisms at higher depths. It is also imperative to consider the influence of tectonic activities on the Irati Formation during the selection of depths for CO_2 storage. Seismic images will aid to delineate the surface area of the selected storage sites and reservoir geometries considering faults distribution/orientations, seals/traps integrity and reservoir thicknesses.

According to the Intergovernmental Panel on Climate Change (IPCC, 2005) special report, the recommended depths for CO_2 storage are 800m and above. However, considering the buoyancy of supercritical CO_2 concerning the reservoir rocks, temperatures and pressures, fluid can migrate to the surface even at these depths (Matter and Kelemen, 2009). The buoyancy of CO_2 threatens the long-time storage of CO_2 within geologic structures except for the high integrity of traps and seals mechanisms. However, to overcome issues related to buoyancy, CO_2 may be dissolved in water by releasing it as bubbles of gas within the injection well at some intervals of depths as the water flows down (Galison et al., 2014). Another factor that may affect CO_2 storage (especially in the carbonate units) is water saturation (Sw). However, based on the spontaneous potential (self-potential) log and the charts [modified from Asquith and Gibson (1982) and Allied-Horizontal Wireline Services (2015)], water saturations are low at higher depths in the Irati Formation at the southwestern region of Saõ Paulo. Reservoir depths higher than 900m show Sw of <14%, while those below 800m indicate ≥40%. Therefore, CO_2/S_w ratios may determine the choice of the carbonate units for CO_2 storage.

6. PREDICTION OF FLOW UNITS

Figure 5 shows the average limits of porosity (Φ) and permeability K defined for the shale and carbonate reservoir units within the Irati Formation. The reservoir quality index (RQI) and flow zone indicator (FZI) (Figures 6 and 7) are essential to provide the theoretical estimation of the distribution of the reservoirs pore integrity, grains and pore-throats, grain sizes and sorting, textures and structures of grains. These parameters define the porosity and pore spaces interconnectivity within a given reservoir unit. The injection rate and transmissibility of fluid within the reservoirs also depend on these factors.

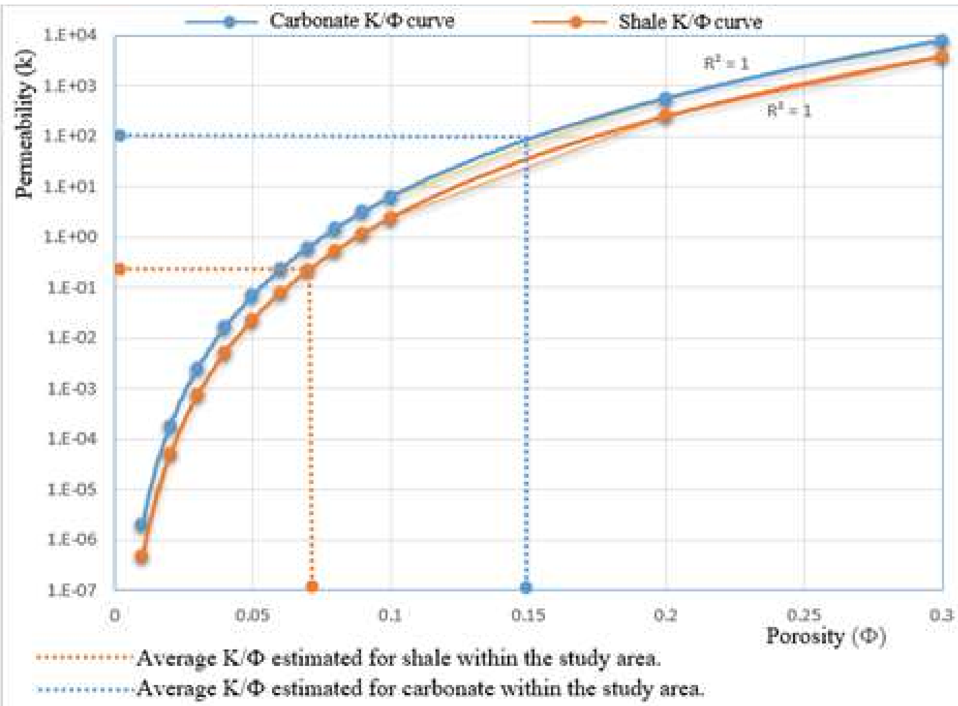

Figure 5. Showing the average values K based on shale and carbonate rocks

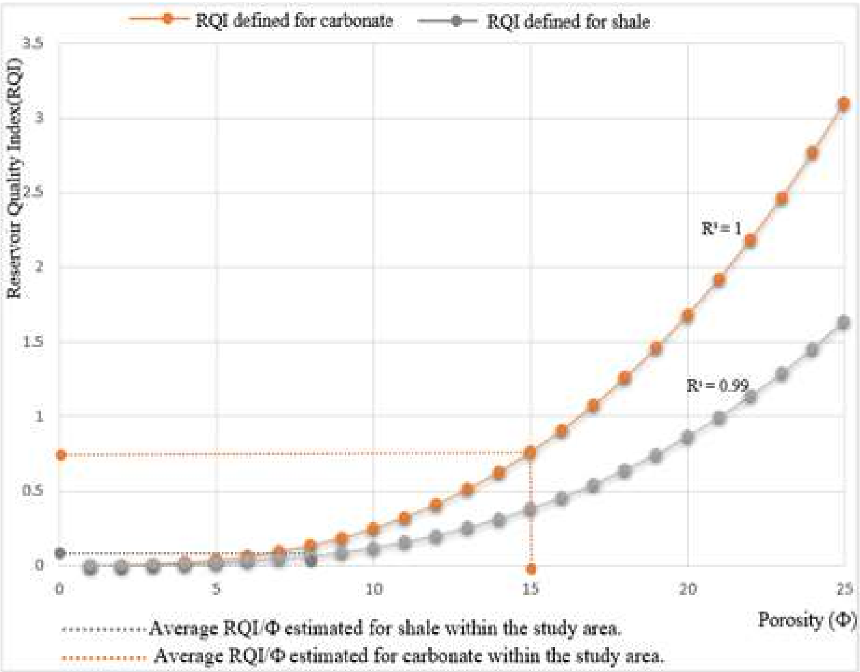

Figure 6. Showing the average RQI predicted for shale and carbonate rocks

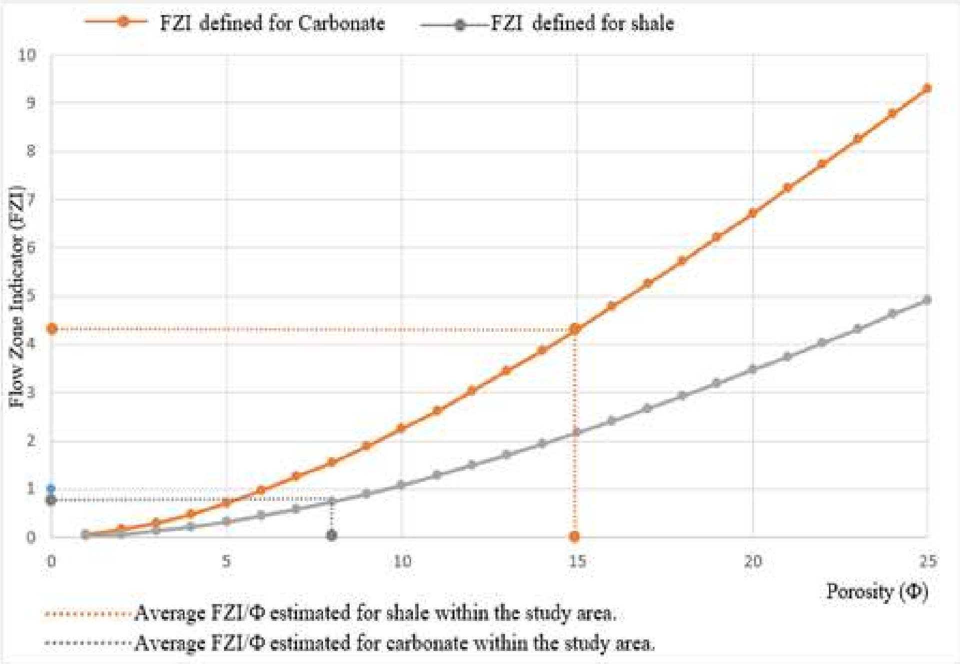

Figure 7. Showing average FZI estimated for shale and carbonate rocks

7. INJECTION, STORAGE AND SECURITY OF CO_2 WITHIN THE IRATI FORMATION

Geologically, the injection, storage, and security of fluids depend on the targeted reservoirs' flow units and geological/geochemical trapping mechanisms. The flow unit factors in the rock units in-situ are not as significant in shale reservoirs as presented by the carbonate rocks. Regardless, on a large scale, based on the flow units and the need for carbon capture and storage (CCS), the shale and carbonate reservoirs in the Irati Formation are recommendable for CO_2 storage. The flow units represent the intrinsic elements that define some of the storage efficiency factors.

Fault orientations and the integrity of seals/traps are factors that define the geometry of reservoirs and the security of the fluids in them. Therefore, they are crucial concerning CO_2 storage in geological structures. Evaluating these parameters is essential to predict the CO_2 storage potentials of the reservoirs within the Irati Formation. The security of CO_2 within the geological reservoirs will depend on the prevalent structural styles within the Parana Basin (Rostirolla et al., 2003). While the pore spaces in the reservoir rocks provide the largest capacity for CO_2 storage, rock surfaces will adsorb some quantities of the fluid depending on the total organic content (TOC) of the rock units (especially shales) and reservoir pressure. Therefore, geological and geochemical trapping mechanisms will secure the injected CO_2 within the reservoir units of the Irati Formation of the Parana Basin. Geochemical trapping mechanisms contributing to the CO_2 storage potentials of the reservoirs include hydrodynamic trapping, residual trapping, solubility trapping and mineral trapping (Rosenbauer and Thomas, 2010; Zhang and Song, 2014). The effectiveness of some of these geochemical trappings (e. g., solubility and residual trappings) depends on the presence of brine (salt-water) within the Formation. Therefore, in the absence of brine within the Irati Formation, hydrodynamic and mineral trappings are likely to be more active.

Other factors concerning CO_2 injection, storage and security are gross thicknesses (h) and depths of the reservoir units. The wireline logs show that the Irati Formation thickness ranges from ≥ 20m to ≤ 80m across the study location (southwest of São Paulo). Therefore, considering that the shale and carbonate units are predominant within the Irati Formation, the shale-carbonate hybrid geological reservoir will provide sufficient thicknesses for CO_2 storage in agreement with existing standards and proven atlases. The depths of occurrence of the Irati Formation across the study location is higher than the recommended depth (above 800m) (IPCC, 2005; Chadwick et al. 2008; IEA-GHG, 2009; Smith et al., 2011). The wireline logs also reveal that towards the southwestern region of São Paulo, the Irati Formation depths are above 800m (more than 2500m in some cases); therefore, they meet the recommended depth of reservoirs for CO_2 injection and storage.

The average values presented for the evaluated flow units suggest that the Irati Formation should support the injection (probably considering higher pressure in shale because of low flow units) and storage of CO_2. The flow unit factors are significant in carbonates when compared with the shale. Carbonates-CO_2 chemical interaction is imperative in the storage potential evaluation. The carbonate-CO_2 reaction may not constitute concerns in the Irati Formation, considering the low water saturations with depth increases indications. Therefore, the shales may form the required seals and traps for the carbonate reservoirs to serve as CO_2 storage tanks. Basalt sills are not uncommon within the sedimentary layers of the southwest of São Paulo. Basalt consists mainly of pyroxene (augite), plagioclase and olivine with silica content between 45% and 52%. It has good potentials for CO_2 mineralisation (McGrail et al., 2008; Oelkers et al., 2009; Goldberg and Slagle, 2011). The mineralisation of CO_2 means a chemical reaction between certain minerals and CO_2, leading to the transformation of CO_2 in the rock. Therefore, the associated basalt could contribute to the overburden or seal integrity or present itself as a potential reservoir. Considering the combined shale and carbonate rocks of the Irati Formation as a storage unit such that the overlaying Serra Alta Formation forms the required seal is also a conceivable idea. However, the Serra Alta Formation consists of porous rock units (e. g., carbonate), debunking its possibility as a potential overburden layer for the entire Irati Formation. It is also promising to consider the portions within the Irati Formation overlying by shale and basalt sills for CO_2 storage, provided other factors support the system.

8. FINAL REMARKS

The shale and carbonate reservoir units within the Formation of Irati Formation within the southwest of São Paulo can support storage, especially with a delineated large area, provided other geologic and environmental factors are favourable. The associated basalt sills of the Sera Geral Formation intruding the study location (Irati Formation) and the siltstones of the Irati Formation may contribute to the quality reservoirs concerning |CO_2 storage. However, geology-based limitations exist involving low shale permeability, water saturations in carbonates, thin-bedded layers, overburden integrity/continuity, and fault styles/distributions. The engaged wireline logs for this study dated from the mid-60s to the 80s. Therefore, if further exploration activities based on modern/improved equipment and expertise reveal significant shale gas, fracturing to enhance gas production will increase CO_2 storage potentials in shales. The reduction in the water saturation (Sw) with depth increase may also boost carbonate storage potentials depending on CO2/water ratios. Seismic interpretations involving 2D-4D data to evaluate the geometry of the reservoirs and capacity estimation for storage are pertinent. Further formation evaluations may use the presented hydraulic units as hydrocarbon exploration input data to verify possible oil or gas production, thereby boosting CO_2 storage capacity within the Irati Formation.

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CHAPTER 8

RESERVOIR MODELLING AND SIMULATION: INITIAL APPROACH FOR CO_2 STORAGE CAPACITY ESTIMATION IN IRATI FORMATION, PARANÁ SEDIMENTARY BASIN

Nathalia Weber

ABSTRACT

With the production increase of its energy resources in the last decade, shale gas reservoirs have become an object of a technical feasibility study for geological carbon storage projects. In Brazil, Irati Formation stands out for its high potential for natural gas generation and its strategic location in the Paraná Basin due to its proximity to regions with higher concentrations of stationary carbon dioxide (CO_2) emission sources. For initial estimates of the CO_2 storage potential in this geological formation, this chapter presents the results of reservoir modelling and numerical simulations for an injector well project with a geological model based on Irati. For a geological unit with dimensions of 1,200 m X 600 m X 40 m, the storage capacity results are close to 800,000 tons of CO_2, considering established safety parameters. The sensitivity analysis as a function of the maximization of the injection indicated the most significant influence of the reservoir's pressure, thickness, and gas saturation for this evaluation.

Keywords: Geological Carbon Storage; Unconventional Reservoirs; Numerical Reservoir Simulation.

1. INTRODUCTION

Evaluating CO_2 storage capacity and injectivity potential in deep geological formations can be performed by applying several estimation methods based mainly on porosity, fluid saturation in the pores, and depth. The use of numerical reservoir simulation software allows to include elements related to fluid dynamics and parameters of well engineering and operation of the injection process, among other benefits in the analysis.

Numerical reservoir simulation is one of the methods traditionally used in petroleum engineering to predict the behaviour of oil and gas reservoirs from numerical solutions. Generally, numerical reservoir or flow simulators use the formulation and solution of mathematical equations that describe physical processes through (i) the application of a set of fundamental laws, such as the mass conservation, energy conservation, and momentum conservation; (ii) the mathematical description of a transport phenomenon linked to the nature of the process; and (iii) the appropriate state equations (Rosa et al., 2006). With the introduction of information on geological data, rocks and fluids properties, and the production and completion method, numerical reservoir simulators are applied to analyse the reservoir's behaviour, determine the best field for a development scheme, and improve knowledge of the reservoir's geology, among other possibilities.

Several authors used numerical reservoir simulation for studies related to capacity, safety, and injection strategies for geological CO_2 storage, with higher frequency in saline aquifers. Studies focused on shale reservoirs as potential CO_2 receptors are significantly smaller in quantity, with few exceptions, based on advanced gas recovery processes due to the shale's preference of adsorption by CO_2 over methane (CH_4). These studies cover feasibility analysis of CO_2 storage (Kalantari-Dahaghi, 2010; Zhan et al., 2017), comparisons of advanced recovery methods strategies (Eshkalak et al., 2014; Jiang et al., 2014; Kim et al., 2017), analysis of factors of influence on injection efficiency (Kim et al., 2017) and studies applied to specific geological regions/formations (Schepers et al., 2009; Liu et al., 2013; Liu et al., 2016). As a study focused exclusively on carbon storage, without considering gas production, Chen et al. (2015) estimate CO_2 storage capacity in a depleted shale gas reservoir, based on the New Albany Formation, with sensitivity analysis of storage capacity.

2. RELEVANT ASPECTS TO SHALE GAS RESERVOIRS MODELLING AND SIMULATION

Predicting shale gas reservoirs' behaviour by numerical simulation presents additional challenges for modelling the system in comparison to conventional reservoirs. Among other reasons, the order of magnitude of permeability stands out, varying from nano to microDarcy. In addition, the little experience with the production of these resources so far, compared to the experience with conventional ones, leads to the lack of empirical knowledge of these reservoirs' behaviour (Houzé et al., 2018).

Beyond the low permeability, the challenges of modelling unconventional reservoirs are the intricate flow geometry, the combination of transport processes and the strong interactions between rocks and fluids (Wu et al., 2014). The different gas transport mechanisms, such as non-Darcyan flow, Knudsen diffusion and adsorption/desorption processes, are caused by complex networks of natural shale fractures and geochemical properties, such as the gas storage mechanism by adsorption (Javadpour et al., 2007; Sun et al., 2013; Wu et al., 2014). The interaction between the reservoirs' natural fractures with the hydraulic fractures from the well contributes to this complexity and non-planarity (Cipolla et al., 2010).

Based on the raised concerns, the construction of a geological model for reservoir simulation should cover relevant aspects such as natural fracture networks, gas adsorption, and diffusion mechanisms. In addition, to maximize CO_2 injection, the model must consider a horizontal well with hydraulic fracturing due to the low vertical permeability characteristic of shale gas reservoirs.

3. METHODS

In the first group of activities, the main factors that influence the capacity of geological carbon storage were identified based on a literature review. This identification was engaged in defining geological characteristics and CO_2 injection parameters for the simulation. Due to the low exploitation activity in the targeted region of Irati Formation in Paraná Basin and the absence of production history in the Formation, it was necessary to complement geological data with another formation of black shales. The Barnett Formation in the United States of America was selected due to its use by the Brazilian National Agency for Petroleum, Natural Gas and Biofuels (ANP) as a reference for estimating the potential of Brazilian formations of black shales for hydrocarbons, in addition to the excellent availability of information in the literature. In addition, other general parameters for known shale formations were considered in the model.

The geological base model (M0) was constructed in the Builder module of the Computer Modelling Group simulator (CMG-2017) and a horizontal well with hydraulic fractures. The CO_2 injection rate in this proposal is limited by the injection pressure, which respected the formation fracture pressure, assumed based on the fracture gradient of 16.97 kPa/m, referring to the median value between 11.31 kPa and 22.62 kPa estimated for shale formations by Halliburton (2008).

Numerical simulations were then performed in the Compositional Module GEM (Generalized Equation-of-State Model Compositional Reservoir Simulator) of CMG in 1,000 years to determine the total theoretical capacity of CO_2 injection. A sensitivity analysis was performed with the maximization of CO_2 injection as an objective function to understand the influence of geological characteristics on capacity injection.

Due to geological uncertainties, pessimistic and optimistic boundary models were created, with minimum (M-) and maximum (M+) possible values of the main relevant characteristics to CO_2 storage capacity, based on estimated values from other black shale formations in the world. Variations in Irati Formation's porosity were also included in the boundary models. These models were then submitted to numerical simulation in GEM to obtain the range of results for theoretical CO_2 injection capacity potential.

3.1 Geological base model

The three-dimensional base geological model (M0) was created in the Builder module of CMG, with an area of 1,200 m x 600 m, sufficient to safely incorporate the volume of influence of a horizontal injector well with hydraulic fracturing. The thickness was determined as 40 m, pointed out by Milani et al. (2007) as an average value for the Irati Formation. Due to the low permeability, CO_2 storage potential is restricted to the volume stimulated by the wells and the hydraulic fractures, allowing the analysis through reservoir simulation to be focused only on the influence of the injector well, considering no major faults in the region. The reservoir is initially composed only of CH_4 and water.

Generally, reservoirs with natural fractures are represented in a simplified form by double porosity, which classifies the values between matrix porosity and fractures to reduce the simulation time considerably. This simplification was adopted in this study, considering the presence of natural fractures in Irati. The approximated pore space in percentage was calculated concerning the total area of

Irati Formation's MEV images presented in De Souza (2018) for the matrix porosity. The base model's intermediate value of 6% was adopted, while the boundary models' porosity range of 4% and 8% was used. These numbers are within the field of average porosities of potential reservoirs of the known black shales in the world. The survey of porosities estimated in studies by the United States Energy Information Administration (EIA, 2011 and 2013), which evaluated recoverable hydrocarbon resources of shale formations in 137 formations worldwide, presented 1.6% to 12%. Due to the absence of data or reference for porosity calculation of the natural fractures of Irati, an average value found in 0.5% shales was adopted, pointed out in Wang and Reed (2009).

Two main conditions supported the determination of the depth for the base model the first concerns the physical state of CO_2 to be injected. To maximize the volume to be injected for storage, CO_2 must be in a supercritical state, i. e., at pressures and temperatures above 7.38 MPa and 31.1 °C, assuming more significant potential for compression. This point is reached at depths between 800 and 850 m (van der Meer, 2005; Holloway and Savage, 1993). It was also considered a safety margin of 1,000 m of distance from the Guarani Aquifer, which has an average depth of 320 m, according to 50 wells registered in the Hydrogeological Database of the extinct Water Resource Development Superintendence and Environmental Sanitation of the State of Paraná. Thus, the selected depth was 1,320 m, meeting the mentioned conditions. Although Irati Formation reaches the depth of 3,000 m, this value with more significant potential for CO_2 storage was chosen to expand the scope of this study.

Regarding reservoir pressure, an average hydrostatic pressure gradient of 0.475 psi/ft was assumed as used in Barnett (Vidas and Hugman, 2008). This number is not different from generally adopted mean values since EIA (2013) uses pressure gradients from 0.35 to 0.6 psi/ft depth – later used in the boundary models. Since 1 psi/ft is equivalent to 22,621 kPa/m, the reservoir of the base model with a 1,320 m depth was established at a pressure of 14,183 kPa.

Gomes (2010) brought results of geothermal resources of up to 64 ºC for a depth of 1 km in the Paraná Basin. The temperature adopted was 49 ºC based on a conservative approach. Permeability values, considered extremely low for shales, were extracted from Bhandari et al. (2015) with values for Barnett of 0.0000963 mD and 0.0000023 mD for horizontal and vertical permeabilities matrix, respectively. For the permeability of natural fractures, the value assumed was applied in reservoir numerical simulation in Zhu et al. (2017), based on Heller and Zoback (2014).

Given the absence of references for water saturation to the determined depth, a 55% gas saturation was defined, and its impact was included in the later analyses. The relevant aspects for shale gas reservoir modelling observed in the theoretical survey of the present study – a network of natural fractures, adsorption, and diffusion mechanisms – were also incorporated into the models used for a simplified representation of Irati. The networks of natural fractures were integrated using a model with double porosity, distinguishing porosities and permeabilities between matrix and fracture, whose values have already been treated in this description of the method.

The Langmuir parameters from Weniger et al. (2010) analysed isotherms of samples from the Irati Formation were adopted. For this base model, the results of sample 08_170 were adopted since it represents intermediate values. Converting the pressure numbers from MPa to kPa-1 and maintaining the importance of substance quantity (mmol/g equal to gmol/kg), it was obtained for CH_4 Langmuir pressure and volume equivalent to 0.25 gmol/kg and 7.062x10-5 kPa-1 and, for CO_2, 1.25 gmol/kg and 7.45x10-5 kPa-1.

Incorporating diffusion mechanisms based on the nanometric scale was considered a non-darcy flow and constant diffusion coefficients for CH_4 and CO_2. The CH_4 and CO_2 diffusion coefficients analysis in Wang et al. (2017) showed variations from 1.4x10-7 to 1.6x10-6 cm^2/s. Another considered point was the difference between the two values. The diffusion coefficient of CO_2 is lower than CH_4 under the same pressure (Wang et al., 2017). Thus, the values determined were 1.0x10-6 and 0.8x10-6 for CH_4 and CO_2, respectively.

Finally, other essential characteristics for shale gas reservoirs behaviour analysis were added to the model, based on assumptions from reservoir simulation studies in shale formations, (i) density, assumed at 2,550 kg/m^3 by Aguilera (2016) for the Barnett, Marcellus, and Haynesville Formations; and (ii) matrix compressibility, established at 4.4x10-7 in simulation for Yu et al. Fm. Barnett (2014). Table 1 presents a summary of the data used in the construction of the M0 base model.

Feature	Value	Reference
Dimensions (m)	1,200 x 600 x 40	(a)
The porosity of the matrix (fraction)	6%	De Souza (2018)[1]
Porosity of natural fractures (fraction)	0,5%	Wang and Reed (2009)

Horizontal matrix permeability (nD)	96,3	Bhandari et al. (2015)
Vertical matrix permeability (nD)	2,3	Bhandari et al. (2015)
Permeability of natural fractures (MD)	0,01	Zhu et al (2017) and Heller and Zoback (2014)
Depth (m)	1.320	(b)
Pressure (kPa)	14.183	(c)
Temperature (°C)	49	Gomes (2010)[1]
Initial gas saturation (fraction)	55%	Aguilera (2016)
Langmuir CH_4 volume (gmol/kg)	0,25	Weniger et al. (2010)
Langmuir CH_4 pressure (kPa-1)	7.06215x10-5	Weniger et al. (2010)
Langmuir CO_2 volume (gmol/kg)	1,25	Weniger et al. (2010)
Langmuir CO_2 pressure (kPa-1)	7.45x10-5	Weniger et al. (2010)
Diffusion coefficient CH_4 (cm2/s)	1x10-6	Wang et al. (2017)
Diffusion coefficient CO_2 (cm2/s)	0.8x10-6	Wang et al. (2017)
Compressibility (kPa-1)	4.4x10-7	Yu et al. (2014)
Density (kg/m³)	2.550	Aguilera (2016)

Table 1. Values used for the m0 base model reservoir.

[1] Calculated values based on the references;

(a) Area of 1,200 m x 600 m based on the dimensions of the horizontal well with fractures and width of 40 m (from Milani et al., 2007);

(b) Respecting a minimum of 800 m depth and the safe distance from the aquifer;

(c) Calculated based on the pressure gradient of Vidas and Hugman (2008).

3.2. Injection well

In addition to the data selection from the reservoir´s geological characteristics, it was also included definitions of parameters related to the injector well engineering.

The well length and hydraulic fracturing stages density were established based on the example of wells with more recent completions used in Barnett, applied by

EIA (2013) as a reference to stablish well stimulation parameters for estimating recovery factors. It was modelled a horizontal well (90º) with 1,000 m of extension and 11 stages of hydraulic fractures. The fractures' wing reaches 140 m, and the inner thickness is 0.6096 m (standard GEM value). The fractures' height was set at 10 m above and below the well, leaving a safety margin to not cover the total 40 m reservoir's thickness.

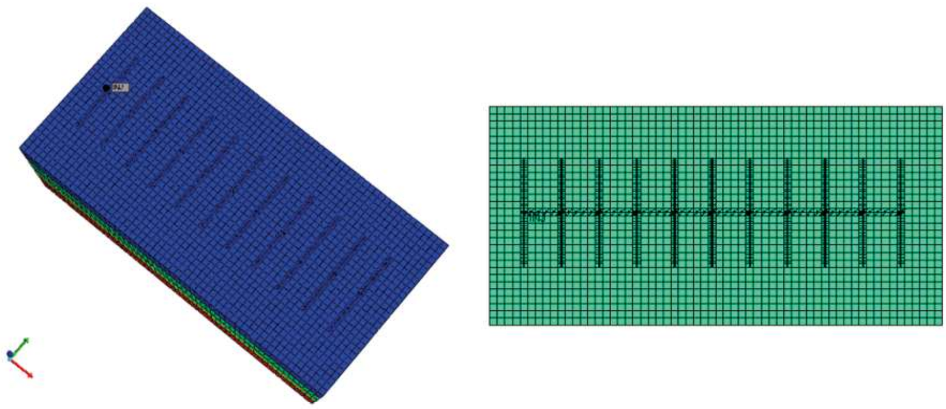
The determination of the potentially more critical item of the project, the bottom pressure of the well, is related to the formation's stress fracture pressure, which, by safety, should be higher than the total pressure of the reservoir during and after the end of the CO_2 injection period. Injection pressure is also the main factor that limits the injection rate. In a review of CO_2 injection studies in depleted shale gas reservoirs, Du and Nojabaei (2019) report definitions of injection rate restriction between 100 and 5000 Mscf/d, the same as 2,832 283,168 m^3/d. However, these studies seek to determine the rate limit to maximize enhanced oil or gas recovery, which tends to result in lower injection rates when compared to the injection proposal specifically for CO_2 storage. Hoteit et al. (2019) use injection rate limits between 15 and 50,000 Mscf/d (424,753 and 1,415,842 m^3/d) for CO_2 injection analysis exclusively for storage. For injection in non-depleted reservoirs, it is possible to establish a parallel with studies of saline aquifers since depleted hydrocarbon reservoirs are traditionally studied and targeted for CO_2 injection. Generally, the CO_2 injection rate for saline aquifers is limited by injection pressure, which respects the formation fracture pressure (Szulczewski, 2009). This approach can be considered conservative if one believes that the spread of fractures can benefit storage capacity, although it can be a reasonable parameter considering storage security.

For the calculation of fracture pressure, due to the absence of studies with this purpose at Irati, an average fracture gradient for shale formations was considered, ranging from 0.5 to 1.0 psi/ft (11.31 to 22.62 kPa/m) (Halliburton, 2008). These values were then considered for the boundary models, while the mean value of 0.75 psi/ft (16.97 kPa/m) was selected for the base model. Therefore, multiplying this gradient by the depth determined in the previously mentioned (1,320 m), a fracture pressure of 990 psi was obtained, equivalent to 22,395 kPa. The related condition between calculated fracture pressure and the original reservoir pressure is parallel to the associated requirements of Zhao et al. (2018) and Wanniarachchi et al. (2017). In the first analysis involving the impact of depleting shale gas reservoirs on fracture pressure, fracture pressures are 10% to 80% higher than the initial reservoir pressures, considering possible anisotropies of geomechanical parameters. In Wanniarachchi et al. (2017), this proportion reaches up to 160%. Thus, the calculated value for fracture pressure considering a hypothetical reservoir of the Irati Formation is within this range, with a ratio of 60%. This comparison and identification of compatible values with studies in other formations is an essential indication of the choice of conservative and adequate numbers since this parameter – fracture pressure – has a significant impact on the potential for CO_2 storage capacity. Finally, considering a safety margin of 1,000 kPa, the well bottom hole pressure was set to 21,395 kPa for the base model.

Table 2 summarizes the values assumed for the well included in the base model, and Figure 1 displays images of the model on Builder.

Feature	**Value**
Well length (m)	1.000
Number of stages of hydraulic fracturing	11
Wings of fractures (m)	140
Internal thickness of fractures (m)	0,6096
Height of fractures (m)	20
Maximum pressure on well bottom (kPa)	21.395

Table 2. Values used for the injection well with hydraulic fracturing of the M0 base model.



1. Image of model M0, referring to the hypothetical reservoir in Irati and two-dimensional layer view with the well, in builder

3.3. Parameters for sensitivity analysis

The study involves the influence of the geological characteristics of the reservoir on CO_2 storage capacity. Since this is a relatively new approach, few studies have this purpose applied to shale reservoirs. It is possible to establish parallels with essential factors in evaluating hydrocarbon accumulations in conventional reservoirs, such as porosity, permeability, and pressure. However, because these are unconventional reservoirs, we also consider volume stimulation by hydraulic fracturing and geochemical properties, notably the ability to adsorb CO_2 on the organic matter.

To contribute to the knowledge of unconventional reservoirs' behaviour as potential CO_2 storage units, a sensitivity analysis of geological characteristics was performed according to the maximization of the CO_2 injection volume. Thickness, porosity, permeability, pressure, temperature, initial gas saturation, CO_2 diffusion coefficient, compressibility, and rock density were varied in 20%, considering ten (10) years of injection. Pressure variations followed proportionally by variations in well bottom hole pressure, and 60% higher.

3.4 Geological boundary models

Considering the geological uncertainties of the base model M0, the boundary models were also used in the simulations. It considers the minimum (M-) and maximum (M+) values based on other formations of black shale reservoirs worldwide. For this analysis of the potential range of CO_2 storage capacity of the Irati Formation, the following characteristics were varied from the base model (M0):

- Porosity, according to the estimated values Irati, from 4% to 8% (based on De Souza, 2018);
- Permeability, based on the maximum variation assumed in EIA (2013), from 0.00001 to 0.001 mD;
- Pressure, with variations in pressure gradients, assumed in EIA (2013) for sub pressure of 0.35 psi/ft and overpressure of 0.6 psi/ft, applied to a depth of 1320 m;
- Due to the difficulty to find values for water saturation in the literature, initial gas saturation was set at the values calculated in Aguilera (2016) for the Barnett, Marcellus and Haynesville formations, ranging from 35% to 45%, with safety margin, resulting in 30% to 50%;
- Langmuir parameters were extracted from Weniger et al. (2010) for the Irati Formation, with samples 08_168 and 08_154. The pessimistic model was set to 0.04 gmol/kg and pressure of 1.77x10-4 kPa-1 for CH_4 and 0.65 gmol/kg and 5.03x10-5 kPa-1 for CO_2. The optimistic, with 0.37 gmol/kg and 1.19x10-4 kPa-1 for CH_4 and 2.02 gmol/kg and 6.67x10-5 kPa-1 for CO_2;

● Rock bottom pressure, following the same reasoning established for M0, with fracture gradients ranging from 0.5 to 1.0 psi/ft (Halliburton, 2008).

Table 3 presents the values used in the construction of the boundary models.

Variable	M-	Base	M+	Reference
Porosity (fraction)	4%	6%	8%	Dias (2018)[1]
Permeability (mD)	0,00001	0,0000963	0,001	EIA (2013)
Pressure (kPa)	10.451	14.183	17.916	(a)
Gas saturation (fraction)	50%	55%	70%	Aguilera (2016)
Langmuir CH_4 volume (gmol/kg)	0,04	0,25	0,37	Weniger et al. (2010)
Langmuir CH_4 pressure (kPa-1)	1.77x10-4	7.062x10-5	1.19x10-4	Weniger et al. (2010)
Langmuir CO_2 volume (gmol/kg)	0,65	1,25	2,02	Weniger et al. (2010)
Langmuir CO_2 pressure (kPa-1)	5.03x10-5	7.45x10-5	6.67x10-5	Weniger et al. (2010)
Pressure at rock bottom (kPa)	13.930	21.395	28.860	(b)

Table 3. Definition of minimum and maximum values of geological characteristics for the composition of the M- and M+ boundary scenarios.

[1]Calculated based on the table reference.

(a) Calculated based on EIA pressure gradients (2013);

(b) Calculated based on the conditional relation between fracture pressure and training pressure.

4. RESULTS

The numerical reservoir simulation for a thousand years of the M0 base model indicated a theoretical potential of injection capacity of approximately 783,000 tons of CO_2, as identified in Figure 2a. The total CO_2 injected annually starts with about 25,000 tons, with a decline of 47% in the first ten (10) years. From twenty years, the reduction is around 17% every ten years, with less stable variations after

260 years of injection. In the 136th year, the CO_2 injection rate is already below 1,000 tons per year and below ten tons in the 278th year of injection.

These results show that the injection time to achieve the total CO_2 storage capacity of the hypothetical reservoir exceeds the period of a commercial project since it seems unlikely to have a project with more than 136 years of planning. The injection rate was within the established parameter limits in other CO_2 injection studies in shale gas and oil reservoirs, reviewed in Du and Nojabaei (2019), peaking at 35,000 m^3/d in the first year. The injection rate behaviour is presented in Figures 2d and 2e for 1,000 and 20 years injection time, respectively.

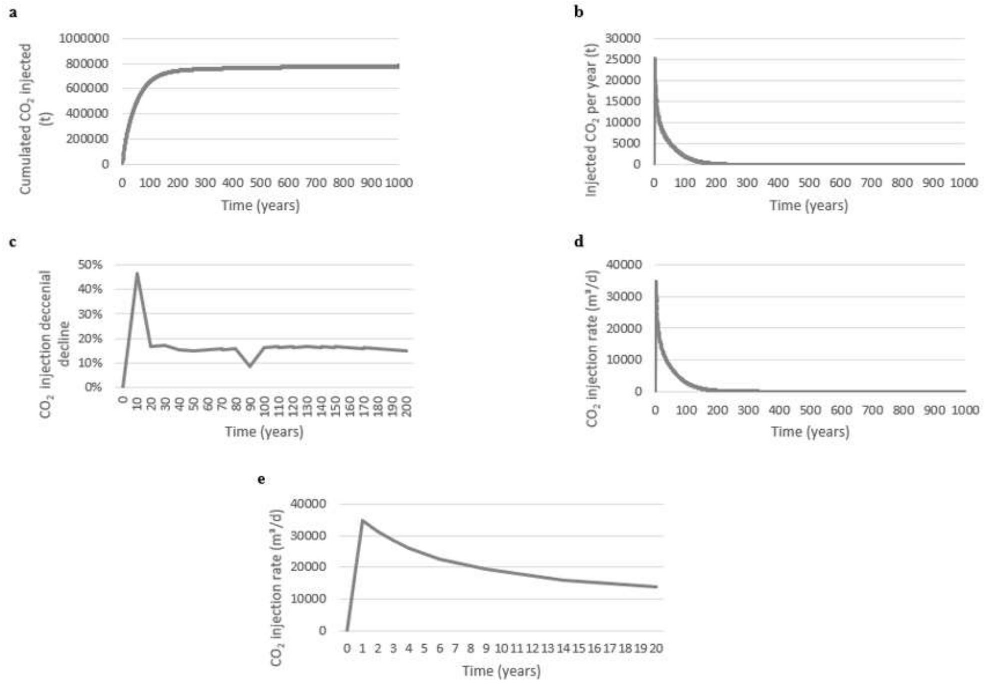


Figure 2. Simulation results for 1,000 years of injection to evaluate storage capacity: (a) accumulated CO_2 injected; (b) CO_2 injected per year; (c) decennial decline of CO_2 injection; (e) CO_2 injection rate.

Figure 3 shows the CO_2 proportion evolution in the gas phase in the four layers of the reservoir, each with 10 m. From "layer 1", the CO_2 fraction is kept almost evenly between 20% and 30% at the end of the injection period. However, the small portions related to the upper part of the injector well passage and hydraulic fractures, the fraction can reach 60% of the gas phase. The same percentages stand in layer 2, where the well is located, but with the regions around the well reaching more blocks. The third layer (top to bottom) has almost homogeneous proportions of 20% to 30% of CO_2.

On the other hand, the last layer brings an entirely different pattern of CO2 distribution concerning the total gas phase. The region around the well and hydraulic fractures with the highest CO_2 fraction occupies the entire area virtually, with values around 30% to 70%, leaving only the extremities with percentages from 0 to 20%. The higher water saturation can justify this behaviour concerning the other upper layers and, therefore, by the presence of extremely low amounts of CH_4. Considering the low compressibility of water, the injected CO_2 that reached the fourth layer was entirely stored under the adsorbed phase.

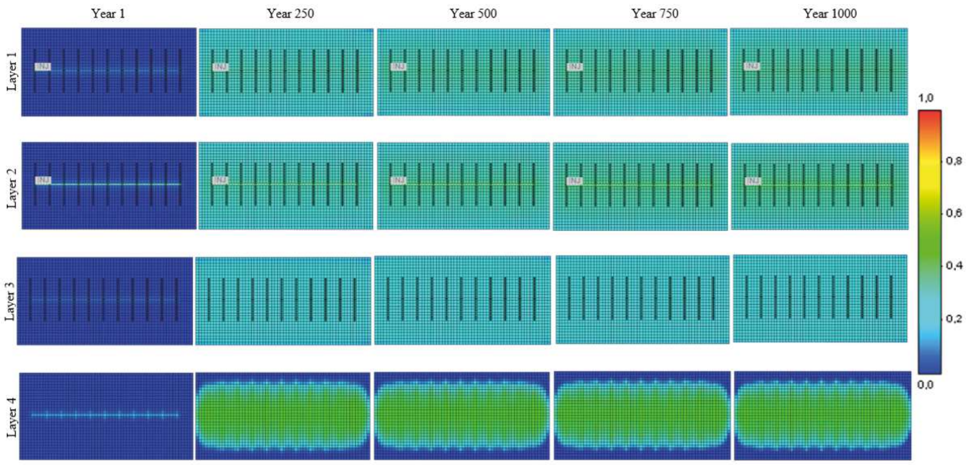


Figure 3. Plan view of the reservoir in four layers, identifying the evolution of the CO_2 fraction in the gas phase, up to the end of the CO_2 injection period, in selected years.

At the end of the injection period, the CO_2 adsorbed phase concerning the total stored ranged from 70% to 80% in the two upper layers and 80% up to 100% in the lower layers(Figure 4). Figure 5 shows the evolution of CO_2 adsorption in gmole/m^3 in the injector well layer until year 136, in which the injection flow was less than 1,000 tons of CO2 per year.

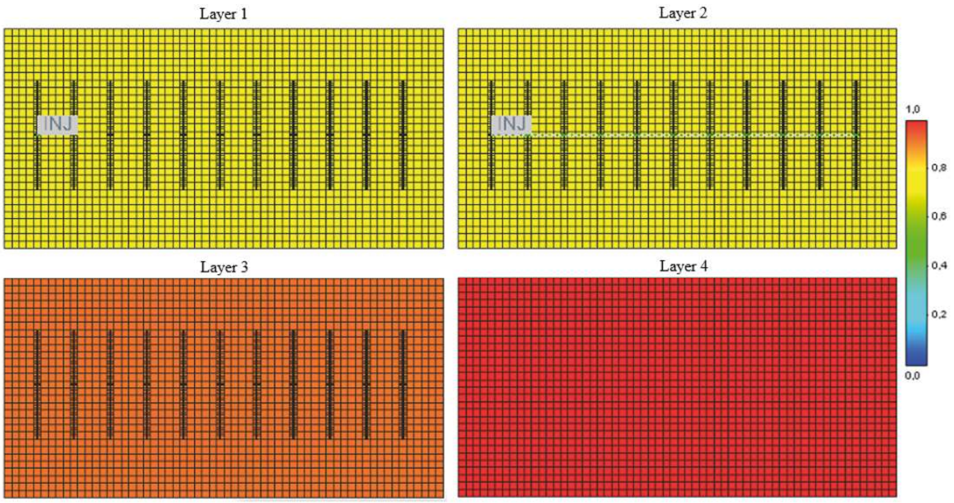


Figure 4. Plan view of the four layers of the reservoir at the end of the injection period,

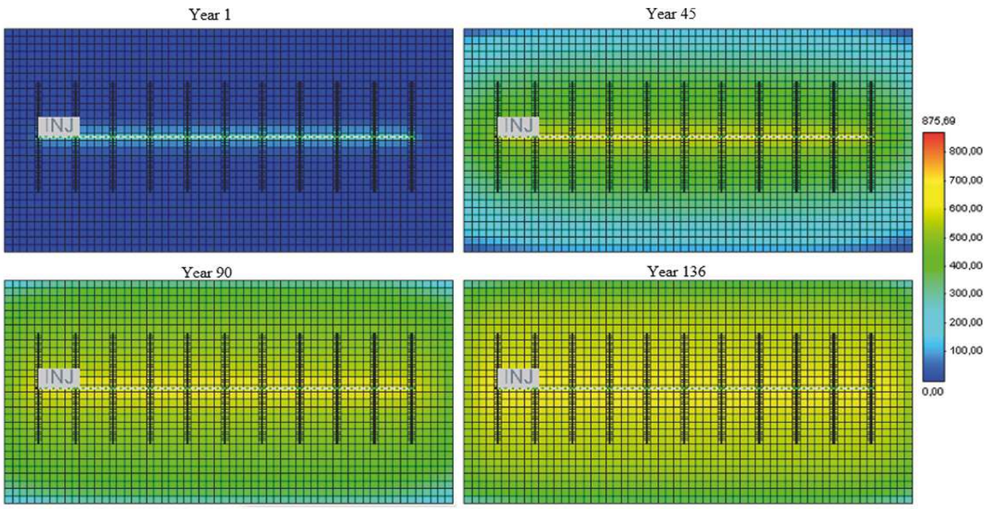


Figure 5. Plan view of layer 2, where the injector well is located, identifying the concentrations of CO2 by volume, in gmole/m³, in selected years, up to the 136th year.

The total effectiveness of CO_2 storage in the adsorption phase presented 40% to 77%, as observed in Figure 6. At the end of the simulation period, approximately 13.68x109 CO_2 gmole were adsorbed, and 0.92x109 CH_4 gmole underwent a desorption process. However, it is impossible to establish a CO_2/CH_4 displacement ratio, as it is unknown whether CH_4 reached the maximum adsorption potential before CO_2 injection was initiated.

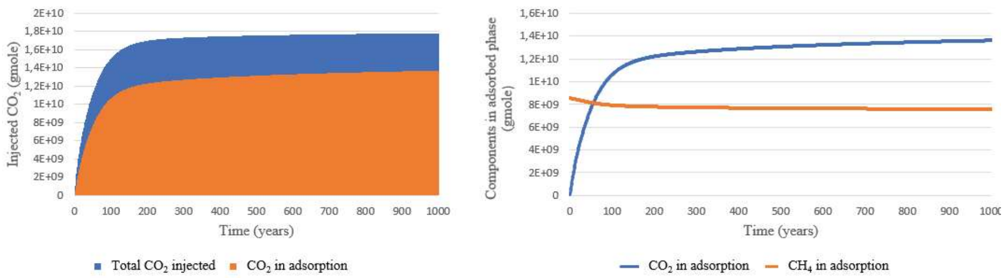


Figure 6. Evolution of the CO2 in adsorption based on the total injected and CH_4 in adsorption in the reservoir, in M0.

The sensitivity analysis of the reservoir properties concerning CO_2 injection capacity indicated the most significant influence involving pressure, thickness, gas saturation, density, porosity, and permeability, in that order based on the results. The temperature, compressibility and CO_2 diffusion coefficient showed little influence, as shown in Figure 7. The variation of the reservoir pressure had more expressive results due to its established relationships with the variation of the injection pressure.

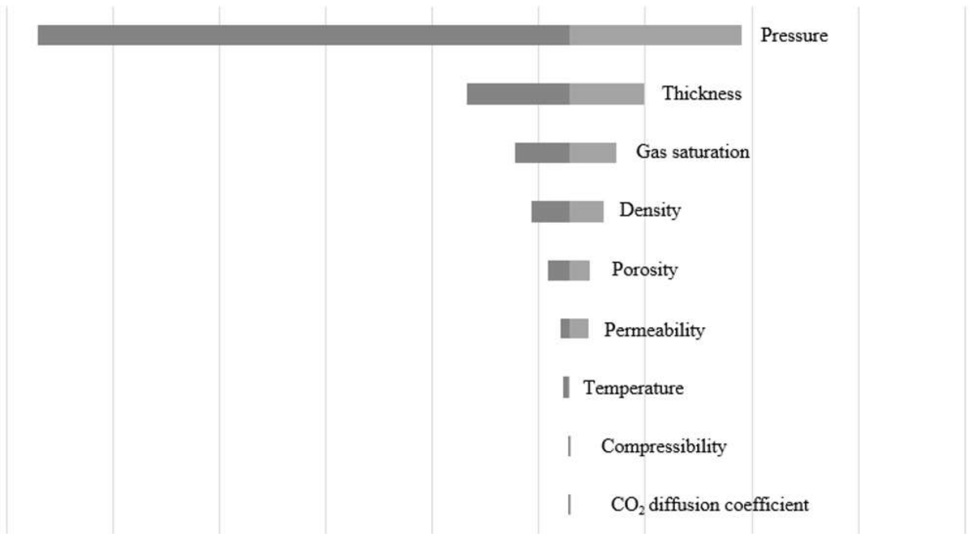


Figure 7. Sensitivity analysis of reservoir properties concerning CO_2 injection considering; pressure, thickness, gas saturation, density, porosity, permeability, temperature, compressibility, and CO_2 diffusion coefficient.

Storage safety was not impaired; the final reservoir pressure stayed below the fracture pressure. Only in the year 760, the reservoir reaches the value equivalent to the final pressure with the total CO_2 injected, 21,507 kPa, as identified in Figure 8.

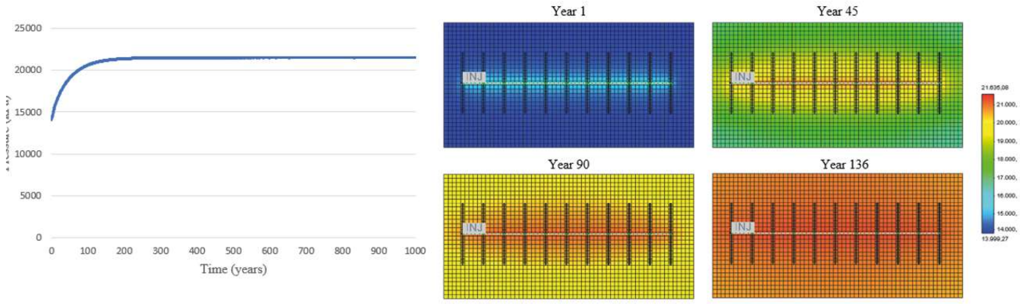


Figure 8: Evolution of pressure in the injection period, with a maximum value of 21,507 kPa reached in the year 760 and plan view of the layer with the well showing the evolution of pressure (in kPa) in selected years, in M0.

Regarding the simulations' results for M- and M+ boundary models, storage capacity was found between 166,000 and 1193,000 tons of CO_2, demonstrating the extent of the impact of characteristic geological variations on the result when considered a virtually unrestricted injection time. Results for storage capacity and final CO_2 storage percentages in the adsorbed phase of 56% in M- and 69% in M+ are shown in Figure 9.

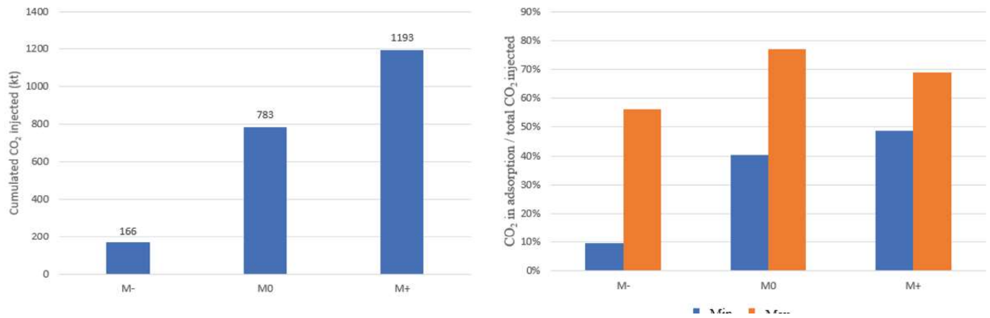


Figure 9. Comparison of CO_2 stored in the boundary models (M- and M+) and base model (M0), and comparison of the effectiveness of CO_2 storage in the adsorbed phase concerning the total injected, in the boundary models (M- and M+) and base model (M0), in 1000 years.

The capacity intervals between the pessimistic and optimistic scenarios demonstrate the significant influence of the variation of the reservoir properties, notably the pressure and gas saturation, since the thickness and density were not altered concerning the base model. Therefore, the relevance of obtaining refined data to construct the geological model is clear, reducing uncertainties. Assessing the total potential of the Irati Formation for CO_2 storage requires further studies to provide the entire area in which CO_2 injection activities can be carried out, considering the adequate spacing between wells. Because the thickness used in the model is the average of the entire formation, the determined area would be multiplied by the results of this work, providing an estimate for the whole length of the Irati Formation.

The comparison of this potential with other shale formations is limited by the differences in literature approaches to date. In general, the CO_2 injection in shale gas reservoirs is studied for reservoirs that have already been the target of production and are almost always associated with enhanced recovery. If, on the one hand, storage capacity tends to be lower in non-depleted reservoirs, on the other hand, the objective of enhanced recovery tends to minimize CO_2 injection.

Despite the uncertainties of the applied parameters, the present study indicates estimates for the potential of CO_2 storage capacity in Irati without considering oil or gas production, based on the possibility of CO_2 injection up to a safety pressure lower than the reservoir fracture pressure. From this concept, the possibility of storing carbon in shale gas reservoirs is raised without the need for local production of fossil fuel resources.

5. CONCLUSIONS

The present study aimed to estimate the geological CO_2 storage capacity of Irati Formation in the Paraná Basin by a unit of geological volume based on numerical reservoir simulations. Essential characteristics were incorporated into the geological modelling of the shale gas reservoirs, such as a network of natural fractures, gas diffusivity, adsorption and hydraulic fracturing. The CO_2 injection pressure was limited to stay lower than the assumed formation's fracture pressure, with a injection period of 1,000 years, allowing it to reach the total theoretical storage capacity. The project was restricted to an injector well in a reservoir representative volume comprising the horizontal well extension with hydraulic fracturing, covering an area of 1,200 m for 600 m, with a thickness of 40 m.

The simulation results presented a capacity of 783,000 tons of CO_2. The values may fluctuate between 166,000 and 1,193,000 tons, considering the pessimistic and optimistic scenarios of the reservoir properties .77% of the injected CO_2 was stored in the adsorbed phase at the end of the injection period. The sensitivity analysis indicated the reservoir's pressure and thickness as factors of more significant influence on total capacity, followed by gas saturation and formation density.

The presented results and methodologies may serve as references to predict CO_2 injection and storage in other areas where the depth and thicknesses are close to those showcased by this study.

ACKNOWLEDGEMENT

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CHAPTER 9

CLAY MINERALS AND CO_2 GEOLOGICAL STORAGE IN THE PARANÁ BASIN

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Haline de Vasconcellos Rocha
Fábio Palma de Lima

ABSTRACT

CO_2 geological storage is the segment within the CCS chain that plays a significant role in mitigating the worst impacts of climate change due to its considerable CO_2 abatement capacity. Overall, the effectiveness of CO_2 geological storage depends on the combination of geological factors, including clay mineralogy. Clay minerals are relevant to CO_2 geological storage since they affect the gas sorption capacity of rock formations. For instance, the concentration of expandable clays, such as smectites, adds to reservoirs' overall CO_2 storage capacity by favouring the development of CO_2 adsorption sites due to interlamellar swelling. In this chapter, the contribution of clay minerals to CO_2 geological storage is discussed. In addition, the Paraná Basin, south and southeast Brazil, was selected as a case study for determining potential reservoirs and caprocks to CO_2 geological storage, based on identified clay mineral assemblages. The result is that the clay mineralogy of various geological formations within the Paraná Basin favours the overall effectiveness and safety of CO_2 geological storage and the deployment of CCS technologies in the region.

Keywords: Clay minerals, CO_2 geological storage, Panará Basin

1. INTRODUCTION

The increase in carbon dioxide (CO_2) concentration in the Earth's atmosphere, especially from the 1950s to the present day, has been scientifically proven with data from different proxies (IPCC, 2021) and widely disseminated in various media. Special attention has been given to CO_2 emitting sources, the greenhouse effect of this gas in the atmosphere, and the possible consequences on the planet's surface in different environments.

On the other hand, the technologies developed to capture the CO_2 released from stationary sources, compress it, transport it, and store it in geological formations placed at depths greater than 500 m are still relatively less known (Tomic et al., 2018). The combination of these technologies is known as CO_2 capture and storage (CCS). According to the IPCC (2005), CCS is an important option to reduce the release of CO_2 into the atmosphere, contributing to stabilizing its concentration. It may lead to a critical emission reduction in a zero-carbon transition scenario (IEA, 2020).

In this chapter, the focus is to evaluate the potential for CO_2 geological storage, also known as CO_2 geological sequestration, of some sedimentary formations of the Paraná Basin, based on the contribution of its clay minerals for the retention of this compound.

2. CLAY MINERALS

Clay minerals are common minerals on the Earth's surface, constituting many soils, sediments, and sedimentary rocks. In sedimentary basins, they are abundant constituents of siliciclastic and some sedimentary carbonate rocks. In these materials, most clay minerals are clay-sized particles, usually less than 2 µm.

Clay minerals' chemical composition and crystal structure classify them as hydrated aluminium phyllosilicates (Guggenheim & Martin, 1995), divided into two groups (1:1 and 2:1), which differ by the number of tetrahedral sheets linked to an octahedral sheet (CMS, 2020). 1:1 clay minerals are formed by repeating the stacking of a tetrahedral sheet and an octahedral sheet. 2:1 clay minerals contain an octahedral sheet between two tetrahedral sheets and interlamellar material (usually cations or chemical compounds) between the 2:1 layers.

The adsorption capacity of clay minerals is one of the most important characteristics to be determined to operate efficiently CO_2 sequestration (Fripiat et al. 1974). The interlamellar distance is a critical parameter determining the sorption of molecules, including CO_2 (Hong and Romanov 2018). This distance depends on the charge and composition of the clay mineral and the size of the charge-compensating cations in that space (Busch et al. 2016, Grekov et al. 2020). For instance, expandable clays, such as clays from the smectite group, lead to higher CO_2 storage capacity (Bertier & Rother, 2016; Busch et al., 2017) due to its volumetric expansion and consequent development of adsorption sites. Additionally, such interlamellar swelling in smectite clays associated with CO_2 adsorption contributes to storage safety and a reduction in reservoir pressure (Busch et al., 2020).

Regarding the sorption capacity of different clay mineral assemblages, Ca-exchanged smectite can adsorb the most significant amounts of CO_2, followed by Na-exchanged smectite, illite, and kaolinite, and negligible amounts of CO_2 adsorbed to chlorite (Busch et al., 2020; Busch et al., 2008).

Overall, clay minerals are essential to CO_2 geological storage due to their gas sorption capacity. In low-permeability reservoirs, such as shale formations, clay minerals contribute to the gas sorption capacity of these unconventional reservoirs and, consequently, its overall CO_2 storage potential (Busch et al., 2008). Clay minerals in conventional reservoirs determine the caprock integrity, storage safety, and effectiveness (Busch et al., 2017). Therefore, determining mineralogical assemblages, especially clay mineral content, type, and composition, is essential to characterize potential CO_2 reservoirs and caprocks.

3. POTENTIAL GEOLOGICAL FORMATIONS FOR CCS IN THE PARANÁ BASIN BASED ON THEIR CLAY MINERALS CONTENT

The Paraná Basin is a Paleozoic-Mesozoic cratonic basin (Ordovician to Cretaceous) that occupies a significant and wide area in the central portion of South America, located mainly in southern Brazil (just over 1,120,000 km^2) (REATE 2020). The basin is filled, essentially, with siliciclastic rocks, and subordinately, with sedimentary carbonate rocks, adding up to about 6 km in thickness.

Volcanic igneous rocks of the Serra Geral Formation, about 1700 m thick, complete the stratigraphic column of the basin. They present themselves as spills, sills, and dikes (Melfi et al. 1988) and close the evolutionary history of the Paraná Basin in the Early Cretaceous (Riccomini 1995).

In total, the sedimentary and igneous rocks of Paraná Basin amount to just over 7600 m, according to the thicknesses mentioned by Milani et al. (2007). They are overlaid by the sedimentary deposits of the Bauru Basin, at least 300 m thick.

Clay minerals are present in siliciclastic rocks along the entire stratigraphic column of the Paraná Basin, with variations in their types and proportions. The most comprehensive study of the characterization of clay minerals was carried out by Ramos & Formoso (1975), who analysed 1052 samples collected in 43 drill cores drilled by Petrobrás until 1967, as shown in Figure 1.

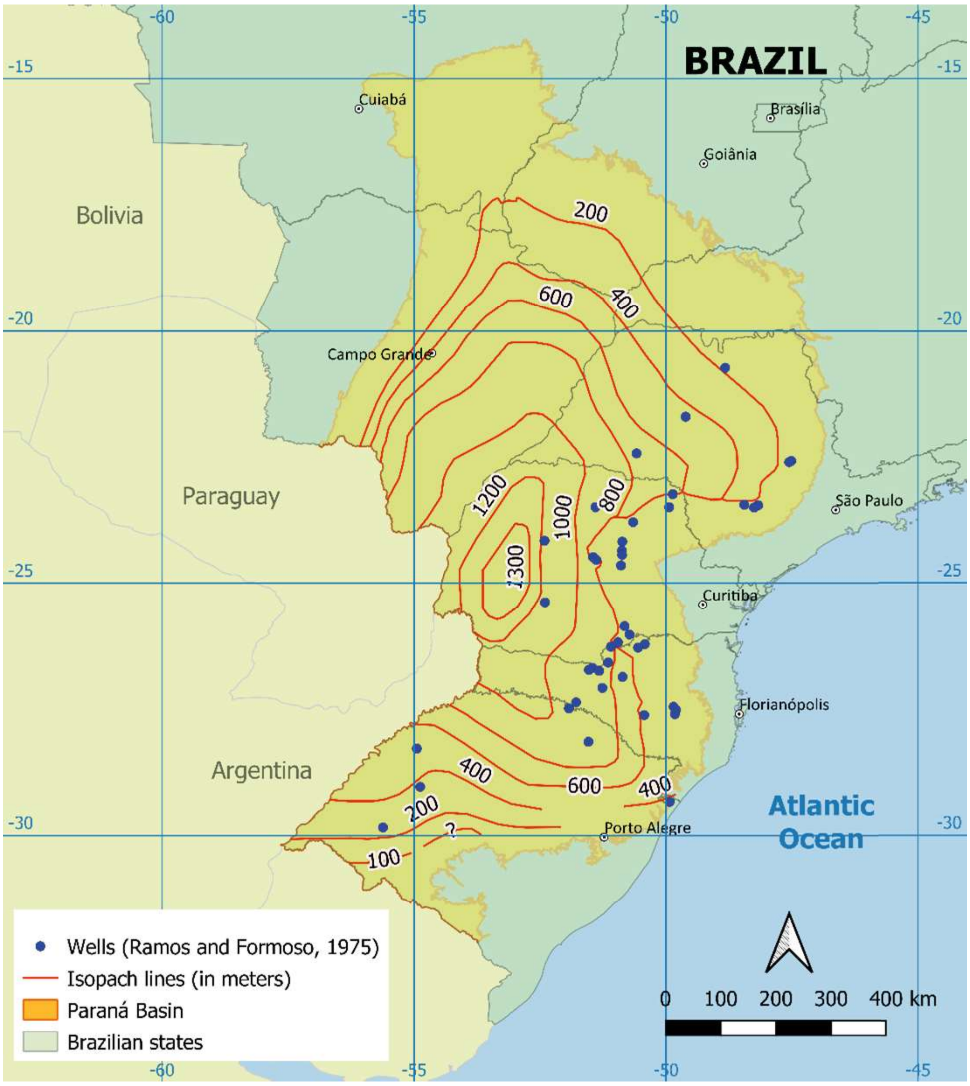

Figure 1 - Isopaque map (in meters) of the Permian section above Irati Formation and the location of the 43 wells analyzed by Ramos & Formoso (1975) in the Paraná Basin (Source: Lima 2021).

The boreholes used by the authors were drilled in the southern (Paraná, Santa Catarina, and the Rio Grande do Sul states) and east (São Paulo state) parts of the basin, reaching a depth of 4378 m in a sample collected in the core 2-CM-1-PR (Paraná state). The authors analysed the clay fraction (< 2µm) by X-ray diffraction (Cu K alpha radiation, 35 kV, 20 mA, Ni filter, goniometer speed of 2o 2Ө/min), using oriented preparations and conventional treatments (natural drying, solvation with ethylene glycol and calcination at 490oC). The lithology of the samples accompanies the mineralogical results for groups of clay minerals. Several similar types of research by later authors complement this collection, carried out with samples collected from natural exposures and mine fronts in the outcropping area of the basin along its borders, and in shallow cores drilled close to this area.

The set of information collected is presented in Table 1 and considered representative of the lithological variation and assemblage of clay minerals from various geological formations in the Paraná Basin, given the geographic coverage of the boreholes and exposures as the wide vertical distribution of the samples.

Due to the differences in the methods used for the semi-quantification of mineral phases in the X-ray diffractograms used by the various authors, table 1 shows the dominant clay mineral and those with subordinate presence in each geological formation. Since the objective of this work is to indicate the training potential for deploying CCS technology based on the clay mineral content, the lack of absolute values does not affect this analysis. Thus, information regarding the maximum thickness, dominant and subordinate lithologies, and principal and secondary clay mineral assemblages were compiled for the geological sedimentary formations of the Paraná, Itararé, Guatá, Passa Dois, and São Bento groups (Table 1).

The total thicknesses recorded for each group are hundreds of meters (Table 1): i) Paraná Group with 996 m; ii) Itararé Group reaching 1281 m, the thickest in the basin; iii) Guatá Group with a thickness of 586 m, the thinnest in the basin; iv) Passa Dois Group with 1159 m, and v) São Bento Group with 800 m only in the sum of sedimentary units (Pirambóia and Botucatu formations), not including the volcanic rocks of the Serra Geral Formation, which can reach 1500 m in maximum thickness.

The dominant lithologies are psammitic (sandstone) to pelitic (siltstone, claystone, and shale) (Table 1). Psephytic rocks (diamictite and conglomerate) are only important in the Itararé Group. Subordinately occurring lithologies include carbonate rocks (limestone, oolitic limestone, and marlstone), calcareous concretion, nodular flint, and coal.

Among the clay minerals mentioned by the consulted authors, illite, interstratified illite/smectite, and smectite are cited as the main phases in several geological formations where they are associated or isolated, constituting the main mineralogical composition. Chlorite is the main clay mineral only in the Rio Bonito and Irati formations. Assemblages of clay minerals that are more varied, with subordinate occurrences, are recognized in the different formations and commonly include kaolinite, in addition to pyrophyllite (Grupo Paraná), palygorskite (Grupo Itararé), and corrensite (Grupo Passa Dois).

The presence of smectite as the main or subordinate clay mineral in several geological formations of the Paraná Basin meets one of the critical criteria for selecting the reservoir rock for CO_2, that is, the presence of appropriate mineralogical composition for the interaction with the carbon dioxide. Several studies have demonstrated the role of this expandable clay mineral in CO_2 adsorption.

In addition, the presence of interstratified illite/smectite and corrensite may be important for the effectiveness of the geological storage of CO_2 in the Paraná Basin. These clay minerals are still poorly studied in their interactions with CO_2, but both contain interstratified smectite and are expandable, which suggests a good sorption capacity. The other clay minerals (illite, kaolinite, chlorite) interact with CO_2, although lesser (e. g., Hu et al. 2019).

The varied lithology of sedimentary formations that contain expandable clay minerals as dominant or subordinate clay suggests that the study to determine the potential for CO_2 storage will have a local character. The characterization of sedimentary facies and mineralogical composition, together with other local geological attributes (e. g., deformation structures), will be the basis of information for selecting reservoir rocks.

4. CONCLUSION

The geological storage of CO_2 is a technological alternative to reduce the emission of greenhouse gases worldwide. It may eventually compensate for the various stationary sources that emit this gas in Brazil's southeast and south regions. Several geological sedimentary formations within the Paraná Basin contain lithologies that might be suitable for CO_2 retention. The overall suitability of reservoirs to CO_2 storage depends on their clay mineralogy among various geological aspects. This dependence is due to the gas sorption capacity of clay minerals, which affects the CO_2 storage potential of clay-rich geological formations. Inthe Paraná Basin, the occurrence of expandable clays, such as smectites, contributes to the overall potential for CO_2 geological storage and CCS deployment in the region. However, the lithological and compositional heterogeneity of geological formation suggests that a local scale approach will be necessary to determine its behaviour as a reservoir and/or caprock and its real contribution to emissions mitigation.

<table>
<tr><th rowspan="2">Group</th><th colspan="2">Formation</th><th colspan="2" rowspan="2">Maximum thickness (m)</th><th colspan="2" rowspan="2">Main lithology</th><th colspan="2" rowspan="2">Other lithologies</th><th colspan="2" rowspan="2">Main clay mineral(s)</th><th colspan="2" rowspan="2">Other clay minerals</th></tr>
<tr><th>SSE</th><th>NNW</th></tr>
<tr><td rowspan="2">São Bento</td><td colspan="2">Botucatu</td><td colspan="2">450 [5]</td><td colspan="2">sandstone [1]</td><td colspan="2">claystone [1]
clayey sandstone</td><td colspan="2">smectite [1]</td><td colspan="2">illite, chlorite, I/S, kaolinite [1]</td></tr>
<tr><td colspan="2">Pirambóia</td><td colspan="2">350 [3]</td><td colspan="2">sandstone [3]</td><td colspan="2">claystone, siltstone [3]</td><td colspan="2">smectite, I/S [6]</td><td colspan="2"></td></tr>
<tr><td rowspan="4">Passa Dois</td><td>Rio do Rasto</td><td rowspan="3">Corumbataí</td><td>650 [5]</td><td rowspan="3">130 [7]</td><td colspan="2">siltstone [3]
claystone</td><td>sandstone [1]
limestone
silex</td><td rowspan="3">shale [3]
sandstone
oolitic limestone</td><td>illite [1]
smectite</td><td rowspan="3">smectite [2]</td><td>I/S, chlorite, corrensite, kaolinite [1]</td><td rowspan="3">illite [2]
chlorite
I/S</td></tr>
<tr><td>Teresina</td><td>318 [3]</td><td colspan="2">siltstone, shale, claystone [1]</td><td>oolitic limestone, silex, sandstone [1]</td><td>illite [1]</td><td>I/S, smectite, chlorite, corrensite [1]</td></tr>
<tr><td>Serra Alta</td><td>120 [1]</td><td colspan="2">shale, siltstone, claystone [1]</td><td>calcareous concretion [1]</td><td>illite [1]</td><td>I/S, chlorite, smectite, corrensite, kaolinite [1]</td></tr>
<tr><td colspan="2">Irati</td><td colspan="2">71 [3]</td><td colspan="2">claystone, shale [1]</td><td colspan="2">limestone, nodular silex [1]
calcareous concretions, siltstone</td><td colspan="2">illite, I/S, chlorite [1]</td><td colspan="2">smectite, corrensite, kaolinite [1]</td></tr>
<tr><td rowspan="2">Guatá</td><td>Palermo</td><td rowspan="2">Tatuí [4]</td><td>300 [5]</td><td rowspan="2">70 [4]</td><td>siltstone [1]</td><td rowspan="2">siltstone [4]</td><td>shale [1]
sandstone</td><td rowspan="2">limestone [4]
silex
sandstone</td><td>I/S [1]</td><td rowspan="2">illite [9]</td><td>chlorite [1]
illite
kaolinite
smectite</td><td rowspan="2">kaolinite [9]
smectite</td></tr>
<tr><td>Rio Bonito</td><td>286 [1]</td><td>sandstone [1]</td><td>shale [1]
siltstone claystone
marlstone coal</td><td>I/S [1]</td><td>kaolinite [1]
chlorite
illite smectite</td></tr>
<tr><td rowspan="3">Itararé</td><td>Taciba</td><td rowspan="2"></td><td rowspan="3">1281 [1]</td><td rowspan="2"></td><td colspan="2" rowspan="3">diamictite [1]
conglomerate
sandstone
claystone</td><td colspan="2" rowspan="3">shale, siltstone [1]</td><td rowspan="3">illite [1]
chlorite</td><td rowspan="2"></td><td rowspan="3">smectite [1]
kaolinite, I/S, palygorskite</td><td rowspan="2"></td></tr>
<tr><td>C. Mourão</td></tr>
<tr><td>Lagoa Azul</td><td>Aquidauana</td><td>799 [3]</td><td>smectite, illite [8]</td><td>kaolinite
chlorite [8]</td></tr>
<tr><td rowspan="2">Paraná</td><td colspan="2">Ponta Grossa</td><td colspan="2">653 [1]</td><td colspan="2">shale [1]</td><td colspan="2">siltstone, sandstone [1]</td><td colspan="2">illite [1]</td><td colspan="2">chlorite, I/S [1]
kaolinite, pirofilite</td></tr>
<tr><td colspan="2">Furnas</td><td colspan="2">343 [3]</td><td colspan="2">sandstone [1]</td><td colspan="2">siltstone [3]</td><td colspan="2">illite [1]</td><td colspan="2">kaolinite, chlorite [1]
I/S, pyrophyllite</td></tr>
</table>

Table 1 – Maximum thicknesses, lithologies and assemblages of clay minerals from geological sedimentary formations in the Paraná Basin. The information in each frame comes from: 1 Ramos and Formoso (1975); 2 Ramos and Formoso (1976); 3 Schneider et al. (1974); 4 Soares (1972), Assine et al. (2003), Chahud (2011); 5 Milani et al. (2007); 6 Gesicki (2007); 7 Zanardo et al. (2011), 8 Gesicki (1997); 9 Curtolo (2019).

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CHAPTER 10

REGULATION, COMPLIANCE AND BEST INSTITUTIONAL PRACTICES FOR CO_2 ONSHORE AND OFFSHORE GEOLOGICAL STORAGE: SANTOS AND PARANÁ SEDIMENTARY BASINS CASES

Raíssa Moreira Lima Mendes Musarra
Hirdan K. de Medeiros Costa
Mariana Ciotta

ABSTRACT

This chapter addresses the regulatory and institutional framework for geological carbon storage in Brazil, especially in the Santos and Paraná Basins, in terms of important territorial peculiarities for the regulatory context. Thus, it addresses the general perspectives for incorporating international normative criteria and the pertinence of internal norms to CCS technologies, showing the current internal legal and regulatory issues, using them as a locus of application. To this end, the deductive analytical method will be adopted for research elaboration, combined with the systematic and teleological approach for legal hermeneutics and the comparative method for the exposition of best practices. The analysis of the basins shows that they require long-term storage and monitoring planning. In this sense, the research techniques will be documentary and theoretical analysis and institutional composition.

Keywords: Geological Storage of CO_2, CCS (Carbon Capture and Storage), CCS Regulation, Oil and Gas depleted fields, Santos Basin.

1. INTRODUCTION

Legal and Regulatory aspects involving safety, control, and licensing for CO_2 transport and storage are combined with other criteria for the characterization and assessing potential carbon geological storage complexes. The surrounding areas involving depleted oil and gas fields are also essential factors for implementing CCS (Carbon Capture and Storage) technologies in territories where they are not yet consolidated, as in Brazil. First, it is worth distinguishing between legal and regulatory. Therefore, the text aims to present both legal and regulatory aspects and good practices related to the geological storage of carbon dioxide. Legal is that which, in a broad sense, not only expresses what is authorized or enabled by law but also everything that can be done or everything that complies with use and custom is understood by jurisprudence. Regulatory is a term that refers to a set of rules, laws and guidelines that regulate the functioning of the sectors in which agents provide utility services.

Carbon sequestration can be accomplished through natural means, through photosynthesis, carbon removal from the atmosphere, or by artificial means, through Carbon Capture and Storage Technologies. Once captured, the carbon dioxide is compressed and transported to suitable reservoirs (IEA, 2018). Carbon dioxide can be withdrawn from the atmosphere to the hydrosphere, through ocean storage, also through the biosphere, with storage by biomass, finally, through the lithosphere, with the geological repository. The geological storage of CO_2 can be done in the national territory depending on economic, technological and logistic vectors (Costa e Musarra, 2020).

Brazilian Post-2015 Development Agenda to the SDGs, called "Guiding Elements of the Brazilian Position", established the plan intended by 2030. Concerning energy, the intention is to promote an efficient, safe and quality supply that contributes to economic growth, poverty reduction, and social inclusion. It also includes increasing capacity building, promoting innovation and the transfer of modern energy technologies, developing quality, reliable, sustainable and resilient energy infrastructure to support economic development and human well-being, focusing on equitable and affordable access for all (MRE, 2014).

Promoting treatment of climate change by including it in related objectives and goals is pertinent to atmospheric CO_2 reduction and climate change mitigation. These objectives should: emphasise that combating climate change is essential for promoting sustainable development and eradicating poverty; emphasise the centrality of the principles and provisions of the United Nations Framework

Convention on Climate Change (UNFCCC), including the principle of common but differentiated responsibilities. They should also promote the deployment of clean energy, including low or zero-emission technologies, and support the transfer of technology to low-carbon infrastructure and industry solutions (MRE, 2014).

Considering Sustainable developments goals (SDG) 7, 13, and 14 as well as the Paris Agreement (United Nations Organization, 2015), to avoid climate change, carbon capture and storage activities can be an instrument to mitigate the anthropogenic emission of greenhouse gases (Costa and Musarra, 2019; Costa, 2019; Costa and Ladeira, 2019). As soft law, the literature considers the Paris Agreement for its applicability once each contracting state incorporates it into its internal regulations (Bastian, 2016).

However, geological storage may result in ecological damage, such as CO_2 leakage, making risk assessment and specific regulation necessary (Mikunda and Dixon, 2017). So far, there is no specific legislation for those activities in Brazil. Still, the entire national legal system may be triggered through systematic interpretation to make up a framework for CCS in Brazil (Morbach and Costa, 2020). The study of these factors applied to onshore and offshore carbon geological storage is justified by the need to adapt the national regulatory system and internationally adopted standards to the local Brazilian context for potential storage sites.

2. METHODOLOGY

The research-based method is monographic with a case study, bibliographic, documental (official statistical data) and normative research techniques, and analogy supported by Brazilian and international legislation. Socio-political criteria, norms and previous judicial and administrative decisions directed to other activities are considered in analogy to possible concrete cases for the definition of potential sites in Brazil (in Decree-Law Nº 4657 of 1942, Law of Introduction to Brazilian Law Norms). Therefore, in the absence of specific legislation dedicated to carbon storage, the Law institutions decide the case according to the law's analogy, customs, and general principles. The analysis of the regulatory compliance based on legal hermeneutics and analogy of norms considers, in principle: Federal Constitution of 1988; ANP Resolution 37/2001, CONAMA Resolution No. 23/1994, Federal Decree No. 8437, MMA Ordinance 422/2011 (which establishes procedures for federal environmental licensing of activities and projects of exploration and production of oil and natural gas in the marine environment (offshore) and onshore in the land-sea transition zone), Directive 2009/31/EC of the European Parliament and the Council, 23/04/09, and other norms related to the matter, directly or indirectly.

3. HEALTH, SAFETY AND ENVIRONMENTAL ISSUES

Various countries and organisations published different guidelines for implementing carbon storage projects in the environmental legislation debate; however, according to Tavakkolaghae and Meneghini (2019), policies are generally provided for specific conditions. Typically, these rules do not apply to different areas. Practices are usually affected by the laws of certain countries. Environmental regulations involving the project's location are considered for enforcement in the concerned states. Instructions for storage are limited and do not cover all environmental challenges. The literature on risk mitigation shows that some of the targeted objectives are: Ensuring the efficiency of the CCS project; Protecting the health of the workforce and those who live in the vicinity of the project; Limiting degradation of ecosystems in CCS sites; Elaborating comprehensive and responsive regulatory structure (Tavakkolaghae and Meneghini, 2019; Costa and Musarra, 2020; Costa et al., 2018). In this way, the purposes of monitoring are to assess the following concerning CCS: verify injected and stored quantities of CO_2; record the thermodynamic properties of stored CO_2; ensure the acceptable range of pressure inside the underground reservoir; detect and measure any leakage in the storage on early steps; monitoring the efficiency of the remediation; tracking the operated and shut-in wells for leakage (Nunes and Costa, 2020). This can be achieved by active and passive seismic monitoring, including gravimetry methods, temperature logs, geoelectrical approaches; microbiology; and geochemical sampling (Tavakkolaghae and Romano, 2019).

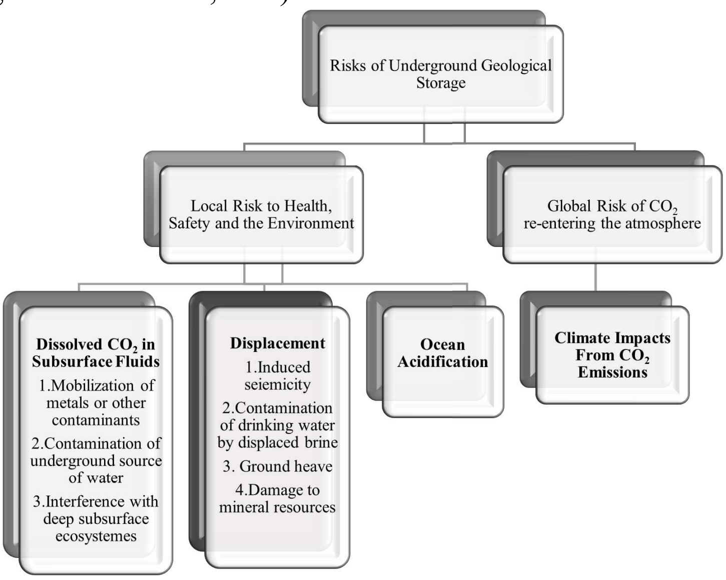

Figure 1: The schematic of risk chart of underground storage (Tavakkolaghae and Meneghini, 2019).

CCS outlines the risk of water contamination due to leakage of an injection well (IPCC, 2005; Solomon, 2006). Undetected geologic faults allow the CO_2 to migrate into water zones, elevate CO_2 levels, and contaminate groundwater and underground aquifers near the leakage. Contamination has a secondary impact on aquatic plant life and any other life forms that use the groundwater or aquifer as a source of drinking water. It could be lethal to plant and animal life, making remedial measures and intercepting CO_2 leakage essential to avoid aquifer contamination (Sawey, 2008; Tavakkolaghae and Meneghini, 2019).

4. REGULATORY FRAMEWORK

From a normative point of view, Brazilian law 9.478 / 97 aims to protect the environment, promote energy conservation, and propose measures to mitigate emissions of greenhouse gases and pollutants in the energy and transportation sectors. Law 9478/97 and its articles present the scope of the theme in Brazil still to be discussed and examined, demonstrating that, since its creation, the National Energy Policy has been connected to strategic topics such as CO_2 Capture and Storage.

Also worthy of mention is the edition of Law 12,187, of December 29, 2009, which establishes the National Policy on Climate Change - PNMC (MMA, 2018).

It is essential to understand the relevance of Law 12,187 of 2009 in the historical context of the government of ex-president Luís Inácio Lula da Silva. At the time, Brazil made commitments under the United Nations Framework Convention on Climate Change, the Kyoto Protocol and other documents on climate change, and the country became a signatory.

Thus, in art 5 stands out the promotion and development of scientific and technological research and the diffusion of technologies, processes, and practices aimed at mitigating climate change by reducing emissions by anthropogenic sources and strengthening anthropogenic emission removals through gas sinks.

The decree that regulates the policy is currently 9578/2018 that provides action plans for prevention, mitigation and adaptation to climate change .[2] Industrial

[2] Art. 17. For the purposes of the provisions of this Decree, the following action plans for the prevention and control of deforestation in biomes and sectorial plans for mitigation and adaptation to climate change are considered:

I - Action Plan for Prevention and Control of Deforestation in the Legal Amazon - PPCDAm;

II - Action Plan for Prevention and Control of Deforestation and Burning in the Cerrado - PPCerrado;

III - Ten-Year Energy Expansion Plan - PDE;

emissions were not planned, except for those related to the steel industry. However, paragraphs 2 and 4 of article 19 of the decree announce the possibility of instituting new mitigation plans and technologies, especially regarding those established by the United Nations Convention, as in the case of CCS .[3]

In Brazil, the main environmental policies are defined in the National Environmental Policy Law (Federal Law 6,938 of 1981) and the various resolutions of the National Environment Council (CONAMA). For example, Resolution 01 of 1986, which requires an assessment and an environmental impact report before granting environmental licensing by the environmental regulatory agency or Resolution 420 of 2009, sets out rules and tools for managing contaminated areas. Although generic, the Normative Instruction IBAMA 12/2010 can be considered an important milestone for institutionalising CCS activities in Brazil. Its art 2nd determines that the IBAMA council evaluates, in the process of licensing activities capable of emitting greenhouse gases, measures proposed by the entrepreneur to mitigate these environmental impacts in compliance with the commitments assumed by Brazil in the United Nations Framework Convention on Climate Change.

Adopting the National Policy on Climate Change, it is believed that it would be more appropriate to adopt a structure in which the structures provided there are used to head the CCS technology technologies in Brazil, always owing to the Ministry of the Environment. Ambiente act as a consultant and regulator of environmental issues. It means that the assessment of mitigation measures constitutes merit in the licensing of activities. To this end, Article 3 of the Normative

IV - Sectoral Plan for Mitigation and Adaptation to Climate Change for the Consolidation of a Low Carbon Economy in Agriculture - ABC Plan; and

V - Sectorial Plan for the Reduction of Emissions from the Steel Industry.

[3] Art. 19. To achieve the voluntary national commitment referred to in art. 12 of Law No. 12,187, of 2009, actions will be implemented that aim to reduce between 1,168 million ton CO2eq and 1,259 million tonCO2eq of the total emissions estimated in art. 18. (. . .)

§ 1 In order to comply with the provision in the caput, the following actions contained in the plans referred to in art. 17

§ 2 Other mitigation actions that contribute to the achievement of the voluntary national commitment provided for in the caput will be defined in the plans referred to in art. 6th and art. 11 of Law No. 12,187, of 2009, and in other government plans and programs.

§ 3 The actions referred to in this article will be implemented in a coordinated and cooperative manner by government agencies and should be reviewed and adjusted, whenever necessary, to achieve the intended final objectives, subject to the provisions of § 1 and § 2 of art . 3rd.

§ 4 The actions referred to in this article may be implemented even through the clean development mechanism or other mechanisms under the United Nations Framework Convention on Climate Change, promulgated by Decree No. 2,652, of July 1, 1998.

Instruction required that the Term of Reference issued by Ibama should guide Environmental Impact Studies for the licensing of projects capable of emitting greenhouse gases and include measures to mitigate or compensate for such impacts (Costa et al., 2018b).

During the eventual implementation process, the ideal is that civil society's participation is encouraged to build legitimacy in promoting CCS activities and that this participation is deliberative. According to the International Energy Agency (IEA, 2016), legal and regulatory frameworks are essential to ensure that the geological storage of CO_2 is safe and effective and that the storage locations and accompanying risks are managed.

With this highlight, the need to follow up with the actions of actors interested in carrying out, monitoring, approving and regulating CCS activities in Brazil is emphasised to allow the manifestation of these technologies as soon as possible to mitigate climate change.

During geological storage, the pore spaces are filled with carbon dioxide gas while displacing the original gas for permanent trapping. The implementation of CCS requires infrastructure to transport and permanently store CO_2, which requires significant capital investment, especially for projects storing CO_2 in offshore storage reservoirs (TOWNSEND et al., 2020). The literature points out that storage at the international level has typically occurred in the following structures: (i) saline aquifers, (ii) depleted reservoirs, and (iii) fields still in production.

However, the choice of geological formations should be based on the absence of a significant risk of leakage or of significant environmental or health hazards (Art. 4 Directive 2009/31/EC). Fields still in production have questionable 'storage' capacity, and the CO_2 stream classified for this purpose is best referred to as 'use' (Carpenter; Koperna, 2014) for enhanced oil and gas recovery.

5. PROVISIONS FOR THE SANTOS BASIN

Studies based on literature review and data of the rock formations of the Santos Basin and criteria pointed out as desirable in a CO_2 reservoir compared to the available information of the rocks point out that storage in the depleted fields of this basin is geologically favourable (CIOTTA, 2019). The choice of these formations is made concomitantly with the mapping of areas and their situation as producers.

However, the feasibility of this storage implies the consideration of the legal issues involving the use of depleted fields for CO_2 storage and criteria recommended in international legislation. There are existing related Brazilian standards and their adequacy to concrete cases, considering possible legal consequences and application in fields located in potential sites, such as those of this nature in the Santos basin.

Depleted fields are oil or gas production fields that are at the end of their lives. They provide opportunities to reuse existing oil and gas infrastructure, repurposing it for CO_2 transport and storage, providing benefits such as reducing the cost of building transportation and storage infrastructure and potentially reducing permitting time (Townsend et al., 2020). Reusing infrastructure can also defer the costs and environmental impact of decommissioning, freeing up resources that can be invested in other value-creating activities. According to Townsend et al. (2020), worldwide decommissioning expenditures are projected to amount to $85 billion between 2019 and 2028, with the most significant component of costs associated with oil wells decommissioning. Thus, oil and gas wells may be suitable for CO_2 injection.

However, the same authors point out that the design standards and operational criteria for oil and gas production wells differ from CO_2 injection, meaning that remedial actions will be required to modify well equipment. Hence, operators need to weigh the additional repair work costs and any other risks associated with using existing wells against the time and cost of drilling a new well. Currently, well reuse is being considered for the Porthos project in Rotterdam (Townsend et al., 2020).

Based on the analogy concerning Oil and Gas production, valid for being the storage of gas (CH_4) admittedly more harmful to the environment (ABNT, 2007) than CO_2, the operation and buffering of storage facilities would follow the existing Brazilian rules, such as ANP Resolution 37/2001, CONAMA Resolution No. 23/1994, Federal Decree No. 8437 and MMA Ordinance 422/2011.

There are international criteria for characterization and assessment of potential areas and surrounding areas of storage complexes (Directive 2009/31/EC of the European Parliament and Council, 23/04/09, which consider three phases: 1. data collection; 2. construction of three-dimensional static geological model; 3. characterization of the dynamic storage behaviour, sensitivity characterization, risk assessment. This regulatory benchmark will serve as a basis for future CCS operations in depleted fields in the Santos Basin.

The choice of the Santos Basin as the base for a CCS project may be explained by the basin's proximity to the region with the highest greenhouse gas emissions in Brazil (Southeast Region), an area of significant economic development. This financial interest also results in greater availability of local companies to operate in this type of project, whose local CO_2 emissions can also be directed to local storage projects.

The Santos Basin fields are recent ventures, allowing for a storage project in depleted fields with long-term planning; however, with an important field that is approaching the desired stage (decommissioning phase), the Merluza Field. Ketzer et al. (2007) proposed that the Santos Basin has a total storage capacity of 167 $MtCO_2$ in oil fields. In 2016, Brazil committed to reducing greenhouse gas emissions by 37% below 2005 levels by 2025 (MMA, 2018, p. 03). In Brazil, in 2016, the exploration and use of oil, natural gas, or derivatives generated 296 million tonnes of CO_2 (SEEG, 2018), so the Santos basin could store more than half the sector's amount in annual emissions.

Geologically, the viability of the formations is, at first, intrinsically associated with the use of oil and gas depleted fields. Adapting previously available structures, e. g., depleted reservoirs and oil and gas pipelines to implement CO_2 storage, come with economic importance; it saves time and costs. According to Article 5, item II of the Federal Constitution, "no one will be forced to do or not to do something except by force of law". It is equivalent to saying that individuals have ample freedom to do whatever they want, provided it is not an act, behaviour, or activity prohibited by law. Strictly speaking, CCS activities are not prohibited by law; on the contrary, they fit the second-order as mitigation technologies, encouraged by the Brazilian National Policy on Climate Change (PNMC) Law No. 12.187/09).

However, as it is an activity with potential interference with the environment, it must respect rules provided for in this area, such as the National Environmental Policy (Federal Law No. 6.938/81), Federal Law No. 6.514/08, which includes violations and administrative penalties to the environment; Federal Law No. 9.605/98 (Environmental Crimes Law); Federal Law No. 9.966/00 (prohibits the discharge of hazardous or harmful substances in national waters (according to the classification of substances); Complementary Law No. 140/11, which provide for the distribution of licensing powers among the federative entities.

The carbon dioxide stream has not yet been classified as a hazardous substance in our legislation, however, if so classified, activities related thereto are subject to the collection of the Environmental Control and Inspection Fee - TCFA, whose taxable event is the regular exercise of the police power vested in the Brazilian Institute of the Environment and Renewable Natural Resources - IBAMA to control and inspect potentially polluting activities and users of natural resources (Federal Law no. 6.938/81), and, by the same law, it is understood as degradation of the environmental quality, the adverse change of the characteristics of the environment and as pollution that which harms the health, safety and welfare of the population, creates adverse conditions to social and economic activities, adversely affects the biota or affects the aesthetic or sanitary conditions of the environment, or, still, the release of materials or energy in disagreement with the established environmental standards, considering the polluter, the individual or legal entity, of public or private law, directly or indirectly responsible for an activity that causes environmental degradation.

Within the chain of activities, the individuals involved are liable, without prejudice, to the penalties defined by federal, state, and municipal legislation for failure to comply with the measures necessary to preserve or correct the inconveniences and damages caused by the degradation of the environmental quality. Regardless of fault, the polluter is obliged to indemnify or repair the damage caused to the environment and third parties affected by its activity (article 14, §1).

CO_2 currents in the offshore environment have not yet established environmental standards, and, as this occurs, they must be respected. And all damages eventually resulting from the activity must be repaired by our legislation, regardless of possession, ownership, or time of participation of the subjects in activities considered degrading or polluting to the environment.

Internationally, however, it has been adopted for CCS some standards for liability for damages caused to third parties, ranging from 15 to 60 years, in most jurisdictions, followed by certification proving the safety of the storage for subsequent transfer of responsibility to state entities (MUSARRA et al., 2019). At the current stage of the Brazilian regulatory framework, this possibility of transferring responsibilities is not yet a reality.

Since 2007, the international regulatory framework has evolved notably in Europe with the European CO_2 Storage Directive. The EC Storage Directive deals with monitoring to assess whether the injected CO_2 is behaving as expected, whether any migration or leakage occurs and whether this damages the environment or human health. OSPAR (named after the original Oslo and Paris conventions ("OS" for Oslo and "PAR" for Paris) focuses primarily on detecting and preventing leakage and emissions and, therefore, identifies several objectives for a monitoring program

The absence of standards is not a reason for the inertia of the activity operators since the Law of "Introduction to Brazilian Law" allows court decisions to be resolved based on analogy. Thus, considering the Brazilian normative concerning the exploration of Oil and Gas (normative attributions granted to the ANP - NATIONAL

AGENCY OF PETROLEUM, NATURAL GAS AND BIOFUELS by force of Law no. 9.478 of 1997), and more specifically, of storage of CH_4, already existing, we may conclude that, if provided for in exploration contracts as additives (and, knowing that depleted fields already have environmental impact studies, approved development plans and previous licensing), it is possible to carry out Simplified Licensing (Ministry of the Environment Ordinance 422/2011) for the specific requirements of the inspection agency. And, in the case of fields located in the Santos Basin, storage, as an offshore activity, would have the competence assigned to IBAMA (according to Supplementary Law 140/11), subjecting the activities to the resolutions of its Council (CONAMA).

Regarding the Underground Storage of Natural Gas (ESGN), the internal regulations state that there must be a Development Plan, which must include in the forecast of Underground Storage of Natural Gas (ESGN) aspects (ANP Resolution 17/2015) as a description of the Reservoirs and Storage Processes.

These parameters are associated with the criteria established in Directive 2009/31/EC of the European Union, especially regarding the risk assessment, which should include the following: characterization of the leakage potential of the storage complex, determined through dynamic modelling and security characterization described above.

Considering its location, capacity, concession regime, licensing, and environmental impact studies already carried out, depleted fields in the Santos Basin present conditions for the short-term storage of CO_2 in Brazil. The knowledge of national and international standards can help the eventual CCS operator meet the most relevant safety and other legal requirements for applying CCS technology according to local and national standards.

6. PROVISIONS FOR THE PARANÁ BASIN

As Pelissari (2021) pointed out, on the geological aspect, there are main geological formations that present potential for CO_2 storage in the basin. They include the coal, saline aquifer and sandstones of the Rio Bonito Formation and Itarare Group, black shales of the Irati and Ponta Grossa Formations, and the Sierra General Formation basalts. However, the associated risks must be foreseen and duly mitigated because, in addition to the national regulatory framework, there are specific adjustments regarding the state of Paraná. There are specific adjustments concerning the Paraná State that should be addressed.

In 2019 (Law 19878 - July 3, 2019), the state of Paraná issued a controversial law that prohibits the exploitation of shale gas by the hydraulic fracturing method. There is room for interference in possible activities in the subsoil of the state. In the sole paragraph of the first article it describes, the law says: In addition to the method in this article (shale gas), the ban extends to other types of soil exploration that may cause groundwater contamination and other environmental or health-damaging accidents. It may include carbon dioxide geological storage, making frameworks and institutional positions even more important.

Although the constitutionality of this Law has not been questioned, it is essential to emphasize the union's private competence to legislate over - deposits, mines, other mineral resources and metallurgy (article 22, XII of the CF). Still, it is important that the mineral resources, including those of the subsoil, are assets of the Union (article 20, item IX of the Federal Constitution), which allows, in principle, that decisions regarding CCS in the onshore environment are the responsibility of the Union. There may be questioning involving the judicial. However, the fact that competence to legislate about the environment can be claimed makes it competitive among all entities of the federation (including the states), making the measure of the state of Paraná valid regarding the impediment of underground activities.

In addition to the provisions of the Constitution, it is essential to go through the legislative and normative framework. It starts with the Civil Code, which prescribes a complete and exclusive property until proven otherwise (Art. 1,231). Also, art. 1,229, thus, says: the ownership of the soil covers that of the corresponding airspace and subsoil, in heights and depths, useful for the exercise, and the owner cannot oppose activities that are carried out, by third parties, at such a height or depth, that he has no legitimate interest to stop them.

However, according to art. 1,230 "The ownership of the soil does not cover deposits, mines and other mineral resources, hydraulic energy potentials, archaeological monuments and other assets constituted by special laws".

Therefore, when considering CCS activities as part of the concept of deposits, mines, resources or other assets, it can be understood that this property is not presumed, needs to be proven and does not necessarily fit as full.

Law no. 12,305, of August 2, 2010, institutes the National Solid Waste Policy. Because, when classifying a CCS activity as residual, there is the application of the principles, objectives and instruments of compliance with the Law, as well as the references related to integrated management and management, the responsibilities of generators and public authorities and the instruments applicable rules.

Suppose the CCS activity is conceived as dangerous. In that case, it is necessary to install and operate it; it can only be authorized or licensed by the competent authorities "if the responsible person proves, at least, technical and economic capacity, in addition to conditions to provide the care necessary for the management of this waste. " (art. 37).

Legal entities are required to prepare a hazardous waste management plan and submit it to the competent body of the National Environment System (SISNAMA).

However, the CCS activity is not seen as dangerous, as the leakage of carbon and causing the damage reported in session 3 is consistent with the intensification of the greenhouse effect.

Within the scope of Mining Law, there is Decree-Law no. 227/67, which defines the Union's competence "to manage mineral resources, the mineral production industry and the distribution, trade and consumption of mineral products".

If carbon storage is considered as mining; therefore, this activity is governed by this Code, and "the exploitation of the deposits depends on a permit for research authorization, by the Director-General of DNPM, and a mining concession, granted by the Minister of State for Mines and Energy. " (art. 7).

Therefore, when CCS activities are accepted within the mining profile, the matter is governed within that specific legislation. On the other hand, if it is seen as a complementary activity to the oil and gas sector, the Petroleum Law will be applied, viewing CCS as a form of advanced well recovery. Anyway, all these choices and profiles followed the environmental legislation, outlined in the National Environment Policy, as well as in the Resolutions of the National Environment Council (CONAMA), which are: Resolution no. 237/97, which deals with environmental licensing and Resolution no. 001/86, on environmental impact.

Ministry of Mines and Energy, National Agency of Petroleum, Natural Gas and Biofuels, jointly launched, in 2020, Resolution 817/2020, on decommissioning of oil and natural gas exploration and production facilities, the inclusion of land area under contract in the bidding process, the sale and reversal of assets, the fulfilment of remaining obligations, the return of the area and other measures related to decommissioning. In its annexes, it provides for specific requirements for decommissioning onshore (annexe III) and offshore (annexe IV), for both, it gives, in annexe V, that there must be basic environmental information;

a) owner of the area where the facilities to be decommissioned are located,

b) maps, data and georeferenced information of the areas where the facilities are to be decommissioned and their surroundings are located, including water bodies, protected areas, land use and the location of the production facilities to be decommissioned and

c) future use of the area where the facilities to be decommissioned is located.

Suppose the decommissioned regions are used for geological storage. In that case, the project for the future use of the area for this purpose must be provided for in the decommissioning plan for existing oil and natural gas exploration and production facilities.

7. CONCLUSIONS

Sustaining the recovery of ecosystems and economic growth are premises that should guide activities of production, circulation and distribution of goods and services, and the existence of standards gives a positive value to economic growth by sustaining the recovery of ecosystems.

And among actions that intend to meet the criteria of sustainable development for the recovery of ecosystems, maintaining economic growth and mitigating undesirable effects of anthropic origin in the environment, such as climate change and acidification of the oceans, are the activities of carbon capture, storage, and transport.

Again adopting a global plan around the decarbonization project gained momentum as part of the Paris Agreement in 2015. CCS (Carbon Capture and Storage) activities are among the options to achieve these goals (IPCC, 2019).

Verifying the feasibility of this type of undertaking requires analysis at different levels. This work was dedicated to deepening the regulatory and geological feasibility of applying CCS projects. The Santos Basin region is an economically favourable area for the adoption of this measure. The use of depleted fields is interesting for the prior availability of infrastructure and the lower environmental impact, lower costs and more excellent technical knowledge. To Paraná basin, the potential can guarantee the permanent carbon abatement, increased by BECCS harmful emissions. For both basins, legal and regulatory frameworks are critical to ensuring that geological CO_2 storage is safe and effective and that storage location and accompanying risks are responsibly managed.

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This book presents the latest studies of the CNPq Research Group (Estudos para Armazenamento Geológico de Carbono – CCS) of the Institute of Energy and Environment/Research Centre for Greenhouse Gas Innovation, at the University of Sao Paulo. The studies are related to the technical and regulatory issues for implementing Carbon, Capture and Storage (CCS) technologies, especially CO_2 geological storage in the Paraná and Santos Basins. The parent project, entitled "Carbon Geological Storage in Brazil: "Perspectives for CCS in unconventional petroleum reservoirs of onshore Paraná sedimentary basin and turbidites from offshore sedimentary basins in southeast Brazil", was funded by SHELL and FAPESP.

The book intends to provide an overview of the potential for secured long-term CO_2 storage in the Paraná and Santos basins with high prospects for CCS. The central academic findings refer to CO_2 reservoir properties and main criteria for site selection to improve the Brazilian CCUS development's decision-making process and contribute to the R&D plan for greenhouse gas emissions mitigation of the Southeastern Region, with geological evaluations and regulatory analyses.

The book aims to improve the decision-making process in greenhouse gases mitigation and energy/environmental governance; therefore, it captures the specialized and non-specialized audience.

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