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RUBENS COUTINHO TOLEDO

Technical analysis of Calcium Looping process applied to natural gas power plant

Guaratinguetá
2026

Rubens Coutinho Toledo

Technical analysis of Calcium Looping process applied to natural gas power plant

Thesis presented to the Faculty of Engineering and Sciences at the Guaratinguetá Campus, State University of São Paulo, for obtaining the title of Doctor in Engineering - Mechanical.

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POTENTIAL IMPACT OF THIS RESEARCH

This research aligns with SDG 7 (Clean and Affordable Energy) by supporting low-carbon power generation through calcium looping in natural gas plants. It contributes to SDG 9 (Industry, Innovation and Infrastructure) by advancing technological pathways for industrial decarbonization, and to SDG 13 (Climate Action) by enabling CO_2 emissions reduction and supporting climate mitigation strategies in Brazil.

IMPACTO POTENCIAL DESTA PESQUISA

Esta pesquisa está alinhada ao ODS 7 (Energia Limpa e Acessível) ao promover geração de energia de baixo carbono via looping de cálcio em usinas a gás natural. Contribui para o ODS 9 (Indústria, Inovação e Infraestrutura) ao avançar soluções tecnológicas para descarbonização industrial, e para o ODS 13 (Ação contra a Mudança do Clima) ao viabilizar a redução de emissões de CO_2 e apoiar estratégias de mitigação no Brasil.

RUBENS COUTINHO TOLEDO

Technical analysis of Calcium Looping process applied to natural gas power plant.

Tese apresentada à Universidade Estadual Paulista (UNESP), Faculdade de Engenharia e Ciências de Guaratinguetá, para obtenção do título de Doutor em Engenharia.

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To the boy who one day dreamed of being a scientist and my dear wife.

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ABSTRACT

The global effort to mitigate greenhouse gas emissions has intensified the development of carbon capture technologies compatible with low-carbon energy systems. In this context, the growing role of natural gas–fired (NG) power plants in the Brazilian energy matrix poses specific challenges for carbon capture due to the low concentration of carbon dioxide (CO_2) in their flue gases. Calcium looping (CaL) emerges as a promising alternative; however, no experimental studies addressing Brazilian limestone under NG combustion conditions have been reported to date. This thesis aims to develop a technical assessment of the CaL process applied to natural gas power plants using a Brazilian dolomite as a CaO-based sorbent. The study investigates whether laboratory-scale experimental approaches can establish operational criteria and demonstrate the technical feasibility of CaL under low CO_2 concentration conditions. N_2 adsorption porosimetry was employed to correlate sorbent pore structure with process performance. An integrated methodology combining thermogravimetric analysis (TGA) and a bench-scale Dual Interconnected Fluidized Bed (DIFB) reactor was adopted. A Rotatable Central Composite Design (RCCD) method was used to optimize and evaluate key experimental parameters in both TGA and DIFB systems. The results demonstrate that Brazilian dolomite exhibits promising carbon capture performance under low CO_2 partial pressures, provided that appropriate operational windows are applied. Pore structure analysis revealed a critical pore size range between 30 and 100 Å, governing both initial capture efficiency and cyclic degradation. TGA experiments showed that most of the fast carbonation occurs within the first 2.5 min, whereas longer carbonation times are dominated by diffusion-controlled regimes. Carbonation temperature was identified as the dominant operational parameter, with optimal conditions at 580 °C for 7.5 min and 550 °C for 10 min, yielding IEC$10, c$ values of 1.34 and 1.20, respectively. In the DIFB system, increased elutriation and thermal degradation resulted in lower capture efficiencies, with maximum values on the order of 0.0177 kg CO_2/kg $CaCO_3$, indicating that scale-up introduces additional degradation mechanisms not observed in fixed-bed systems. The originality of this thesis lies in the integrated experimental evaluation of CaL under conditions representative of NG combustion using a Brazilian dolomite, a context that remains scarcely addressed in the literature. The combined use of pore structure analysis, TGA, and DIFB provides novel insights into the relationship between sorbent microstructure, operational conditions, and performance degradation, demonstrating that the limitations observed in fluidized bed systems are primarily associated with intrinsic sorbent properties rather than low CO_2 concentration. These findings constitute a key contribution of this thesis, as they demonstrate that performance limitations in fluidized bed systems are mainly related to intrinsic sorbent properties rather than low CO_2 concentration, while providing a comprehensive analysis of parameter impacts on carbon capture performance and a realistic basis for future studies in pilot-scale reactors and sorbent development.

KEYWORDS: Calcium looping; Natural gas; Dolomite; CO_2 capture; Thermogravimetry;

Fluidized bed; Pore blockage.

RESUMO

O esforço global para a mitigação das emissões de gases de efeito estufa tem impulsionado o desenvolvimento de tecnologias de captura de carbono compatíveis com sistemas energéticos de baixo carbono. Nesse contexto, a crescente participação das usinas termelétricas a GN na matriz energética brasileira impõe desafios específicos à captura de carbono, em razão da baixa concentração de dióxido de carbono (CO_2) nos gases de exaustão. O CaL surge como uma alternativa promissora; entretanto, ainda não há estudos experimentais que abordem o uso de calcários brasileiros sob condições de combustão de GN. Esta tese tem como objetivo desenvolver uma análise técnica do processo CaL aplicado a usinas a gás natural, utilizando uma dolomita brasileira como sorvente à base de CaO. O estudo investiga se abordagens experimentais em escala de laboratório são capazes de estabelecer critérios operacionais e demonstrar a viabilidade técnica do CaL sob condições de baixa concentração de CO_2. A porosimetria por adsorção de N_2 foi empregada para correlacionar a estrutura dos poros do sorvente com o desempenho do processo. Adotou-se uma metodologia integrada combinando análises de TGA e um DIFB em escala de bancada. O método de RCCD foi utilizado para otimizar e avaliar os principais parâmetros experimentais tanto nos ensaios de TGA quanto no sistema DIFB. Os resultados demonstram que a dolomita brasileira apresenta desempenho promissor na captura de carbono sob baixas pressões parciais de CO_2, desde que adotadas condições operacionais adequadas. A análise da estrutura dos pores revelou uma faixa crítica de tamanho de poros entre 30,0 e 100,0 Å, a qual governa tanto a eficiência inicial de captura quanto a degradação cíclica do sorvente. Os experimentos em TGA indicaram que a maior parte da carbonatação rápida ocorre nos primeiros 2,5 min, enquanto tempos de carbonatação mais longos são dominados por regimes controlados por difusão. A temperatura de carbonatação foi identificada como o principal parâmetro operacional, com condições ótimas em 580 °C por 7,5 min e 550 °C por 10,0 min, resultando em valores de IEC$10, c$ de 1,34 e 1,20, respectivamente. No sistema DIFB, o aumento da elutriação e da degradação térmica resultou em menores eficiências de captura, com valores máximos da ordem de 0,0177 kg CO_2/kg $CaCO_3$, indicando que a ampliação de escala introduz mecanismos adicionais de degradação não observados em sistemas de leito fixo. A originalidade desta tese reside na avaliação experimental integrada do CaL sob condições representativas da combustão de GN, utilizando uma dolomita brasileira, um contexto ainda pouco explorado na literatura. O uso combinado da análise da estrutura porosa, TGA e DIFB fornece novos insights sobre a relação entre a microestrutura do sorvente, as condições operacionais e a degradação de desempenho, demonstrando que as limitações observadas em sistemas de leito fluidizado estão principalmente associadas às propriedades intrínsecas do sorvente, e não à baixa concentração de CO_2. Esses resultados constituem uma contribuição relevante desta tese, ao evidenciar que as limitações de desempenho em sistemas de leito fluidizado estão majoritariamente relacionadas às propriedades intrínsecas do sorvente, além de fornecer uma análise abrangente do impacto

dos parâmetros operacionais na captura de carbono e uma base realista para estudos futuros em reatores em escala piloto e no desenvolvimento de novos sorventes.

PALAVRAS-CHAVES: Calcium looping; Gás Natural; Dolomita; Captura de CO_2; Termogravimetria; Leito fluidizado; Bloqueio de poros.

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1 INTRODUCTION

1.1 PROBLEM DESCRIPTION AND JUSTIFICATION

Greenhouse gas (GHG) emissions constitute a central challenge for contemporary society, as climate change increasingly affects daily life through alterations in land use, lifestyle transformations, and evolving patterns of consumption and production across regions and among individuals (FILONCHYK *et al.*, 2024; SHAH *et al.*, 2024; LEE; ROMERO, 2023).

The increase in GHG emissions into the atmosphere causes an increase in the average temperature of the oceans, causing changes in the amount and periods of rain, an increase in periods of drought, a decrease in glaciers, the incidence of storms and rising ocean levels with devastating consequences for biomes and living beings (ALFONSO; GESTO; SADOUL, 2021; ISIAKA; NDUKWE; CHIBUIKE, 2021; MUGWANYA *et al.*, 2022; STRAUSS *et al.*, 2021). Also, temperature increases affect various aspects of crop growth, such as flowering, fruiting, fruit size, quality, and ripening, ultimately leading to reduced productivity and lower costs (SHAH *et al.*, 2024). Furthermore, the variation in the concentrations of certain gases that make up GHGs is the main factor attributed to the increase in temperature, with anthropogenic CO_2 considered the main responsible for global warming (FILONCHYK *et al.*, 2024; MOKHOV, 2022; STIPS *et al.*, 2016).

The escalation in global energy consumption and the associated rise in carbon dioxide (CO_2) emissions to the atmosphere have prompted the scientific community to develop and implement technological strategies aimed at mitigating the contribution of CO_2 to climate change. In this context, substantial investments have been directed toward projects focused on improving energy efficiency, expanding the deployment of renewable energy sources, and advancing low-carbon technologies (ARCE *et al.*, 2017; COSENSE4CLIMATE PROJECT, 2024; CLEVER PROJECT, 2024; CLEANKER, 2017; NATURAL RESOURCES CANADA, 2022; SOCRATCES, 2018). Concurrently, the reduction of anthropogenic CO_2 emissions is recognized as a key measure to attenuate the adverse impacts of climate change (LEE; ROMERO, 2023; MIKHAYLOV *et al.*, 2020).

The energy and industrial sectors are the largest contributors to global greenhouse gas emissions, accounting for approximately 34% and 24% of total emissions, respectively (LAMB *et al.*, 2021). Although policies targeting the phase-out of fossil fuels have intensified, future scenarios such as the Net Zero 2050 pathway still project that about 15% of total primary energy supply will be derived from oil and approximately 5% from coal and natural gas (INTERNATIONAL ENERGY AGENCY (IEA), 2023). Currently, fossil fuels remain the dominant energy sources, supplying around 80–85% of global energy demand. This predominance is associated with several advantages, including abundant reserves, high energy density, operational flexibility, ease of storage, extensive existing infrastructure and relatively low cost (INTERNATIONAL

ENERGY AGENCY (IEA), 2023).

International projections indicate that, during the initial stages of the transition toward a predominantly renewable energy matrix, the use of non-renewable energy sources will temporarily increase to support and enable the structural changes required for this transition, before a sustained decline in their consumption is realized (INTERNATIONAL ENERGY AGENCY (IEA), 2023). National statistics for Brazil show that, in 2024, oil and oil derivatives accounted for 40.7% of the total primary energy supply in the domestic energy mix, while natural gas contributed 7.5%, representing increases of 7.6 and 1.2 percentage points, respectively, compared with the 2023 report (EPE, 2024).

In 2024, Brazil's natural gas consumption was substantial, reaching 77 million m^3/day; of this volume, 36.5% was consumed by the industrial sector and 18.3% by the energy sector (EPE, 2024). In the context of the continued exploration and development of Brazil's "pré-sal" offshore reserves, public policies have been oriented toward expanding natural gas utilization across multiple sectors, with a particular emphasis on industry. Projections indicate that industrial natural gas demand alone could increase to 80 million m^3/day by 2040 (BRAZILIAN DEVELOPMENT BANK (BNDES), 2021).

The Calcium Looping (CaL) process consists of a reversible carbonation-calcination reaction of a CaO-based sorbent (DIEGO; ARIAS, 2020a), mostly using limestone even though many CaO-based substitutes have been researched as replacement to natural limestone (ANTZARA *et al.*, 2018; CHAI *et al.*, 2022; DONG *et al.*, 2020; LI; WANG; LI, 2022). Limestone is an abundant low-cost material suitable for an economically viable process, being natural limestone largely utilized (ANTZARA *et al.*, 2018; BLAMEY *et al.*, 2016; ZHANG *et al.*, 2016).

The main advantages of this CO_2 capture technology, relative to alternative approaches, include its suitability as a short- to medium-term mitigation option due to its compatibility with retrofitting in existing plants; the use of low-cost, naturally occurring sorbents that are abundantly available (e.g., calcitic and dolomitic limestones); the relatively minor efficiency penalty imposed on the combustion process; the possibility of exploiting commercially mature fluidized bed technologies; and its applicability to CO_2 capture in both pre-combustion and post-combustion configurations (CHAMPAGNE *et al.*, 2016; DEAN *et al.*, 2011; VALVERDE; SANCHEZ-JIMENEZ; PÉREZ-MAQUEDA, 2015).

For CaL systems applied to natural gas-fired power plants, the techno-economic feasibility is still under active investigation. Most modeling studies consider several process configurations in which CaL could serve as a substitute for coal-based systems. Previous study (SCHAKEL *et al.*, 2018) reported improved performance in natural gas applications, mainly attributable to the lower sulfur content of the fuel, which decreases sorbent purge requirements. Other study (PILLAI *et al.*, 2022) observed that Natural Gas Combined Cycle (NGCC) plants integrated with CaL can be further enhanced by coupling with renewable energy sources, although economic concerns related to natural gas price volatility remain (MOORE; CRISTINA; KULAY, 2019). Numerous studies have sought to achieve NGCC–CaL efficiencies comparable to those of coal-fired plants;

however, they frequently lack a detailed characterization of the carbonator gas atmosphere and, in some cases, adopt flue gas parameters derived from coal combustion instead of those specific to natural gas. (HU; AHN, 2017) suggested that regenerating the calciner outlet stream to increase CO_2 concentration could reduce the thermal energy demand of the process.

From the limited number of experimental studies available (SYMONDS *et al.*, 2016), a natural gas combustor was employed to supply CO_2 (8.59 vol.% wet) to the carbonator. However, the primary objective of that work was the comparison between synthetic pellets and natural limestone, rather than the investigation of the effects of low CO_2 concentrations. In another study (HAAF *et al.*, 2020a), Solid Recovered Fuel (SRF) was tested in the calciner, while lignite and natural gas–derived flue gases were used in the carbonator. A CO_2 concentration of 9.5 vol.% in the flue gas was reported, with no observable adverse impact on CO_2 capture efficiency. Additional experiments were performed at different pressures using simulated coal and natural gas flue gases in a TGA system, with a CO_2 concentration of 16.7 vol.% wet during carbonation cycles (DUHOUX *et al.*, 2020). Although natural gas was considered in these studies, the specific influence of low CO_2 concentrations on the CaL process was not systematically examined. In practical applications, natural gas flue gases typically exhibit substantially lower CO_2 concentrations (approximately 4.0 vol.% wet), which may significantly affect CaL performance.

Fluidized bed reactors are widely employed for gas–solid reactions owing to the excellent gas–solid contact within the bed, the efficient heat and mass transfer between gas and particles, and the high heat transfer coefficients at the bed walls and internal surfaces (WERTHER, 2000). Calcium-looping processes are particularly noteworthy because they are associated with superior sorbent conversion performance (HAAF *et al.*, 2020b; TREGAMBI *et al.*, 2018). At the industrial scale, numerous studies have implemented experimental configurations consisting of two independent reactors (ALONSO *et al.*, 2018; ARIAS *et al.*, 2018; DIEGO; ARIAS, 2020a; HAAF *et al.*, 2020b; HILZ *et al.*, 2018; HILZ *et al.*, 2019). Furthermore, several studies have sought to improve the techno-economic feasibility of calcium looping through the integration of solar energy (TREGAMBI *et al.*, 2018), the development of CaO-based laboratory-fabricated pellets with enhanced properties (MA *et al.*, 2021), the design of high-capacity carbonators (DIEGO; ARIAS, 2020a), and the application of indirect heating strategies (HOFMANN *et al.*, 2024).

One of the most critical milestones in the advancement of calcium looping (CaL) technology is the demonstration and optimization of the process at industrial scale (ERANS; MANOVIC; ANTHONY, 2016; DIETER *et al.*, 2014; HOFMANN *et al.*, 2024). Although the technology can be implemented in various process configurations, it remains unclear which specific configuration is best suited for a given application, industrial sector, or scale of operation (TAN *et al.*, 2024; PAPALAS *et al.*, 2024). Furthermore, sorbent materials still do not exhibit sufficiently robust performance, primarily due to their progressive deactivation over multiple carbonation–calcination cycles (HOFMANN *et al.*, 2024; PEREJÓN *et al.*, 2024). In this context, the design and con-

struction of fluidized bed reactors equipped with advanced particle classification systems should be prioritized in laboratories working on CaL processes, in order to accurately characterize and demonstrate the complete decay behavior of CO_2 sorbents under conditions representative of industrial-scale CaL operation (JAYARATHNA *et al.*, 2019).

In this context, the present study is motivated by the need to mitigate the environmental impacts associated with climate change through research on carbon capture and storage (CCS) technologies, as recognized by the Intergovernmental Panel on Climate Change (IPCC), thereby providing a potential pathway for reducing CO_2 emissions. Accordingly, the central research question guiding this work is: *How can laboratory-scale experimental investigations support the establishment of operational criteria and demonstrate the technical feasibility of the calcium looping process, employing Brazilian dolomite as a sorbent, for carbon dioxide capture under conditions representative of natural gas–fired power plants?*

1.2 OBJECTIVES

The general objective of this thesis is to conduct a comprehensive technical assessment of the calcium looping (CaL) process, employing a domestically sourced dolomite, through experimental investigations based on thermogravimetric analysis (TGA) and a laboratory-scale fluidized bed reactor, specifically a Dual Interconnected Fluidized Bed (DIFB) system. The aim is to define suitable operating criteria and evaluate the feasibility of CO_2 capture under conditions representative of a natural gas-fired power plant.

To achieve that, these objectives will follow:

1. To characterize the nationally sourced dolomite used as a CO_2 sorbent in the CaL process and to assess the effects of CO_2 concentration in the reaction atmosphere and bed compaction on the thermodynamic and kinetic behavior of the calcination and carbonation stages, as well as to evaluate pore structure blockage and sorbent deactivation during carbonation.

2. To study the CaL process via thermogravimetric analysis, employing a rotatable central composite design to identify key response variables, optimize operating conditions, and evaluate sorbent behavior over multiple calcination–carbonation cycles;

3. To compare the behavior of the CaL process in TGA and in a downer-interconnected fluidized bed reactor, identifying performance differences associated with distinct reaction dynamics, sorbent degradation mechanisms, and the representativeness of each experimental system.

5 CONCLUSION

A Brazilian dolomite was evaluated in both TGA and DIFB systems under a simulated natural gas exhaust atmosphere, with particular emphasis on its overall performance, technological feasibility, and the influence of gas velocity and temperature on process behavior. The TGA results indicated that optimization of the CaL process using this dolomite in low CO_2-concentration flue gas—characteristic of natural gas-fired thermoelectric power plants—exhibits substantial potential for efficient CO_2 capture within Brazil's power generation mix. Nonetheless, the findings strongly indicate the need for further investigations in fluidized bed reactors to evaluate the sorbent's performance at a larger and more industrially representative scale. Such studies would enable a more accurate assessment of energy consumption, sorbent elutriation, and sintering phenomena, all of which can critically affect the long-term cyclic stability and overall effectiveness of the capture process.

The fluidized bed investigation was carried out in a reference laboratory in Naples, Italy, to evaluate the performance of the sorbent. During testing in the DIFB configuration, the dolomite exhibited an unexpectedly high degree of elutriation even at relatively low gas velocities, which directly impaired the CO_2 capture performance, yielding a maximum value on the order of 0.0177 kg CO_2/kg $CaCO_3$ under the most favorable operating conditions. Consistent with previous studies, the scale-up of the system introduced additional challenges for the sorbent, indicating that this material may not be suitable for conventional CaL configurations, particularly for the specific calciner design employed in this work.

Although several limitations were identified in this study regarding performance under large-scale operating conditions, these constraints are attributable exclusively to the sorbent employed. When assessing the overall behavior, the tests conducted under a simulated natural-gas-derived flue gas were consistent with expectations for a typical CaL process, exhibiting only a slightly reduced, if any, CO_2 capture efficiency.

All key phenomena reported in previous CaL investigations were also observed in this work, including: a successful and reversible carbonation–calcination cycling; a decline in capture efficiency over repeated cycles, following the characteristic deactivation profile; and the occurrence of sorbent elutriation.

From this perspective, it is possible to conclude that:

1. Initial material characterization revealed an elevated SiO_2 content, a feature not commonly reported in existing literature. Particle size exerted a measurable influence on the calcination behavior, with smaller particles lowering the temperature required to achieve complete calcination. The CO_2 concentration affected both calcination and carbonation reactions, indicating that the gaseous atmosphere is a critical parameter in the kinetic and mechanistic analysis of these processes.

BJH analysis indicated a unimodal pore size distribution in the range of 17–150 Å, with the lower bound of the pore size notably smaller than those reported in other studies, which typically describe larger minimum pore diameters. As carbonation proceeded, progressive pore closure was observed: initially, a relatively uniform reduction in pore volume occurred across the entire diameter range up to approximately 10 min, followed by preferential closure of pores in the 30–100 Å interval. This led to a shift of the distribution toward smaller pores, with larger pores being more readily occluded.

When characterization data are compared across different experimental scales, the results suggest that sorbent performance and behavior can be predicted on the basis of chemical composition, crystalline structure, and pore size distribution. Although additional experimental validation is required to robustly confirm this hypothesis, the capacity to forecast sorbent behavior and performance constitutes a promising strategy for reducing development costs in carbon capture technologies.

2. Carbonation temperature is identified as the most critical parameter governing the process. When comparing temperature and carbonation time based on TGA experiments, it is observed that, even after accounting for the energy consumption during the process, temperature remains the dominant factor influencing carbon capture efficiency, as higher temperatures yield superior energy performance under the investigated conditions.

   From the RCCD design, the optimal operating conditions were determined to be 580 °C for 7.5 min (IEC = 0.89), 550 °C for 10 min (IEC = 1.01), and 475 °C for both 11 min (IEC = 0.83) and 7.5 min (IEC = 0.88). Among these, less surface damage was observed at 475 °C compared with 580 °C and 550 °C. Nevertheless, in multi-cycle tests, superior performance was obtained at 580 °C for 7.5 min and 550 °C for 10 min, with $\mathrm{IEC}_{10,c}$ values of 1.34 and 1.20, respectively, corresponding to an improvement of approximately 40

   Within this framework, the best overall performance was achieved at 580 °C for 7.5 min, which exhibited a lower E_{sp} (33.48 kJ) and a CO_2cap value comparable to that obtained at 550 °C. However, for scale-up purposes, the condition of 550 °C for 10 min appears more suitable, as it provided robust performance (E_{sp} = 37.97 kJ and CO_2cap = 9.80 mg) without any observable signs of sintering on the sorbent surface. This latter aspect is particularly relevant for enhancing process feasibility in a fluidized bed system.

3. In the analysis of the interaction between temperature and fluidization velocity, temperature appears to exert a predominant influence, largely independent of the fluidization velocity. According to the RCDD results, the optimal operating window corresponds to the highest attainable carbonation temperature that does not yet trigger the onset of calcination. The saddle-shaped response surface obtained from the RCCD further indicates that additional

factors may be affecting the system response, thereby underscoring the necessity for a more comprehensive exploration of the parameter space.

The observed lack of fit is attributed to the abrupt transition between the carbonation and calcination regimes, a phenomenon that cannot be adequately represented by a second-order polynomial model. Nevertheless, within the investigated domain that excludes the transition to calcination (570 °C < T < 675 °C and 0.23 m/s < v < 0.78 m/s), the model exhibits good agreement with the experimental observations. For example, it yields values of 0.009240 (experimental) and 0.010778 (predicted) for ξ_{mean}.

4. TGA experiments indicate that the capture capacity declines sharply within the first 2.5 min of carbonation, confirming that the majority of the fast reaction occurs at the early stages; this observation is further corroborated by DIFB tests. Contrary to the expectation that no fast reaction phase should remain after 7 min, samples carbonated for up to 15 min still exhibit signatures of it, possibly due to thermal shock effects associated with rapid transfer between the VTR and ambient conditions. In contrast, longer carbonation times are characterized by extended diffusion-controlled phases and a concomitant reduction in overall performance.

   Pore-structure deformation analysis demonstrates that the fast carbonation phase terminates between 5 and 7.5 min, and its duration is directly proportional to the initial pore volume in the 30–100 Å range. The loss of efficiency is primarily attributed to the closure of these pores, as additional pore blockage at later stages exerts only a minor influence on CO_2 capture.

   The evaluation of the Beta probability density function (PDF) parameters, α and β, suggests a two-step pore closure mechanism. The presence of SiO_2 appears to adversely affect the pore structure by decreasing the total pore volume and constraining the formation or preservation of smaller pores. Overall, these findings indicate that factors beyond the sorbent pore size distribution and SiO_2 content influence the resistance to performance decay and therefore warrant further investigation.

5. Residence time has a substantial impact on the overall energy consumption where 3.5 min per cycle had and increase of 8% of total energy spent during the 475 °C multi-cycle tests, underscoring the importance of identifying an optimal balance to maximize net carbon capture efficiency;

6. At smaller scales, the variability in chemical composition and particle size associated with the selected Brazilian dolomite was critically important, as it posed challenges to experimental reproducibility. Tests employing this dolomite should preferably be conducted within narrow particle size fractions and with larger sample masses. Although DIFB tests were performed using both a restricted particle size range and an increased

sample mass, the variability in the results remained high, underscoring the necessity of conducting replicate experiments when using this material.

7. The DIFB system was not able to retain the entirety of the fine particles using the current experimental methodology. The requirement to employ two filters per experiment proved to be labor-intensive, thereby underscoring the need for the development of a more efficient and robust solution. Elevated temperatures (> 475 °C) exerted a pronounced influence on the surface degradation of the dolomite, whereas the influence of residence time was comparatively negligible. In accordance with the impact test design, the optimal operating window for minimizing elutriation lies between 580 °C and 680 °C at fluidization velocities exceeding 0.55 m/s.

8. The deactivation curves obtained in DIFB exhibit a performance trend characteristic of limestone, which may be partially attributable to temperature-induced degradation. Most samples reached their deactivated state by the fifth cycle, a behavior that is not typically observed for dolomite. In contrast, TGA measurements did not attain a clear deactivation point even after ten cycles, thereby supporting the hypothesis that temperature degradation plays a significant role in the observed behavior. Moreover, the deactivation curves measured in the TGA do not indicate any interaction between partial carbonation and variations in deactivation performance when compared with data reported in the literature, as all tested conditions followed the expected decay-curve profile. Nevertheless, a more detailed investigation directly comparing complete and partial carbonation is required to rigorously validate this hypothesis.

5.1 FUTURE WORKS

Although the feasibility of operating the calciner at lower temperatures was confirmed and the life cycle assessment yielded promising results, the investigated dolomite exhibited a significantly high elutriation rate during the experimental tests. The main working hypothesis attributes this behavior to the silica content, which may induce increased brittleness in the sorbent structure rather than the reinforcing effect typically associated with magnesium. Further phase characterization, particularly by X-ray diffraction, is required to clarify the role of silica within the crystalline structure. In addition, when the pore size distribution of this Brazilian dolomite is compared with those of other dolomites reported in the literature, it exhibits an excessively broad distribution, without a pronounced peak and outside the pore size range considered most effective for carbon capture. In this context, the evaluation of alternative sorbent materials emerges as a relevant and necessary step toward mitigating elutriation-related limitations.

A logical next step of this analysis would be the mapping of limestone mines in Brazil and their spatial proximity to natural gas power plants. Building on the findings of this work, the geological formations could be analyzed to identify and select the most promising limestone

sources based on their likely chemical and mineralogical composition. Subsequent characterization analyses should then be performed to establish a ranking of limestone candidates for calcium looping applications in Brazil. Further studies should also incorporate life cycle assessments considering transport distances to existing power plants, as well as an evaluation of the technical and economic feasibility of implementing a pilot-scale calcium looping facility in Brazil.

Brazil has shown increasing interest in supplying its energy matrix to data processing activities, which is expected to significantly raise electricity demand. At the same time, climate-change-driven variability in rainfall regimes poses challenges to the reliability of hydropower generation, thereby increasing the reliance on natural gas power plants. This trend reinforces the urgency of advancing research on carbon capture technologies to non-renewable energy sores such as power plants. As a carbon capture–based approach, it is imperative to rigorously assess the emission efficiency of the process. In this thesis, such evaluation was achievable only at lab scale; therefore, further investigation using larger scales, such as DIFB systems, is essential and should be pursued.

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APPENDIX D – CURRICULUM

Identification	
	Rubens Coutinho Toledo 25/06/1994
Nationality	Brazilian
Name for citations	Toledo, Rubens Coutinho; Toledo, R. C.
Lattes CV	https://lattes.cnpq.br/6754257943749374
ORCID	https://orcid.org/0000-0002-9682-3102
Other identifier	-
Academic Background	
2019–2021	Postgraduate program in mechanical engineer, Thermal and fluids science – EESC/USP
2012–2018	Bachelor's degree Mechanical Engineer – Federal University of Mato Grosso
Bibliographic Production	
TOLEDO, R. C.; ARCE, G. L.; CARVALHO JR., J. A.; ÁVILA, I. Experimental development of calcium looping carbon capture processes: an overview of opportunities and challenges. Energies, Basel, v. 16, n. 9, p. 3623, 2023. DOI: 10.3390/en16093623. TOLEDO, R. C.; MORAES, C. L. de; THANGARASU, V.; CARVALHO JR., J. A. de; ÁVILA, I. Efficiency and energy consumption of partial carbonation process for CO_2 capture from natural gas combustion. Energies, Basel, v. 18, n. 9, p. 2285, 2025. DOI: 10.3390/en18092285.	
Scientific Events	
VI Workshop da Pós-Graduação em Engenharia. Calcium looping em leitos fluidizados: Identificando as principais publicações. 2022. (Simpósio).	