

Evaluation And Identification of Promising CO₂ Photocapture Materials

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Abstract

Anthropogenic CO₂ emissions must be curtailed rapidly, yet prevailing CO₂ capture technologies remain energy-intensive because regeneration relies on large temperature swings powered by heat or electricity. In direct air capture, dilute ambient CO₂ makes regeneration the dominant driver of energy use and cost. Light and electro-assisted desorption could reduce these penalties, but molecular mechanisms are rarely linked to reactor performance. This thesis establishes a materials-to-device framework for photo-assisted CO₂ capture by integrating density functional theory (DFT), fixed-bed breakthrough experiments, and machine-learning (ML) surrogates. DFT calculations map CO₂ adsorption geometries and energies on low-index facets of transition metals under controlled excess surface charge densities as a proxy for photoexcited carriers. Adsorption strength and configuration are strongly charge and composition-dependent, showing that pristine descriptors, such as the d-band center, can be insufficient. Instead, interfacial charge redistribution coupled with structural relaxation yields a photoswitch-like response in which different charge states preferentially stabilize either adsorbed or desorbed configurations. Guided by these insights, a photo-assisted breakthrough reactor was developed, calibrated, and validated using PEI-impregnated silica, with adsorption near ambient conditions and desorption at ~ 110 °C. The platform integrates controlled CO₂/N₂ delivery, thermocouples, quantified LED irradiance, and optional DC biasing. Indirect illumination via a solar-selective lid resulted in more uniform heating and faster desorption compared to direct in-bed lighting, which introduced thermal gradients and accelerated sorbent degradation. The reactor was then used to study open-cell Cu, Al, and Ni foams as conductive model substrates; on a geometric-area basis, illuminated foams reached ~ 0.3 - 1.1 mmol m⁻² per cycle while exhibiting modest gravimetric uptakes ($\sim 10^{-2}$ mmol g⁻¹), with Ni highest on a mass basis. Illumination and applied voltage produced modest but reproducible desorption enhancements, including under isothermal 25 °C/25 °C conditions with $\pm$ DC bias, supporting a role for surface-charge modulation beyond bulk heating. ML models trained on the curated, site-resolved DFT dataset achieved strong accuracy ($R^2 > 0.8$ under alloy-grouped validation), enabling scalable prioritization of alloy-facet-site candidates for screening. Overall, the results motivate hybrid designs that utilize electrically conductive foams to enable the photothermal and electroresponsive regeneration of high-capacity chemisorptive overlayers for photo-assisted CO₂ capture.

I would like to dedicate this thesis to my loving parents ...

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Nomenclature

Acronyms / Abbreviations

AE	All-Electron
ASU	Air Separation Unit
CCS	Carbon Capture and Sequestration
CCUS	Carbon Capture Utilization and Sequestration
COP	Conference of Parties
CP	Critical Point
DAC	Direct Air Capture
DFT	Density Functional Theory
DIET	Desorption Induced by Electronic Transitions
DOS	Density of States
EDX	Energy-Dispersive X-ray Spectroscopy
EOR	Enhanced Oil Recovery
ESM	Effective Screening Medium
GB	Gradient Boost
GGA	Generalized Gradient Approximation
GHG	Greenhouse Gas
GMST	Global Mean Surface Temperature
GPR	Gaussian Process Regression
HFCs	HydroFluoroCarbons
IGCC	Integrated Gasification Combined Cycle

IPCC	Intergovernmental Panel on Climate Change
IR	Infrared Rays
KP	Kyoto Protocol
KS	Kohn-Sham
LAPW	Linear Augmented Plane-Wave
LDA	Local Density Approximation
LED	Light Emitting Diode
LISA	Light Induced Swing Adsorption
LMBTR	Local Many-Body Tensor Representation
LSPR	Localized Surface Plasmon Resonances
MAE	Mean Absolute Error
MBTR	Many-Body Tensor Representation
MEA	Monoethanolamine
MGR	Menzel-Gomer-Redhead
MI	Mutual Information
ML	Machine Learning
MOF	Metal Organic Framework
MP	Montreal Protocol
MS	Mass Spectrometer
MTZ	Mass Transfer Zone
NDCs	Nationally Determined Contributions
NDIR	Non-Dispersive Infrared
NETL	National Energy Technology Laboratory
PAW	Projector Augmented Wave

PCA	Principal Component Analysis
PDOS	Projected Density of States
PEI	Poly-ethyleneimine
PES	Potential Energy Surface
PFCs	PerFluoroCarbons
PP	PseudoPotentials
PSA	Pressure Swing Adsorption
PSD	Photon-Stimulated Desorption
QATIM	Quantum Theory of Atoms in Molecules
QE	Quantum ESPRESSO
RBF	Radial Basis Function
RF	Random Forest
RMSE	Root Mean Square Error
SEM	Scanning Electron Microscopy
SOAP	Smooth Overlay of Atomic Positions
SRM	Solar Radiation Management
STM	Scanning Tunneling Microscope
STP	Standard Temperature and Pressure
TabPFN	Tabular Prior-data Fitted Network
TCD	Thermal Conductivity Detector
TP	Triple Point
TSA	Temperature Swing Adsorption
UNFCCC	United Nations Framework Convention on Climate Change
UV	Ultra-Violet

VASP Vienna Ab initio Simulation Package

VNL Virtual Nano Lab

XRD X-Ray Diffraction

1. Introduction

1.1 Energy and climate constraints on sustainable growth

There is ongoing academic discussion regarding the potential for sustained economic expansion, with specific attention given to elements that could impede growth or precipitate economic decline. Two primary concerns are the limited availability of fossil fuels as a source of energy and the restricted capacity of the natural environment to assimilate the carbon dioxide (CO₂) emitted from their combustion. To illustrate these concerns, let us posit a situation where fossil fuels are the exclusive energy source. If fossil-fuel resources were abundant and elevated atmospheric CO₂ concentrations caused no detrimental climatic effects, then continued reliance on fossil fuels would pose no immediate barrier to sustainable development. However, were fossil fuels to remain plentiful while the atmospheric capacity for CO₂ absorption is limited, emissions would require stringent controls to avert significant climate repercussions. This scenario, an economy possessing ample fossil fuels but constrained by atmospheric limitations, would necessitate emission restrictions that could impede economic growth, particularly if the economy lacks the capacity to readily substitute fossil fuels with alternative energy sources.

Conversely, the issue of climate change diminishes if fossil fuel resources are limited, as the available carbon is insufficient to elevate atmospheric CO₂ to hazardous levels. In this situation, sustainable development faces the challenge of energy scarcity, where the primary constraint on growth is the lack of fuel. In both the fossil fuel-scarce and fossil fuel-rich but atmosphere-limited scenarios, the relationship between energy and economic output is critical. For growth to be sustained, the economy must compensate for energy constraints by either substituting other inputs for energy or by developing technologies that significantly enhance energy efficiency. Without such adaptations, any growth deceleration caused by energy limits may lead to a redistribution of economic output, favoring fossil fuel suppliers at the expense of returns to labor and capital.

Historically, perceived energy crises have been addressed through strategies aimed at expanding energy supply and enhancing efficiency. The energy concerns of the 1970s, for instance,

prompted intensified exploration for new oil and gas reserves, advancements in extraction and mining technologies, and the implementation of policies designed to encourage energy conservation and the substitution of alternative fuels. During this period, substantial initiatives were also undertaken to develop renewable energy sources and nuclear power. Despite these efforts, fossil fuels have remained the primary global energy source. The promise of nuclear fission was not fully realized, as reliable breeder reactors to extend uranium supplies failed to materialize, and nuclear fusion is not expected to achieve commercial viability before 2050. Furthermore, while improvements in energy saving and fuel switching led to increased energy efficiency, these gains were outpaced by concurrent population and economic growth. Consequently, global fossil fuel consumption and CO₂ emissions have continued to rise: the 2024 Global Carbon Budget estimates that fossil-fuel and cement activities released a record 37.4 Gt CO₂ in 2024, up 0.8% compared to 2023 [43]. The persistence of fossil fuels as the dominant energy source is attributable to their convenience, extensive reserves, and the well-established infrastructure supporting their utilization. This sustained dependence presents a significant challenge for climate stability, implying that CO₂ emissions are likely to continue increasing in the absence of substantial systemic changes.

The extensive utilization of fossil fuels has historically led to localized pollution challenges, such as acid rain and urban smog, stemming from emissions of sulfur dioxide and nitrogen oxides. These concerns were largely mitigated through technological interventions applied at the emission source, including flue-gas desulfurization and catalytic converters. The implementation of such controls proved more economically viable than forgoing fossil fuel usage altogether, thus enabling continued economic expansion alongside improvements in air quality. Many analysts suggest this reflects a broader trend: as economies grow, the corresponding increase in energy demand leads to escalating environmental impacts, which society addresses by mitigating those impacts without abandoning the primary energy source. In this view, the current issue of global climate change can be seen as a continuation of this pattern. Decarbonizing fossil fuel emissions, in essence, remediating CO₂ similar to SO₂, appears a logical progression. However, managing CO₂ presents greater technical challenges, considering its distinct physical properties and the substantial volumes that require capture and storage. The quantities involved are orders of magnitude larger: an average coal-fired power plant emits about 1 kg CO₂ per kWh of electricity, whereas pre-scrubber units in 1997 released only $\approx 6 \text{ g SO}_2 \text{ kWh}^{-1}$ and $\approx 3 \text{ g NO}_x \text{ kWh}^{-1}$ [137, 136].

As one such measure, carbon capture and sequestration (CCS) represents a strategy for mitigating atmospheric CO₂ levels through the capture and permanent isolation of CO₂ before its release. The deployment of CCS technologies necessitates considerable capital expenditure and energy inputs, primarily due to the energy-intensive processes of CO₂ separation, com-

pression, and transportation to designated storage locations. Among the proposed storage methodologies are injection into deep geological formations and deposition in deep ocean environments. However, ocean sequestration is generally disfavored due to its inherent risks, potential harm to marine ecosystems, and susceptibility to leakage. In contrast, geological sequestration is perceived as a comparatively safer and more readily regulated alternative. Although fossil fuels have historically been dominant, it is projected that their utilization will eventually reach a maximum and subsequently decrease as reserves become increasingly difficult to access. Certain long-term projections estimate the global peak in fossil energy consumption to occur as late as the mid-22nd century, after which the energy sector will need to progressively transition to alternative energy sources to sustain economic expansion [145, 118, 45]. Essentially, the era of continuously expanding fossil fuel consumption is inherently constrained by the finite nature of these resources. Ultimately, renewable energy technologies are anticipated to advance sufficiently and become economically viable enough to secure an expanding proportion of the energy market, thereby stimulating a fundamental transformation of the economy's energy foundation.

However, the continued reliance on fossil fuels presents a considerable risk to the climate. If all remaining reserves are burned without carbon capture, the resultant CO₂ emissions would greatly surpass current atmospheric levels, potentially leading to catastrophic climate change. Addressing this challenge involves two main strategies: accelerating the adoption of renewable energy and implementing CCS in fossil fuel systems. Each offers a path to climate stabilization but involves trade-offs. Rapidly transitioning to renewables before they are cost-competitive could require significant investments and constrain energy supply, causing economic strain. Conversely, using CCS allows the continued use of fossil fuels as a bridge to cleaner energy but is expensive, risks CO₂ leakage, and may hinder renewable energy innovation and cost reduction. These trade-offs between renewables-focused decarbonization and CCS-augmented fossil pathways are central to debates on achieving sustainable growth under climate constraints.

1.2 Causal chain of climate change

Anthropogenic climate change can be understood as a sequential process (as illustrated in the top row of Figure 1.1) initiated by greenhouse gas (GHG) **emissions** resulting from socio-economic activities. Following their emission, these gases interact with terrestrial and oceanic reservoirs via **natural cycles** (e.g., carbon cycle); however, a portion remains in the atmosphere, thereby disturbing the planetary radiative balance through an enhanced greenhouse effect. This accumulation perturbs the Earth's radiative balance, subsequently

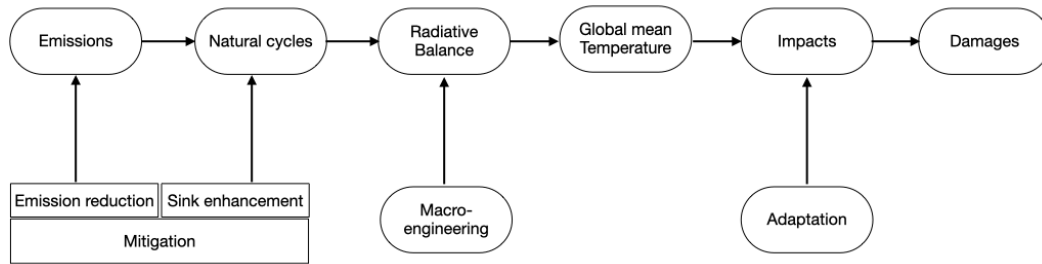


Fig. 1.1 Cause-effect chain of climate change and option reducing impacts [11].

manifesting as an increase in **global-mean surface temperature (GMST)**. This leads to associated shifts in the interconnected atmosphere–ocean–cryosphere system, such as altered precipitation patterns, more frequent and intense extreme weather events, cryosphere retreat, and rising sea levels. These changes then propagate into system-level impacts on sectors like agriculture, water availability, ecosystems, infrastructure, and coastal zones. When these impacts converge with human exposure, sensitivity, and limited adaptive capacity, they manifest as socio-economic and ecological damages, including food insecurity, health burdens, displacement, infrastructure losses, and biodiversity decline.

Article 2 of the United Nations Framework Convention on Climate Change (UNFCCC) advocates for the stabilization of atmospheric GHG concentrations to prevent "dangerous anthropogenic interference" with the climate system, thereby strategically addressing emissions and natural cycles. A more expansive approach involves capping the GMST or enhancing social and institutional resilience to minimize the adverse effects of unavoidable climate impacts. Strategies for addressing climate change can be classified into three main areas (as shown in the lower row of Figure 1.1). First, **mitigation**, in the context of climate change, involves strategies that act upon the **emissions** node by either reducing anthropogenic releases of GHGs or enhancing natural and artificial sinks, thereby limiting the overall atmospheric concentration of these gases. Second, **solar-radiation management (SRM)**, a subset of geo-engineering, seeks to directly offset positive radiative forcing through methods such as stratospheric aerosols, space-based reflectors, or modifications to surface albedo [44, 131, 56]. It seeks to influence the **radiative balance** to offset a portion of the warming effect. It is important to note, however, that SRM does not reduce atmospheric CO₂ levels and introduces its own set of governance and risk-related challenges. Third, **adaptation**, mechanisms are implemented both proximate to and downstream of the **impacts** node, with the goal of fortifying socio-economic resilience. This is achieved via strategies such as coastal defenses, climate-resilient agricultural practices, early-warning systems, and risk-sharing institutions, which collectively aim to reduce the magnitude and intensity of adverse consequences (**damages**) resulting from inevitable climatic pressures.

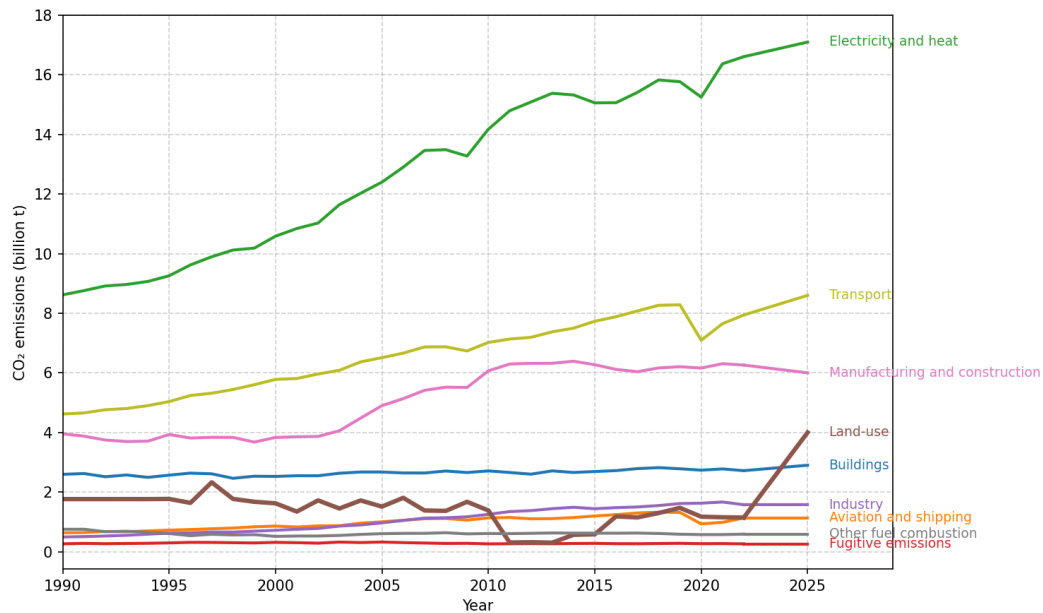


Fig. 1.2 CO₂ emissions by sector [24].

1.3 Source and type of GHGs

It is widely acknowledged that greenhouse gases exert a significant impact on climate change. These gases alter Earth's radiative balance by absorbing infrared radiation emitted from the surface, leading to increased radiative forcing and a corresponding elevation in GMST. Absent the presence of GHGs, the Earth's GMST would approximate -19°C; however, naturally occurring GHGs elevate this temperature to approximately 14°C, fostering conditions conducive to life. The Kyoto Protocol (KP) under the UNFCCC explicitly regulates six key GHGs. Furthermore, the Montreal Protocol (MP) governs other atmospheric gases, notably those implicated in ozone depletion. In addition to these, several other atmospheric constituents influence the chemistry of greenhouse gases without directly inducing radiative forcing. The principal GHGs identified by the KP encompass CO₂, methane (CH₄), perfluorocarbons (PFCs), sulphur hexafluoride (SF₆), nitrous oxide (N₂O), and hydrofluorocarbons (HFCs) [32].

- CO₂ is widely considered the most consequential anthropogenic greenhouse gas due to its substantial contribution to heightened radiative forcing and its accelerated accumulation in the atmosphere. Significant anthropogenic sources of CO₂ emissions encompass the combustion of fossil fuels, cement production, biomass burning, and land-use modifications. In 2023, global CO₂ emissions reached an estimated 37 gigatonnes, indicating a significant and sustained increase in greenhouse gas concentrations.

Key sectors contributing to these emissions (as seen in Figure 1.2) include electricity and heat generation, which account for approximately 42% due to the widespread use of coal and natural gas. The transportation sector contributes 23%, mainly through reliance on petroleum-based fuels, while industrial sectors such as cement, steel, and chemical manufacturing account for 19%, characterized by process emissions and high energy consumption. Residential and commercial sectors are responsible for 10% of emissions, attributed to building energy consumption, and agriculture, forestry, and waste management collectively contribute about 6% [29, 107, 19]. These sectors highlight the diverse and pervasive nature of carbon emissions, reinforcing the necessity for multifaceted and robust mitigation approaches.

- CH₄ is of secondary importance, although it possesses a considerably shorter atmospheric lifetime of approximately ten years. Anthropogenic methane emissions originate from a variety of sources, including agricultural practices, fossil fuel extraction and distribution, biomass combustion, waste decomposition in landfills, coal mining operations, and sewage treatment processes.
- PFCs have very long atmospheric lifetimes (over 10,000 years) and are entirely human-made, mainly from aluminum and semiconductor production [48].
- SF₆, with an atmospheric lifetime around 3,000 years, also comes from human activities like making insulating materials, magnesium, tires, and electrical switchgear [48].
- N₂O primarily comes from farming, especially rice growing, and some industrial activities [38].
- HFCs, used in cooling systems, have atmospheric lifetimes from decades to centuries, with some regulated under the MP.

To enable comparison across various greenhouse gases, the global warming potential metric is used, allowing for the aggregation of emissions into a standardized measure expressed in carbon dioxide equivalents. Examination of global emissions data from the year 2000 indicates that CO₂ emissions constitute the largest proportion of total greenhouse gas emissions. Within CO₂ sources, fossil fuel combustion is significantly greater than emissions arising from land-use changes. Methane and nitrous oxide contribute substantially to overall GHG emissions; however, their impact is considerably less than that of CO₂. The cumulative anthropogenic increase in the concentrations of these gases resulted in an estimated additional radiative forcing of approximately 2.4 W/m² as of 1998 [46].

1.4 Regulations for carbon emissions

Substantial decreases in carbon emissions are crucial to constrain global warming to 1.5 °C above pre-industrial levels, as highlighted in the Intergovernmental Panel on Climate Change's (IPCC) Special Report on Global Warming of 1.5 °C. Recent IPCC assessments underscore the pressing requirement to attain net-zero global CO₂ emissions by approximately 2050 to keep warming within acceptable bounds. Achieving net-zero necessitates equating CO₂ emissions with an equivalent amount removed via technological methods, such as CCS, or natural processes, like afforestation and reforestation. To realize this goal, global CO₂ emissions must be reduced by about 45% from 2010 levels by 2030 and reach net-zero by mid-century. Furthermore, considerable reductions in other key greenhouse gases, including methane and nitrous oxide, are also essential. Immediate and significant emission reductions are emphasized as vital for alleviating the severe consequences of climate change, especially in susceptible regions. The IPCC also emphasizes the swift and widespread adoption of energy-efficient technologies, greater utilization of renewable energy sources, sustainable land management practices, and ongoing technological advancements as essential for fulfilling emission targets.

The 2015 Conference of the Parties (COP21) in Paris marked a turning point in international climate policy with the establishment of the Paris Agreement. This agreement aims to limit the global average temperature increase to well below 2 °C above pre-industrial levels, while pursuing efforts to limit the increase to 1.5 °C. As part of this commitment, signatory nations have pledged to pursue emission reduction targets, primarily focused on decreasing CO₂ emissions, which are recognized as the primary contributor to anthropogenic climate change. These targets involve transitioning to low-carbon energy systems, improving energy efficiency, expanding carbon sinks through afforestation and reforestation, and fostering sustainable development policies to reduce dependence on fossil fuels. Subsequent COP summits, including COP26 in Glasgow and COP28 in Dubai, have reinforced these commitments, emphasizing the importance of strengthening Nationally Determined Contributions (NDCs), ensuring transparent reporting mechanisms, and promoting international collaboration to achieve timely and effective emissions reductions. The Paris Agreement and its subsequent iterations highlight a global consensus on the urgent and comprehensive actions needed to reduce emissions, transition to sustainable energy systems, and protect global environmental stability and human welfare.

1.5 Need for carbon capture

CCS has become a crucial technology for achieving substantial and lasting global emission reductions. The IPCC emphasizes that CCS is essential for scenarios aiming for a 1.5 °C warming limit, especially for industries like cement, steel, and chemical production that face inherent challenges in decarbonization due to unavoidable process-related emissions within current technological capabilities. CCS involves capturing CO₂ emissions at the point of origin or directly from the atmosphere, followed by their conveyance and application across various industrial sectors, or alternatively, secure geological sequestration, thereby diminishing atmospheric greenhouse gas concentrations (refer Figure 1.3). This technological approach serves as a critical adjunct to renewable energy sources and improvements in energy efficiency strategies. Despite its acknowledged potential and essential function, CCS remains substantially under-implemented on a global scale, with current capture rates of only 40–50 million tonnes of CO₂ annually, representing approximately 0.1% of total global emissions [98]. As of early 2025, the operational capacity for carbon capture stands at approximately 50 megatonnes of CO₂ per annum [61], a figure that contrasts sharply with the several gigatonnes per annum deemed necessary by mid-century to align with climate targets. The present infrastructure includes roughly 45 commercial CCS facilities, alongside a development pipeline exceeding 700 projects, reflecting increasing interest and investment in carbon capture technologies. Current projections anticipate an eightfold increase in CCS capacity between 2023 and 2030 [65], indicative of both the urgency and optimism surrounding these technologies. However, this prospective expansion encounters significant challenges, notably the historical precedent of largely unrealized CCS initiatives from the previous decade [65], and the reality that current progress remains considerably below the trajectory required for achieving a net-zero emissions pathway by 2050 [60]. The IPCC has concluded that the deployment of carbon capture is progressing ‘severely behind’ the schedule necessary to meet established mitigation targets [18]. The disparity between current CCS deployment levels and those required to effect meaningful change can be attributed to several key impediments: elevated operational and infrastructural expenditures, considerable energy requirements associated with CO₂ capture and storage processes, infrastructural deficits, the absence of well-defined policy frameworks, regulatory ambiguities, and significant levels of public doubt or opposition [31]. Overcoming these multifaceted challenges through targeted technological innovation, the establishment of coherent and incentivizing policy measures, and improvements in public knowledge and acceptance are essential to expanding CCS technologies to a scale capable of yielding substantial global climate benefits [65, 18].

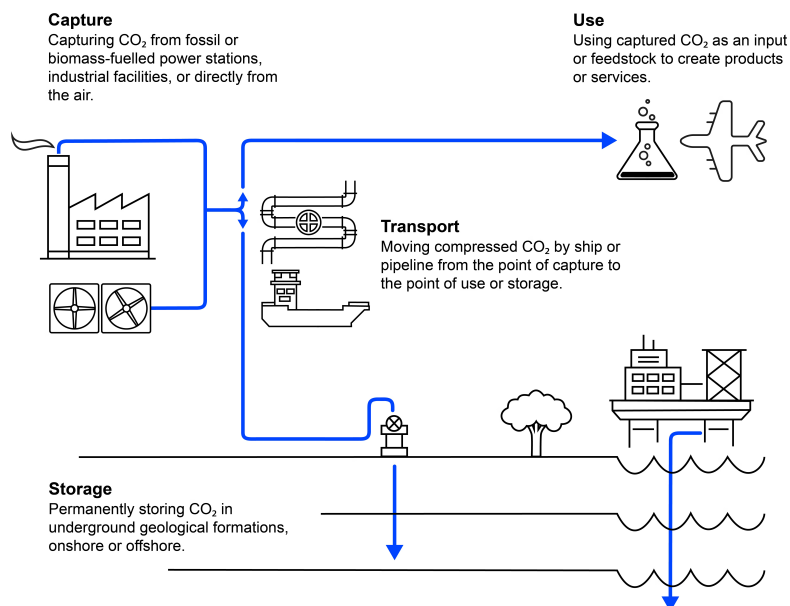


Fig. 1.3 What is CCUS? [59]

1.6 Objectives of the research

This research study is structured around four interconnected objectives that integrate computational modeling with experimental validation and materials optimization in the pursuit of innovative CO₂ capture technologies. The **first objective** concentrates on employing computational modeling to identify potential metals for selective CO₂ adsorption and photodesorption. Specifically, density functional theory calculations will be performed to simulate atomic interactions between CO₂ molecules and the surfaces of diverse pure metals. These simulations will elucidate the CO₂ binding energy on each metal, as well as the preferred molecular adsorption configuration, thus indicating which metal surfaces exhibit a strong affinity for CO₂. Furthermore, adsorption energies will be evaluated both with and without illumination to assess photothermal effects, that is, the extent to which light exposure can weaken the CO₂-surface interaction and facilitate CO₂ desorption. This theoretical approach furnishes a foundation for selecting promising metal candidates that demonstrate robust CO₂ adsorption in the dark and efficient photodesorption under light irradiation.

The **second objective** involves the empirical validation of the computational predictions derived in the preceding phase. To this end, a custom-designed CO₂ capture testing apparatus will be developed and constructed to enable the precise measurement of breakthrough curves under controlled experimental conditions. This apparatus will facilitate meticulous control over the flow rates of CO₂ and N₂ across the metal samples, while also incorporating a light

source to enable direct observation of photodesorption phenomena. Continuous monitoring of the effluent gas composition will allow for quantitative assessment of the extent of CO₂ adsorption by the sample, as well as its temporal evolution. Prior to employing this apparatus with novel metal samples, its performance will be benchmarked using a well-characterized, state-of-the-art CO₂ sorbent material: polyethyleneimine-impregnated silica (PEI-silica). Synthesized via a wet-infiltration technique, as detailed in prior literature, this material exhibits a demonstrably high affinity for CO₂, rendering it an ideal reference standard for validating the functionality of the apparatus. By conducting CO₂ adsorption/desorption experiments with PEI-silica and analyzing the resulting breakthrough curves, the accuracy and reliability of the experimental setup can be rigorously confirmed. Furthermore, complementary characterization of the PEI-silica sample will ensure the appropriate preparation of the reference material and enable the correlation of its structural properties with its expected CO₂ capture performance. Successful validation of the apparatus in this manner will establish a high degree of confidence in the soundness of the experimental methodology before its application to the metals of interest.

Following the validation of the experimental setup, the **third objective** focuses on the experimental validation of the pure metals previously identified. Metals predicted via computational modeling to demonstrate strong CO₂ adsorption and light-responsive desorption will be acquired in suitable forms (e.g., high-surface-area metal foams like copper and aluminum) and characterized comprehensively. Using the CO₂ breakthrough apparatus, the adsorption capacity and photodesorption behavior of these metal samples will be assessed. Each metal will undergo testing under dark conditions to establish baseline CO₂ uptake, followed by testing under illuminated conditions to quantify the extent and rate of CO₂ desorption upon light exposure. The resulting breakthrough curves will yield quantitative metrics for comparison with the DFT simulation results, thus validating the theoretical predictions. A strong correlation between DFT-predicted trends and experimental data would substantiate the effectiveness of the identified metals for selective CO₂ capture and light-driven regeneration. Conversely, discrepancies will provide insights for refining computational models or understanding practical factors influencing performance. In summary, the purpose of Objective 3 is to empirically demonstrate the CO₂ adsorption and photodesorption capabilities of the selected pure metals, thereby linking theoretical predictions with real-world application.

The **fourth and final objective** is an exploration of the potential to enhance CO₂ capture through the utilization of metal alloy compositions. Acknowledging the potential synergistic effects arising from the combination of different metals, this objective entails a systematic investigation of binary metal alloys with the aim of improving both selective adsorption and photodesorption processes. Initially, a range of binary alloy combinations will be identified,

and the respective proportions of each constituent metal within the alloy will be methodically varied to encompass a broad spectrum of compositional possibilities. Subsequently, computational methodologies will be employed to predict the nature of CO₂ interaction with the surface of each candidate alloy, as well as to evaluate the effectiveness of illumination in triggering CO₂ desorption. Recognizing the vast combinatorial space presented by the multitude of potential metal pairings and their respective ratios, evolutionary algorithms, or alternative machine learning techniques, will be integrated into this search process to optimize exploration of the alloy composition space, with the overarching goal of accelerating the discovery of promising alloy candidates. Through an iterative process of modeling and optimization, this study seeks to precisely identify specific alloy compositions that exhibit superior CO₂ binding characteristics in conjunction with efficient photodesorption capabilities. Alloys predicted to exhibit top-tier performance through this computational approach will then be considered strong candidates for subsequent synthesis and experimental evaluation. Upon the conclusion of Objective 4, the scope of this research will have expanded from the investigation of single-metal systems to encompass more complex alloy systems, potentially uncovering novel materials that surpass the performance of their pure metal counterparts.

1.7 Significance of this research

This research provides a notable contribution to fundamental science through enhanced understanding of CO₂ adsorption and desorption at the atomic level. By employing density functional theory (DFT) modeling, the interactions between CO₂ molecules and metal surface atoms are illuminated, offering insight into binding configurations, energy barriers, and the influence of electronic structure on adsorption processes. Such atomic-level detail is critical, for example, advanced simulations combined with machine learning have revealed detailed CO₂ capture mechanisms in sorbents [5]; this work extends this clarity to metal surfaces under photonic excitation. By resolving how CO₂ attaches to and detaches from a substrate atom-by-atom, the study addresses knowledge gaps that cannot be accessed by macroscopic experiments alone, thereby advancing the theoretical framework for CO₂ surface chemistry.

This research introduces a significant innovation by investigating photothermal and photo-assisted CO₂ desorption on metal surfaces, an area that remains relatively underexplored within carbon capture science. In contrast to traditional CO₂ capture systems relying on thermal or pressure fluctuations for CO₂ release, this study explores the application of light as a stimulus to trigger desorption. Recent studies have proposed light-induced swing adsorption (LISA) as a potentially groundbreaking approach, harnessing solar energy to release captured CO₂ rather than relying on external heat or electricity [79]. Prior work, however, has

predominantly concentrated on photo-responsive materials, rather than focusing on bare metal surfaces. By examining how photons facilitate the breaking of CO₂–surface bonds on metals, this study offers novel perspectives into desorption dynamics that have not been previously thoroughly documented. It reveals how photo-excitation or photo-induced surface charge can potentially decrease the energy necessary for CO₂ desorption, presenting a novel mechanism in surface chemistry. This work constitutes an initial systematic investigation into light-driven CO₂ desorption on metal substrates, signifying a notable advancement in the understanding of stimuli-responsive adsorption phenomena.

1.7.1 Potential application

This study's findings hold substantial promise for the advancement of next-generation CO₂ capture systems, particularly those employing light-triggered mechanisms to enhance efficiency and operational flexibility. Given the pressing need to capture CO₂ from industrial flue gases and the ambient atmosphere to mitigate climate change [153], the capacity to utilize light as an energy source for CO₂ desorption introduces new strategies for addressing this challenge. For example, in a power plant environment, a photothermal swing adsorption system could be integrated into flue gas treatment processes. This system could harness concentrated solar irradiation or in-situ lamps to stimulate desorption, rather than depending exclusively on steam or electrical heating to regenerate the CO₂ sorbent. By using a readily available renewable energy source to facilitate CO₂ release, the parasitic energy demand on the plant could potentially be decreased. Enhancing the efficiency of the regeneration phase, light-assisted CO₂ scrubbers can diminish the overall expenses and energy penalties associated with carbon capture in industries such as power generation, cement manufacturing, and chemical production. Consequently, power plants and factories could treat their exhaust streams more cost-effectively, capturing CO₂ with reduced supplemental energy input, thereby promoting the broader adoption of post-combustion carbon capture technologies.

The findings of this study hold significant relevance for direct air capture technologies and modular CO₂ scrubber units, in addition to their implications for large stationary emission sources. Given that DAC systems, which are designed to extract CO₂ directly from ambient air, frequently necessitate deployment in remote locations or require facile transportability, a light-driven desorption mechanism could enable the development of fully autonomous, modular DAC units powered by solar irradiation or low-energy light-emitting diodes. For example, research has demonstrated a "photo-swing" adsorption process that employs an aminopolymer sorbent and a plasmonic titanium nitride light absorber, wherein CO₂ was effectively released from the sorbent upon illumination with low-power LEDs [77]. This prototype achieved CO₂ desorption efficiencies comparable to those of conventional thermal

swing processes and exhibited stable operation over multiple cycles, thus indicating the technical feasibility and reliability of light-triggered regeneration [77]. The capacity to regenerate CO₂ sorbents using light in a robust manner facilitates the development of modular CO₂ scrubbers that can be readily transported to diverse sites or integrated into existing infrastructures in a plug-and-play manner. Such units could capture CO₂ from ambient air or point sources and subsequently utilize solar or lamp-driven illumination to periodically purge the CO₂ for subsequent storage or utilization. The inherent modularity and relatively modest energy requirements of these systems suggest their potential deployment in distributed locations for emissions mitigation. In essence, this study substantiates the conceptual framework for light-responsive CO₂ capture devices characterized by scalability and adaptability across a spectrum of contexts, ranging from large-scale power generation facilities to decentralized capture applications.

This research offers innovations that may lead to more scalable and sustainable carbon capture technologies, aligning with global policy objectives for climate change mitigation. Achieving net-zero CO₂ emissions by mid-century [153], a critical objective of climate policy exemplified by the Paris Agreement, will likely require extensive deployment of carbon capture, utilization, and storage alongside aggressive emissions reductions. The photo-assisted CO₂ desorption mechanisms and integrated discovery approaches developed in this work can aid in this effort by reducing the energy and cost barriers associated with CO₂ capture. For instance, light-driven CO₂ capture systems can leverage renewable energy directly by incorporating photo-responsive materials or linking capture units to on-site solar generators, enabling the photons or electrons produced to power the essential regeneration stage. One method involves photothermal sorbents that absorb sunlight and transform it into localized heat, desorbing CO₂ without the need for an external fossil-fuel boiler. Another approach utilizes photoelectrochemical cells, driven by adjacent photovoltaic panels, applying minimal voltage to an electro-swing sorbent, regenerating it through anodic oxidation instead of high-temperature steam. Both strategies directly supply clean energy to the CO₂-release step, obviating the requirement for grid electricity or natural-gas heat and thereby substantially enhancing the overall carbon balance of CCS operations. Enabling sorbent regeneration with renewable heat, waste heat, or light, these systems facilitate the integration of CO₂ capture with intermittent clean energy sources, which is essential for future large-scale deployment. Furthermore, the materials and insights produced could inform the design of next-generation capture materials and devices optimized for fast cycling and low energy consumption. Such advancements bolster the feasibility of implementing CO₂ scrubbers in sectors that are hard to decarbonize, ultimately supporting a transition to net-zero emissions. In summary, the practical implications of this study suggest more

energy-efficient, versatile, and policy-aligned carbon capture solutions, technologies that use light to help mitigate excess CO₂, contributing to global efforts to stabilize the climate.

1.8 Thesis outline

This thesis is structured into seven chapters, each contributing to a cohesive narrative that progresses from fundamental theory to practical validation and future perspectives.

Chapter 2, titled **‘Background,’** provides an overview of the theoretical and technological underpinnings relevant to the study. This chapter encompasses a review of established carbon-capture methodologies, an examination of the thermodynamic and kinetic principles governing CO₂ adsorption and desorption processes under thermal and photonic stimulation, and a synopsis of density-functional theory, breakthrough-curve analysis, and pertinent machine-learning concepts.

Chapter 3, entitled **‘Computational Investigation of CO₂ Adsorption on Pure Metals,’** integrates the results from the initial peer-reviewed publication derived from this research. It showcases Density Functional Theory (DFT) calculations that quantify CO₂ binding energies and photodesorption characteristics on various transition-metal surfaces, thereby providing a computational foundation for subsequent experimental endeavors.

Chapter 4, entitled **‘Design and Calibration of a Photothermal Breakthrough Apparatus,’** details the preliminary experimental investigation. This section delineates the fabrication of a fixed-bed reactor incorporating in-situ illumination capabilities, provides a comprehensive account of its calibration utilizing polyethyleneimine-impregnated silica, and presents diagnostic characterization data obtained via SEM, XRD, and EDX techniques.

Chapter 5, titled **‘Experimental Validation of Computational Predictions,’** presents the findings of the second experimental investigation, wherein copper, aluminum, and other metal candidates identified via DFT are assessed regarding their capacity for CO₂ uptake and light-induced release. A comparative analysis is conducted between breakthrough curves obtained in both dark and illuminated conditions and theoretical predictions.

Chapter 6, titled **‘Learning Adsorption Energetics on Transition-Metal Alloys,’** encapsulates the second DFT-based investigation. It elucidates an evolutionary-algorithm methodology, integrating quantum calculations with ML models to evaluate binary alloys for superior CO₂ adsorption and photodesorption capabilities, and emphasizes alloys demonstrating enhanced performance relative to their constituent pure metals.

Chapter 7, designated as **‘Conclusions and Future Work,’** synthesizes the key scientific advancements achieved in this thesis, acknowledges the constraints inherent in the methodologies employed, and proposes potential avenues for expanding light-assisted CO₂ capture,

including extended assessments of cyclic stability and incorporation with direct-air-capture technologies.

2. Background

2.1 Overview of Carbon Capture and Storage Technologies

By early 2025, the worldwide deployment of CCS technologies, including carbon capture, utilization, and storage, has experienced marked expansion. Approximately 1,000 projects are at various stages globally, with about 228 facilities in operation and numerous others under development [22]. While these efforts are primarily located in North America and Europe, significant new projects are also emerging across the Asia-Pacific region and the Middle East [22]. The aggregate CO₂ capture capacity of operational CCS/CCUS projects currently exceeds 50 million tonnes per annum and is anticipated to rise dramatically, potentially surpassing 400 million tonnes per annum by 2030, as planned facilities commence operations [61]. This accelerated deployment of CCS is motivated by increasingly stringent climate commitments and net-zero targets, thereby establishing CCUS as a pivotal component in global decarbonization initiatives. CCS is an essential strategy for reducing emissions, involving the capture of CO₂ from point sources and its secure storage to prevent atmospheric release. CCS systems typically comprise three key stages: CO₂ capture, compression and transport, and geological storage. The capture stage, which is the focus of this section, can be implemented at various points in the combustion or conversion process. Indeed, CO₂ capture approaches are commonly classified into three major categories: post-combustion, pre-combustion, and oxy-fuel combustion [135]. Each approach utilizes a unique mechanism for CO₂ separation, offering distinct advantages and limitations. However, techniques such as capture from industrial process streams (steel, cement and chemical) represent an alternative approach, frequently considered a fourth major category [87]. In addition to these methods, direct air capture (DAC) offers a competitive strategy by extracting CO₂ directly from the atmosphere. A brief overview of each category is shown in Figure 2.1. The following section provides a balanced overview of these CCS technologies, detailing key mechanisms, benefits, and drawbacks.

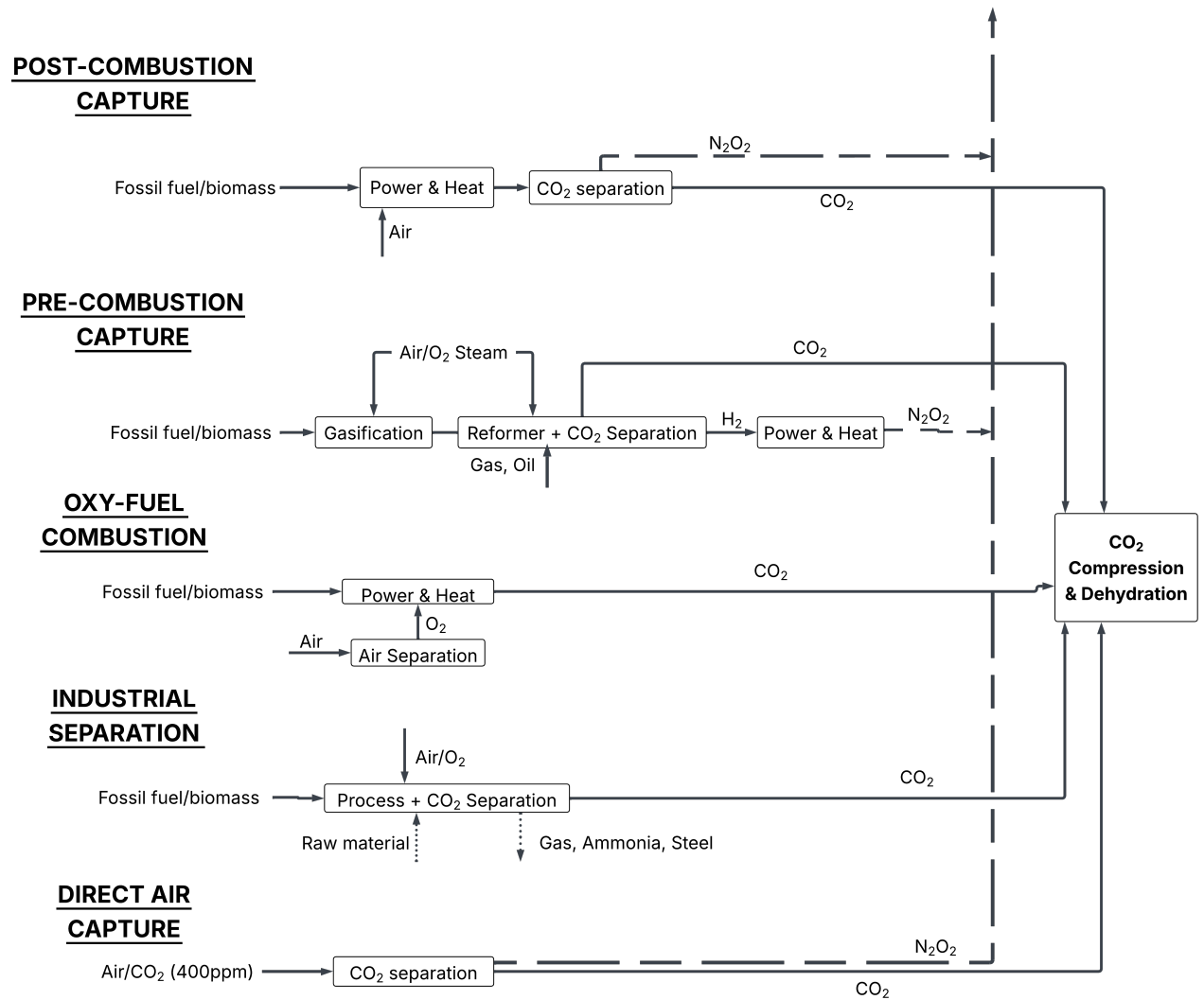


Fig. 2.1 Generic comparison of existing CO₂ capture systems [87, 75].

2.1.1 Post-combustion capture

Post-combustion CO₂ capture involves capturing carbon dioxide from effluent streams following fuel combustion in air. In a typical fossil-fueled power plant (e.g. pulverized coal or natural gas power station), the combustion of fuel with air results in CO₂ diluted within the flue gas (mixed with N₂ and residual O₂) at near-atmospheric pressure [135]. The concentration of CO₂ in flue gas typically ranges from 12% to 15% in coal-fired boilers and approximately 3% to 4% for natural gas turbines, posing separation challenges due to its diluted and low-pressure nature [135]. Chemical absorption using solvents like aqueous amines represents the most established solution, where CO₂ is scrubbed from the flue gas in an absorber column, followed by heating the CO₂-rich solvent in a stripper to release concentrated CO₂ [135]. Although amine-based post-combustion capture technology has been widely adopted in the oil/gas processing and chemical industries for gas stream purification, its application to large-scale power plants has largely been confined to pilot and demonstration projects [135]. Alternative post-combustion capture methods under development encompass solid sorbent filters and polymer membranes designed to selectively separate CO₂ from flue gas. Irrespective of the separation method employed, the captured CO₂ (typically $\approx 90\%$ of the CO₂ in flue gas) requires compression from near-ambient pressure to pipeline pressures (on the order of 150-200 bar) to facilitate transport and storage, entailing substantial energy consumption [135].

Advantages of post-combustion capture

1. *Retrofit Compatibility*: The adaptability of post-combustion systems to established power generation and industrial infrastructures, with minimal disruption to primary combustion processes, positions them as a compelling option for retrofitting existing coal or gas-fueled facilities for emissions mitigation. This is primarily due to the fact that CO₂ is extracted subsequent to conventional combustion and energy production stages. The capacity to integrate a capture unit provides extensive applicability across a diverse range of facility types and operational durations.
2. *Technology Maturity*: Solvent-based CO₂ scrubbers represent a commercially established technology, widely implemented in natural gas sweetening, ammonia production, and hydrogen plants for the removal of CO₂ and other acid gases. The application of this technology to power plant flue gases benefits from a substantial knowledge base [135]. For instance, amine absorption processes have been utilized in refinery and chemical plants for over a decade, indicating a high technology readiness level with respect to fundamental chemistry and engineering.

3. *Fuel Flexibility*: The post-combustion capture method is adaptable to various fuel types, as it operates on the exhaust gas stream, enabling CO₂ capture from the combustion of coal, oil, natural gas, or biomass. This fuel flexibility suggests the potential for implementing a standardized capture system design across multiple sectors (power generation, cement kilns, steel plants, etc.) potentially offering economies of scale in manufacturing standardized equipment.

Limitations of post-combustion capture

1. *Energy Penalty*: A notable disadvantage involves the substantial energy expenditure required for both solvent regeneration and CO₂ compression. Due to the low partial pressure of CO₂ in flue gas, solvents necessitate heating to facilitate CO₂ release in the stripper, which consumes steam from the power cycle. Furthermore, the subsequent compression of the separated CO₂ from approximately 0.1 MPa to around 15 MPa for pipeline transport introduces a significant auxiliary load [135]. Overall, a modern amine capture unit can diminish a power plant's net efficiency by 8–12%. Economically, recent analyses indicate that integrating post-combustion capture could escalate the levelized cost of electricity for a new coal power plant by about 65% [135].
2. *Large Equipment and Solvent Volumes*: Due to the low concentration of CO₂ in flue gas, the capture unit must process substantial gas volumes. This requirement leads to the use of sizable absorbers and strippers, as well as the management of large solvent inventories, consequently escalating capital expenditures. For example, in coal-fired power plants, the flue gas may contain 70–80% N₂ by volume, which must all be processed by the contactor [135]. Moreover, the slow capture kinetics associated with dilute CO₂ necessitate packing or membranes with large surface areas and potentially multiple absorption stages.
3. *Impurities and Degradation*: Flue gas contaminants can negatively impact post-combustion capture systems. Acidic gases, such as SO₂ and NO_x, along with particulates or heavy metals, have the potential to interact with or contaminate solvents and sorbents [135]. SO₂ can degrade amines through the formation of heat-stable salts, while oxygen may oxidize certain solvents. Consequently, effective flue gas pretreatment and/or advanced solvent formulations are essential to minimize losses. The management of solvent degradation and waste introduces additional operational complexities to post-combustion systems.

Despite inherent challenges, post-combustion capture has been successfully implemented in several large-scale projects, and ongoing research seeks to alleviate its limitations. A notable

project is SaskPower’s Boundary Dam Unit 3 in Canada, recognized as the first commercial power plant globally to integrate CCS technology. Since 2014, this facility has been capturing approximately 90% of CO₂ from a 110 MW coal unit using an amine-based system [6]. Another significant undertaking is the Petra Nova project in Texas, which implemented post-combustion amine capture on a portion of a coal plant’s flue gas, capturing around 1.4 Mt CO₂ annually for enhanced oil recovery operations. Petra Nova commenced operations in 2017, underwent a temporary suspension in 2020, and subsequently resumed CO₂ capture in 2023 [60], thereby validating the practical viability of retrofitting post-combustion CCS systems in power generation facilities. In addition to applications in coal-based power generation, there is increasing interest in employing post-combustion capture in natural gas-fired power plants and industrial settings. For example, as part of Norway’s “Longship” CCS initiative, a cement plant in Brevik and a waste-to-energy plant in Oslo are in the process of installing CO₂ scrubbers, with a combined capture capacity of approximately 0.8 Mt CO₂ per year slated for the mid-2020s. The captured CO₂ will then be transported and stored in the North Sea [6]. This represents one of the initial full-scale CCS implementations within the cement sector, thus underscoring the expanding applicability of post-combustion technologies beyond the power generation industry.

2.1.2 Pre-combustion capture

Pre-combustion capture entails the elimination of carbon, specifically in the form of CO₂, prior to the combustion of fuel for energy or heat generation. This process typically involves converting the fuel into a synthesis gas, or reformat gas, which is composed of hydrogen and carbon monoxide. Subsequently, CO₂ is separated following the shifting of CO to CO₂. A representative example is an Integrated Gasification Combined Cycle (IGCC) power plant, or an industrial gasifier, wherein solid or liquid hydrocarbon fuel undergoes partial oxidation with oxygen or air within a gasifier, thereby producing syngas primarily composed of CO and H₂ (plus some CO₂ and impurities) [135]. This syngas is then directed through a water-gas shift reactor, where steam interacts with CO to generate additional CO₂ and H₂ [135].



Following this shift, the syngas may comprise approximately 40% CO₂ and 55% H₂ by volume [135]. The CO₂ is now at an elevated partial pressure, which significantly facilitates its separation. A physical solvent, such as Selexol or Rectisol, can absorb the CO₂ from the high-pressure syngas; subsequently, the CO₂ is released from the solvent through pressure

reduction and stripping, resulting in a concentrated CO₂ stream suitable for compression. The remaining hydrogen-rich fuel gas can be directed to a gas turbine and combusted for power production, or employed in alternative processes as a low-carbon fuel [135]. Fundamentally, pre-combustion capture yields two streams from the original fuel: a near-zero-carbon fuel that can be utilized for energy and a CO₂ byproduct that is captured before it is emitted.

Advantages of pre-combustion capture

1. *High CO₂ Concentrations and Pressures:* The water-gas shift process produces a concentrated stream of CO₂ at elevated pressure, which facilitates a simplified and more economical separation compared to post-combustion methods. This greater driving force for CO₂ capture, approximately 40% of the gas at 2 MPa in shifted syngas versus 12% at 0.1 MPa in flue gas [135], enables the application of smaller equipment and physical solvents that regenerate through pressure swing adsorption. NETL suggests that, due to these advantageous conditions, pre-combustion systems can offer lower capital costs and energy consumption relative to post-combustion systems achieving equivalent CO₂ capture rates [135]. Consequently, facilities employing gasification with CCS often demonstrate a more modest increase in the cost of energy when compared to post-combustion scenarios.
2. *Valuable Hydrogen Product:* A significant advantage of pre-combustion capture is the intrinsic production of hydrogen. This resultant hydrogen can be deployed in gas turbines or fuel cells to generate electricity, achieving zero CO₂ emissions at the point of consumption, or it can be applied across a range of industrial and transportation sectors. The generation of H₂ provides operational flexibility, allowing, for example, an IGCC plant with CCS to co-generate electricity and hydrogen fuel, with the latter potentially sold as a commodity (e.g. for refining or ammonia production). Consequently, pre-combustion capture aligns with the burgeoning interest in a hydrogen economy, facilitating the continued utilization of fossil fuels by transforming them into a lower-carbon energy vector while sequestering carbon byproducts.
3. *Established Industrial Processes:* Established industrial facilities already employ the core principles of pre-combustion CO₂ capture. For example, the Great Plains Synfuels Plant in the U.S. has practiced coal gasification with CO₂ capture for decades, while ammonia fertilizer plants and natural gas processing facilities routinely remove CO₂ from syngas or natural gas. To illustrate, the Great Plains Synfuels Plant in North Dakota gasifies approximately 6 million tons of lignite each year to produce synthetic natural gas, capturing roughly 3 Mt CO₂ annually from the syngas stream at

a low incremental cost (the CO₂ is transported to Canada for EOR) [6]. These cases demonstrate the potential for pre-combustion capture to leverage existing technologies, enhancing confidence in its dependability and scalability.

Disadvantages of pre-combustion capture

1. *High Capital Cost and Complexity*: The inherent demands of gasification or reforming and subsequent shifting processes introduce significant complexity and increase upfront capital investment. An IGCC power plant incorporating CCS is substantially more complex than a conventional power plant, requiring an air separation unit, a gasifier reactor, syngas cleanup systems, shift reactors, and a combined-cycle power block. Consequently, the associated capital expenditure and maintenance requirements are considerably higher. This makes pre-combustion CCS more economically attractive for new power plant construction rather than retrofitting existing infrastructure. Retrofitting an existing pulverized coal boiler to an IGCC configuration is generally not economically feasible, as evidenced by the redirection or cancellation of demonstration projects [6]. The Kemper County project, the only large-scale IGCC with CCS initiative undertaken in the U.S., was terminated in 2017 following multi-billion dollar cost overruns, highlighting the inherent economic risks associated with the complexity of this approach [6].
2. *Efficiency Trade-offs*: Although pre-combustion capture facilitates substantial carbon removal, the process can notably diminish plant efficiency. The energy requirements of gasification and shift reactions, alongside the energy-intensive nature of oxygen production for the gasifier, contribute to this reduction [6]. While an IGCC with capture may potentially achieve acceptable efficiency, it typically remains lower than that of a new supercritical coal plant without capture. Therefore, despite the significant reduction in CO₂ emissions, a greater fuel input becomes necessary for each unit of net electricity produced.
3. *Limited Retrofit Potential*: Pre-combustion carbon capture and storage is optimally suited for nascent projects or specialized industrial processes rather than the modification of existing infrastructure. Sectors that intrinsically generate a concentrated CO₂ stream as a process intermediate, for instance, hydrogen production via steam methane reforming or coal gasification for synfuel synthesis, are particularly amenable to this approach, as CO₂ capture can be integrated with relative simplicity. Nevertheless, the conventional power sector has yet to witness the deployment of large-scale

pre-combustion capture plants due to the considerable capital investments required and the operational uncertainties that have thus far constrained its broader implementation.

2.1.3 Oxy-fuel combustion

Oxy-fuel combustion represents a CO₂ capture strategy that involves combusting fuel in an environment of nearly pure oxygen rather than air. By excluding the substantial proportion of nitrogen typically introduced by air, the resultant flue gas from combustion is largely composed of concentrated CO₂, which is readily purified. Practically, oxy-fuel systems employ pure O₂ (typically >95% O₂) generated from an air separation unit and combine it with recycled CO₂ or H₂O to regulate combustion temperature (since burning in pure oxygen is much hotter than in air) [135]. The fuel (coal, natural gas, etc.) undergoes combustion in this O₂/CO₂ environment, yielding an exhaust gas primarily consisting of CO₂ and H₂O, with only trace contaminants. Following cooling, water vapor is condensed out, resulting in a high-purity CO₂ stream prepared for compression and storage [135]. Fundamentally, oxy-fuel combustion inherently generates a sequestration-ready CO₂ off-gas, thereby obviating the necessity for a separate scrubbing process to extract CO₂ from nitrogen. The primary additional equipment needed includes the air separation unit (ASU) for oxygen supply and downstream CO₂ polishing units (for removing any oxygen or impurity remnants from the CO₂ before storage).

Advantages of oxy-fuel combustion

1. *High Purity CO₂ Stream:* A key advantage of oxy-fuel combustion is the production of a flue gas stream with a high concentration of CO₂ (after moisture removal), which simplifies its subsequent capture. By avoiding nitrogen dilution, CO₂ concentrations of over 80% can be attained in the exhaust gas. This eliminates the need for complex chemical separation processes, allowing CO₂ capture via straightforward phase change (condensing water) and gas clean-up methods. In contrast to post-combustion capture, oxy-fuel combustion reduces the volume of gas requiring treatment by removing N₂ ballast, obviating the need for large absorber/stripper systems.
2. *Pollutant Emission Reduction:* Oxy-fuel combustion has the potential to reduce emissions of certain pollutants compared to traditional air-fired combustion methods. Research indicates that NO_x emissions are significantly reduced (by 60–70%) in oxy-firing scenarios due to the utilization of recycled flue gas and the limited presence of atmospheric N₂ for NO_x formation [135]. Furthermore, the oxygen-rich environment can facilitate a more thorough oxidation of fuel-bound impurities; tests have shown

increased oxidation of mercury in coal oxy-combustion, which simplifies downstream mercury removal [135]. These synergistic benefits suggest that an oxy-fuel plant may more readily comply with stringent air pollutant standards.

3. *Applicability to New and Some Existing Plants:* Oxy-fuel combustion presents a viable option for both new, high-efficiency power generation units designed for CCS integration and the retrofitting of existing boiler systems. The Callide A project in Australia successfully demonstrated the retrofitting of a 30 MW coal boiler to oxy-firing [6], confirming the feasibility of converting existing plants to oxy-fuel operation with boiler modifications and a dedicated oxygen supply. The core components, including cryogenic air separation, flue gas recirculation, and CO₂ handling, are commercially established technologies validated in large-scale pilot settings [135]. Thus, oxy-fuel offers an alternative retrofit strategy to post-combustion capture by removing nitrogen before combustion rather than scrubbing CO₂ from nitrogen-containing flue gas. This approach may be advantageous for some aging plants when carefully integrated with existing infrastructure.

Limitations of oxy-fuel combustion

1. *Significant Oxygen Supply Energy Cost:* The primary drawback of oxy-fuel systems lies in the substantial energy expenditure required for producing pure oxygen. Traditional cryogenic air separation methods are energy-intensive; the oxygen generation necessary for a power plant boiler can consume 10–15% of the plant's gross output as parasitic load [6]. In the context of oxy-coal combustion, the oxygen demand is considerable, with coal combustion requiring approximately 0.2–0.3 tons of O₂ per ton of CO₂ produced. According to NETL analyses, an oxy-coal plant necessitates a significantly larger air separation unit compared to a gasification plant, leading to a marked increase in CO₂ capture costs in oxy-fuel mode [135]. Furthermore, the requirement for high-purity O₂ limits the potential for efficiency improvements through more cost-effective separation techniques. Ongoing efforts are focused on developing advanced, lower-energy oxygen separation technologies to mitigate this challenge [135], though these remain in the experimental or pilot phase.
2. *Process and Control Complexity:* Adapting a boiler for oxy-combustion, whether through retrofitting or new design, necessitates modifications to heat transfer mechanisms and gas dynamics. To maintain flame temperature and heat flux profiles comparable to air combustion, flue gas must be recycled (often 60–70% of flue gas is looped back). This flue gas recirculation, coupled with precise oxygen flow regula-

tion, introduces operational complexity. Materials must be capable of withstanding elevated CO_2 concentrations, which can induce corrosion under specific conditions. Furthermore, adjustments to boiler radiant sections may be required to accommodate variations in gas emissivity. While these engineering challenges are surmountable, they demand meticulous design and operational optimization. Moreover, ensuring the integrity of the O_2 handling system (to avoid fires/explosions in oxygen-rich environments) is paramount. Consequently, despite its conceptual simplicity, oxy-fuel combustion systems necessitate substantial engineering development and have only undergone testing at the pilot scale thus far.

While oxy-fuel combustion has progressed from conceptualization to pilot-scale demonstration over the past decade, its widespread commercial application remains constrained. Pilot projects, including a 30 MWth installation in Germany [128] and the Callide Oxyfuel Project in Australia [27], have validated core principles. Similarly, the OXYCFB300 Compostilla CCS Demonstration Project in Spain [33], alongside the Lacq pilot plant in France [90], have illustrated the viability of oxy-combustion. These initiatives have furnished engineers with practical insights into oxygen-fired boilers, flue gas recirculation, and CO_2 purification methodologies. To date, however, the construction of large-scale oxy-fuel power plants has been hindered, primarily by efficiency losses and the economic burden associated with ASUs. Several proposed projects have been discontinued, notably the White Rose project in the UK, a projected ≈ 448 MW oxy-coal facility designed to capture ≈ 2 Mt CO_2 annually, which was terminated in 2015 due to funding deficits [6].

While various strategies have been presented for capturing and sequestering CO_2 at scale, including post-combustion, pre-combustion, and oxy-fuel approaches, their success is fundamentally dependent on the interaction between CO_2 and the capture medium. Consequently, this discussion will shift from process-level schematics to an examination of CO_2 behavior at the molecular and material levels, focusing on its adsorption and desorption characteristics, and the associated thermodynamic, kinetic, and material challenges for effective carbon capture.

This necessitates the development of materials and operational strategies capable of reducing regeneration energy without compromising capture rates. The integration of compact adsorbent beds, capable of photothermal or photo-electronic regeneration, could substantially reduce both energy consumption and physical footprint.

My research addresses this challenge through the application of DFT to identify pure transition metals where CO_2 binding can be precisely controlled via illumination. Furthermore, we experimentally investigate light-assisted desorption on these metallic substrates to minimize thermal energy requirements. Prior to exploring metal surfaces, polyethylenimine-

Table 2.1 Summary of key physical properties of CO₂ [94, 52, 84, 147].

Property	Value
Molecular structure	Linear, O=C=O
Molar mass	44.01 g/mol; Gas density at STP $\sim 1.98 \text{ kg/m}^3$
Triple point	-56.6°C at 5.18 bar
Critical point	31.1°C at $\sim 7.38 \text{ MPa}$ (73.8 bar); beyond this, CO ₂ is supercritical
Sublimation point	-78.5°C (solid CO ₂ transforms directly to gas)
Solubility in water	$\sim 1.45 \text{ g/L}$ at 25°C (forms carbonic acid in solution)
Other properties	Colorless, odorless, non-flammable; higher thermal conductivity and heat capacity than air (relevant to fire suppression and cooling uses)

functionalized silica serves as a benchmark to establish instrument fidelity and determine a baseline working capacity. This analytical framework is subsequently applied to binary alloys, which are optimized using machine learning techniques to achieve precise control over binding characteristics. Consequently, findings derived from our investigations into metal/CO₂ photo-desorption mechanisms are directly applicable to the design and optimization of point-source emissions, as well as to broader applications in modular carbon capture systems for industrial processes and Direct Air Capture. (DAC)

2.2 Properties and challenges of CO₂ in carbon capture

2.2.1 Physical properties of CO₂

Understanding the physical properties of CO₂ is essential for designing efficient capture, utilization, and storage processes. CO₂ is characterized as a linear, triatomic molecule wherein a central carbon atom is doubly bonded to two oxygen atoms. Possessing a symmetrical configuration with a bond angle of 180° and a C=O bond length of approximately 1.16 angstrom [148], CO₂ lacks a net dipole moment due to the cancellation of partial charges on the oxygen and carbon atoms, thus rendering it a nonpolar species. With a molecular weight of 44.01 g/mol [148], CO₂ presents as a colorless and odorless gas under standard temperature and pressure (STP). Its density at STP ($\approx 1.98 \text{ kg/m}^3$ [148]) is approximately 1.5 times greater than that of air, resulting in its propensity to accumulate in lower-lying areas upon leakage.

At ambient pressure, CO₂ transitions directly from solid to gas (sublimation) at -78.5°C ,

bypassing the liquid phase [148]. The triple point of CO₂ is registered at 216.6 K and 5.18 bar, conditions necessary for liquid CO₂ to exist. The critical point is observed at $\approx 31.1^\circ\text{C}$ and 7.38 MPa [52]. Beyond these critical parameters, CO₂ becomes a supercritical fluid, characterized by a density akin to liquids and a viscosity resembling gases [52]. Supercritical CO₂ is notably effective in applications such as supercritical extraction and pipeline transport for carbon capture and storage, owing to its high density. The relatively low critical temperature and moderate critical pressure of CO₂ facilitate its condensation or supercritical transformation compared to many other gases. The phase behavior of CO₂ dictates that cooling and expanding it below the triple-point pressure can induce solid formation, a factor of concern in cryogenic CO₂ separation processes and pressure regulation valves [84].

CO₂ demonstrates a moderate level of solubility in water, resulting in the formation of an aqueous solution of carbonic acid. Quantitatively, at 25 °C and under a partial pressure of 1 atm, the solubility of CO₂ is approximately 0.034 mol per liter of water (Henry's constant $\approx 3.3 \times 10^{-2}$ M/atm) [94], corresponding to roughly 1.5 g L⁻¹. While sufficient to exert influence on natural aquatic systems, this solubility is modest when compared to gases exhibiting higher solubility. CO₂ is commonly referred to as an 'acid gas' due to its reaction with H₂O, which leads to the production of carbonic acid and a subsequent reduction in pH. In the context of carbon capture technologies, CO₂ solubility can be augmented through chemical reactions that facilitate its binding as bicarbonate or carbamate, effectively sequestering CO₂ within the solution. In contrast, CO₂ exhibits reduced solubility in the majority of non-polar solvents; however, supercritical CO₂ serves as a competent solvent for a range of organic compounds, a property attributed to its liquid-like density coupled with low surface tension. Relevant physical constants for CO₂ are compiled in Table 2.1, and its phase equilibria as functions of temperature and pressure are depicted in a corresponding phase diagram (Figure 2.2).

2.2.2 Chemical properties of CO₂

From a chemical standpoint, CO₂ exhibits substantial stability due to carbon's maximal oxidation state. The creation of CO₂ from its constituent elements is a highly exothermic process ($\Delta H_f \approx -393.5$ kJ/mol), with a standard Gibbs free energy of formation around -394 kJ/mol [50]. This inherent stability is evident in the robust chemical bonds, where each C=O double bond possesses a bond enthalpy of approximately 750-800 kJ/mol [110]. In comparison to the O-H bond in H₂O (≈ 460 kJ/mol) [110], significantly more energy is required to break a C=O bond in CO₂. Consequently, CO₂ is frequently considered a thermodynamic sink, representing the low-energy endpoint of complete combustion, which makes converting CO₂ into other chemicals an energy-intensive endeavor. Indeed, CO₂'s

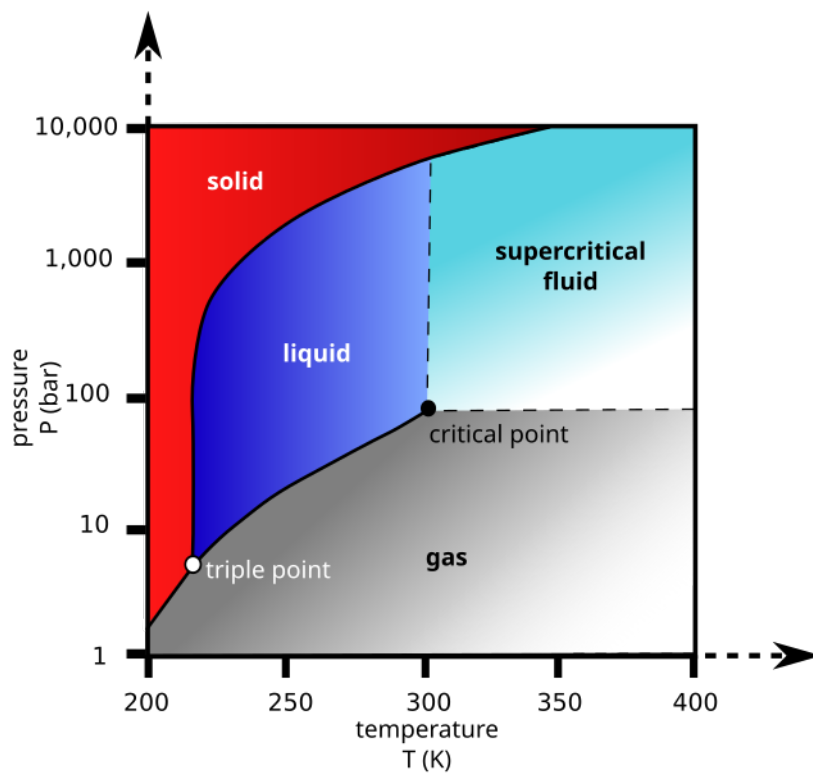
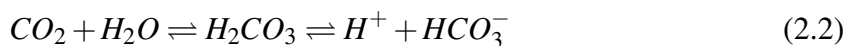


Fig. 2.2 Pressure–temperature phase diagram of CO₂, highlighting the triple point (TP) and critical point (CP) [147]

highly oxidized state and thermodynamic stability necessitate considerable energy input or catalysis to facilitate reactions [138]. It neither combusts nor supports combustion, displaying minimal reactivity under ambient conditions. These characteristics emphasize CO₂'s kinetic inertness: reactions with CO₂ proceed slowly, even when thermodynamically feasible, unless catalyzed or conducted under specific conditions.

Despite lacking a permanent dipole moment, CO₂ possesses polar C=O bonds, resulting in a notable quadrupole moment. This quadrupolar characteristic influences its non-covalent interactions. The molecule's linear structure, coupled with its delocalized electron configuration, contributes to its low reactivity, as evidenced by fully occupied bonding orbitals and the absence of low-lying unoccupied orbitals. CO₂ can be described as a relatively inert oxide in terms of polarity, typically not undergoing spontaneous reactions under ambient conditions except with strong nucleophiles or bases. For example, basic oxides and alkalis react with CO₂ to generate carbonates or bicarbonates. CO₂ readily combines with metal oxides or hydroxides, yielding metal carbonates or hydrogen carbonates, a reaction crucial in processes such as CO₂ scrubbing using lime or soda lime, as well as natural weathering. In aqueous environments, CO₂ reversibly forms carbonic acid:



Carbonic acid, formed when CO₂ dissolves in water, is a weak diprotic acid, with only a small proportion of the dissolved CO₂ present as H₂CO₃ at equilibrium [125]. In the absence of a catalyst, the hydration reaction proceeds relatively slowly; biological systems utilize the enzyme carbonic anhydrase to facilitate the rapid interconversion of CO₂ and HCO₃[−] for respiration. However, in water or amine solutions used for carbon capture, chemical reactions significantly enhance CO₂ uptake. Amines (e.g. monoethanolamine, MEA) react with CO₂ via a two-step, base-catalyzed mechanism to form carbamate species, exhibiting second-order rate constants in the range of 10³-10⁵ M^{−1} s^{−1} for fast-reacting amines [120, 12]. These reactions ($\text{CO}_2 + 2\text{RNH}_2 \rightarrow \text{RNHCOO}^- + \text{RNH}_3^+$) are both exothermic and reversible. Consequently, while CO₂ typically exhibits low reactivity, it readily reacts with strong nucleophiles such as amine and hydroxide ions, a principle employed in chemical absorption methods for CO₂ capture.

2.2.3 Challenges in capturing and handling CO₂

The challenges associated with CO₂ capture and management are directly related to its inherent physical and chemical properties. Its presence as a dilute component in most emission streams, coupled with its exceptional stability, renders its separation and compression

for subsequent storage or utilization a complex and energy-intensive endeavor. The key challenges include:

- *Separation and capture efficiency*: Post-combustion flue gas from power plants typically contains CO_2 at a concentration of approximately $\approx 10\text{--}15\%$ by volume, whereas atmospheric CO_2 levels are only around $\approx 0.04\%$. The capture of such low CO_2 concentrations requires the processing of substantial gas volumes and the attainment of high selectivity. Due to CO_2 's nonpolar nature and molecular size similarity to N_2 and O_2 , direct physical separation presents a significant challenge. Advanced sorbents and membranes leverage CO_2 's enhanced condensability and quadrupole moment to preferentially bind CO_2 . Although CO_2 has no net charge and no permanent dipole, its linear $\text{O}=\text{C}=\text{O}$ structure produces an uneven electron distribution. Electron density is concentrated toward the O atoms and depleted around the central C atom. This gives CO_2 distinct regions of partial negative and partial positive charge, which interact favorably with local electric fields and polar/charged sites inside porous adsorbents (e.g., extra-framework cations in zeolites, polar functional groups, or open metal sites in metal-organic framework (MOFs)), leading to stronger electrostatic interactions and enhanced adsorption relative to N_2 . In contrast, N_2 and O_2 are homonuclear diatomics with far more uniform charge distributions and comparatively weak quadrupole moments, so they interact mainly through weaker dispersion forces and are typically adsorbed less strongly under similar conditions[15]. The presence of moisture can impede CO_2 adsorption, as water exhibits a strong affinity for many sorbents (due to a strong permanent dipole and can hydrogen-bond). It often binds very strongly to the same polar/cationic sites that preferentially adsorb CO_2 , thereby competing for adsorption sites and in some cases reacting chemically with sorbents. Furthermore, the low partial pressure of CO_2 in exhaust gases or ambient air diminishes the driving force behind adsorption or absorption, necessitating either substantial sorbent volumes or energy-intensive regeneration processes. Direct air capture systems, addressing CO_2 concentrations as low as 0.04% , may require approximately $1500\text{--}2400\text{ kWh}$ of energy per ton of CO_2 captured, reflecting the significant entropy cost associated with isolating such dilute CO_2 [25]. In contrast, concentrated point sources (flue gas, $\approx 12\% \text{ CO}_2$) present a less intensive challenge, yet even modern amine-based post-combustion capture plants consume around $250\text{--}300\text{ kWh}_{electric}$ per ton of CO_2 solely for the capture stage [62]. This considerable energy demand (often $20\text{--}30\%$ of a power plant's output) arises directly from CO_2 's inherent stability and the energy needed to disrupt CO_2 , sorbent bonds or release physically adsorbed CO_2 .

- *Thermodynamics v/s kinetics in capture:* CO₂'s inherent thermodynamic stability dictates that chemical capture methodologies necessitate the utilization of reagents exhibiting robust CO₂ binding capabilities. For example, amines engage with CO₂ to generate stable carbamates, effectively extracting CO₂ from the gaseous phase. However, the subsequent release of CO₂ (for storage) mandates substantial thermal input to reverse this reaction. This exemplifies the inherent energy versus affinity trade-off: potent chemisorbents (like amines, etc.) facilitate CO₂ capture at lower concentrations, albeit at the expense of elevated regeneration energy requirements, whereas weaker physisorbents (activated carbons, zeolites, MOFs with open metal sites, etc.) necessitate less energy for regeneration but may only function optimally at higher CO₂ pressures or require cooling. Reaction kinetics also exert a significant influence: in rapid processes such as industrial flue gas treatment, the sorbent must possess not only adequate capacity but also a sufficient rate of uptake. Materials such as zeolites or MOFs may exhibit diffusion limitations, while liquid solvents can encounter mass transfer constraints, all of which are exacerbated by CO₂'s inherent properties (like diffusion coefficient and solubility). Consequently, the design of efficient contactors (large surface area packing, thin membranes, etc.) is paramount to circumventing kinetic bottlenecks in CO₂ capture.
- *Compression and transport:* Following CO₂ capture, compression is essential for its transport or storage. Elevating CO₂ pressure from approximately 0.1 MPa to levels suitable for pipeline (eg., 10-15 MPa) transport demands a considerable energy expenditure. This is commonly achieved through multi-stage compression, which converts CO₂ into a dense or supercritical phase. This process typically consumes 80–120 kWh_e per ton of CO₂ [62], representing a significant, albeit secondary, energy demand relative to the capture stage. Due to the physical properties of CO₂, careful control during compression is crucial: should CO₂ be expanded or cooled below its triple point, the formation of solid dry ice can result in equipment impairment [84]. Therefore, the design of compressors and heat exchangers must proactively avoid traversing two-phase regions. A further challenge arises from the fact that while pure, anhydrous CO₂ is generally compatible with pipeline materials, the presence of impurities and water can lead to significant corrosion issues. The combination of CO₂ with even trace amounts of water results in the formation of carbonic acid, which exhibits corrosive properties with respect to carbon steel. Operational experience indicates that corrosion is minimal as long as CO₂ is maintained in a dry state and is free from O₂ or sulfur-containing compounds [100]. However, ensuring that pipeline CO₂ is dry and clean typically necessitates additional purification and dehydration

processes post-capture [100], thereby increasing both energy consumption and system complexity. Standard CO₂ specifications for pipelines typically mandate CO₂ purity levels exceeding 95–99% with water content in the parts-per-million range [103] to mitigate pipeline corrosion and hydrate formation. Achieving these specifications may require the implementation of downstream scrubbers or drying units. Moreover, CO₂ is transported under high-pressure conditions, necessitating that pipelines and storage tanks are designed to withstand these conditions. The high density of CO₂ also means that in the event of a leak, it can accumulate in low-lying areas, displacing oxygen and creating an acute asphyxiation hazard for personal and nearby population. Accordingly, robust leak detection and ventilation are essential safety measures.

- *Storage and Utilization Challenges:* For subsurface geological storage, CO₂ is typically injected into deep formations (typically >800 m depth) where the prevailing temperature and pressure maintain it in a supercritical state [139]. Due to its buoyancy relative to formation brine (its density is 50–70% that of water [99]), supercritical CO₂ tends to rise within the reservoir. Therefore, a secure caprock is essential to prevent upward migration and ensure containment. Storage security is enhanced over time through several trapping mechanisms: CO₂ gradually dissolves into groundwater (solubility trapping); it becomes trapped in pore spaces as an immobile residual phase (residual trapping); and it may react with minerals to form solid carbonates (mineral trapping). However, these processes occur over extended timescales.
- *Material Compatibility and Operational Issues:* Although CO₂ is generally inert and does not readily react with pipeline steels or storage materials, it can interact with certain chemicals. For instance, amine solvents used in CO₂ capture can undergo side reactions, leading to the formation of heat-stable salts or oxidative degradation of amines, resulting in solvent loss and the need for replenishment. The propensity of CO₂ to form solid hydrates under high-pressure and low-temperature conditions can also cause equipment blockage if water is present. In cryogenic CO₂ capture or direct air capture systems employing cooling, CO₂ can freeze out, necessitating a thorough understanding of its phase diagram to avoid solidification during process variations. Furthermore, the inherent stability of CO₂ presents a significant hurdle for its utilization, as catalysts for CO₂ conversion to fuels or chemicals must overcome substantial activation energy barriers, often resulting in low yields.

The inherent physical and chemical properties of CO₂, including its moderate physisorption enthalpy, the necessity of strong chemisorptive interactions, low partial pressures in dilute streams, and susceptibility to impurities, present considerable impediments to its effective

capture and regeneration. Resolving these challenges is contingent upon the judicious selection and engineering of adsorption materials, ensuring an optimal equilibrium among capacity, selectivity, kinetics, and stability. Accordingly, the subsequent section will provide a brief overview of the key categories of sorbents, encompassing both traditional porous solids and cutting-edge functionalized frameworks, that underpin state-of-the-art carbon capture technologies.

2.3 Adsorption Materials

Various solid-state materials have been explored for CO₂ capture, each employing either or both of the physisorption or chemisorption adsorption mechanisms. Key categories of CO₂ sorbents include:

- *Carbon-based sorbents:* Activated carbons and carbon molecular sieves are frequently utilized as physisorbents for CO₂ capture. These materials generally exhibit elevated surface areas and micropore volumes, which facilitate CO₂ adsorption through van der Waals forces. Carbon-based materials can be produced from a range of precursors (coal, coconut shell, biomass, etc.) and modified through activation or doping processes. As an example, the introduction of nitrogen-doped porous carbons creates polar sites that enhance CO₂ affinity. Carbon sorbents often demonstrate hydrophobic properties, which is advantageous in flue gas applications where moisture is present. However, their inherent selectivity for CO₂ over N₂ is moderate, making them suitable for bulk CO₂ removal in gas streams with high CO₂ concentrations. Their low cost and thermal stability make them attractive for implementation in both pressure swing and temperature swing adsorption processes.
- *Zeolites and molecular sieves:* Zeolites (crystalline aluminosilicates) are frequently utilized as CO₂ adsorbents in industrial applications. A notable example is zeolite 13X, which exhibits a high cation density and a pore structure that facilitates strong electrostatic interactions with CO₂ (a quadrupolar molecule). Zeolite 13X demonstrates high CO₂ capacity and selectivity over N₂ at ambient temperature, rendering it suitable for CO₂/N₂ separation in flue gas. Generally, zeolites function through physisorption (ion–dipole or ion–quadrupole forces); their heat of adsorption for CO₂ surpasses that of activated carbon due to the presence of charged cation sites (e.g. Na⁺ in 13X). However, zeolites are susceptible to water, as water vapor can compete for adsorption sites, thereby diminishing CO₂ capacity. Consequently, zeolites often necessitate pre-drying of gas or higher regeneration temperatures to eliminate water.

Nevertheless, zeolites are robust and regenerable, and pressure swing adsorption (PSA) units employing zeolite 13X have been implemented for CO₂ capture from natural gas and syngas streams.

- *Metal–Organic Frameworks*: MOFs represent a relatively new class of porous materials. These materials are constructed from metal ion nodes interconnected by organic linkers, resulting in tunable crystalline structures. The considerable interest in MOFs as CO₂ adsorbents stems from their exceptionally high surface areas and the capacity for chemical tailorability. Through design, MOFs can be tailored with specific pore sizes and functionalities to optimize CO₂ adsorption. For example, MOFs featuring open metal sites can bind CO₂ through coordination, which is similar to chemisorption. A notable example is Mg-MOF-74, which demonstrates a strong affinity for CO₂ via coordinative bonding at its exposed Mg²⁺ sites. Other MOFs may also feature amine-functionalized linkers or polar groups to enhance CO₂ interactions. Many MOFs exhibit Langmuir-type isotherms characterized by a sharp initial increase in adsorption, with some displaying step-shaped isotherms (due to framework flexibility or site activation). A significant research focus from 2020 to 2025 has been on enhancing the stability and scalability of MOFs for industrial CO₂ capture, alongside the development of composite materials (MOF on structured supports, etc.). For example, Xu et al.[150] conducted a high-throughput computational screening of over 4000 MOF structures to assess their performance in post-combustion CO₂ capture, identifying 142 MOFs with superior predicted CO₂ separation capabilities in a PSA process (flue gas with 15% CO₂ at 1 bar, 298 K). The most effective MOFs typically featured open metal sites (e.g. Cu²⁺, Co²⁺, Mn²⁺) or functional groups such as amines and halogens that enhance CO₂ binding. This highlights the chemical tunability of MOFs for CO₂ capture, a feature not as readily available in traditional zeolites or carbons. Current research is focused on creating MOFs with increased capacities, improved CO₂/N₂ selectivity, and enhanced stability (e.g. water-resistant MOFs) to meet the requirements of carbon capture applications.
- *Amine-functionalized sorbents*: These materials are composites that integrate a high-surface-area support with chemically reactive amine groups, facilitating CO₂ capture through chemisorption. The supports can be constructed from porous silica, alumina, polymers, or MOFs, with amines introduced via grafting (covalently attached) or infusion (e.g. covalently attached or loaded polyethyleneimine). When these materials encounter CO₂, the amines react, producing ammonium carbamate or bicarbonate compounds, which efficiently extract CO₂ from the gas. These sorbents exhibit notable

CO₂ selectivity and capacity at low partial pressures (they are the basis for some direct air capture systems). In a representative mechanism, a zwitterion intermediate forms, followed by a carbamate ion pair, during the reaction between CO₂ and a primary amine. This process necessitates a second amine or water to act as a proton acceptor. However, this approach results in a high heat of adsorption ($\approx 70\text{--}90$ kJ/mol), akin to liquid amine solvents, necessitating substantial energy for regeneration. Consequently, these sorbents are typically regenerated using temperature swing adsorption (TSA) (heating to 100 °C - 120 °C to break the CO₂-amine bonds) rather than PSA. Current research endeavors in the early 2020s have been dedicated to the optimization of amine type and loading (to maximize CO₂ capacity while minimizing pore blockage and amine degradation) in CO₂ capture systems. Emerging chemisorbents incorporate sterically hindered amines, cyclic amines, or novel polymers to achieve improved performance. Additionally, solid alkali metal oxide/hydroxide sorbents (e.g. Na₂CO₃ on supports, lithium zirconate, magnesium oxide, etc.) are under investigation for their capacity to capture CO₂ through the formation of solid carbonates, such as the reaction between calcium oxide and CO₂ to produce CaCO₃ (a basis of the calcium looping process). These inorganic chemisorbents, which operate at elevated temperatures and are regenerated via calcination (CO₂ release at >800 °C), are typically implemented in pre-combustion or post-combustion capture scenarios. While offering rapid kinetics and high capacity, their high operating temperatures and susceptibility to sintering differentiate them from the low-temperature sorbents utilized in conventional TSA/PSA systems.

In summary, materials used in CO₂ capture applications encompass a spectrum from purely physical adsorbents (activated carbon, 13X zeolite, MOF-5, etc.) to purely chemical adsorbents (liquid amines, CaO, etc.), with a variety of hybrid approaches (amine-loaded solids, MOFs with reactive sites) also under investigation. An efficacious CO₂ adsorbent necessitates a combination of high capacity, adequate selectivity, rapid adsorption kinetics, facile regeneration, and sustained stability over repeated cycles. These benchmarks guide the continuous development of advanced sorbents. For real-world deployment, economic viability and material durability are also of paramount importance; consequently, researchers are focused on improving established sorbents (e.g. modifying carbons or zeolites) and discovering novel materials that can meet performance targets at scale.

Prior to investigating metal-based systems, our reactor system was initially benchmarked using PEI-impregnated silica, a CO₂ sorbent selected for its well-established characterization and widespread use. This calibration was essential for validating the performance and reliability of our experimental setup. The selection of PEI + silica as the benchmark material,

as detailed in Table 2.2, was based on considerations such as its known CO₂ adsorption behavior, commercial availability, and ease of handling.

2.4 Role and advantages of light energy in carbon capture

Harnessing light energy, whether derived from solar radiation or engineered light (e.g., LEDs, lasers, IR lamps) emitters, offers multifaceted approaches to diminish the energetic penalty associated with CO₂ capture and regeneration.

- *Renewable and abundant nature* : Solar energy is widely considered one of the most plentiful renewable resources available. The majority of regions throughout the world receive considerable sunlight, with most of the global population residing in areas that experience an average of 3–5 kWh of solar energy per square meter per day [129]. Even regions exhibiting the lowest solar yields still acquire approximately half the insolation observed in the highest-yield regions, indicating a globally distributed solar resource, albeit with some geographic variation [129]. Consequently, the widespread accessibility of solar power makes it a potentially reliable candidate for driving energy-intensive processes, such as carbon capture, on a global scale.

The potential of solar energy, in theoretical terms, exceeds global energy requirements by several orders of magnitude. It has been estimated that the Earth's surface is exposed to solar irradiation that is approximately 200,000 times the world's total daily electricity demand [133]. Meeting the projected worldwide energy consumption for 2030 could be achieved by covering an area equivalent to the size of Spain with solar panels operating at 20% efficiency [133]. Studies suggest that utilizing only $\approx 1\%$ of the available renewable solar resource could supplant the current reliance on fossil fuels; however, current exploitation levels are at $\approx 0.01\%$ of daily solar irradiance [67]. Furthermore, the technical potential of solar energy is approximately 100-fold greater than the global energy demand of today [67]. These metrics emphasize the practically unbounded capacity of solar power. Solar energy's renewable and carbon-free characteristics, coupled with ongoing improvements in cost-effectiveness and efficiency, establish it as a promising driving force for sustainable carbon capture technologies.

- *Sustainability and environmental impact*: Traditional carbon capture methods often utilize temperature swing adsorption, which involves heating a sorbent to release CO₂, or pressure swing adsorption, which reduces pressure to desorb CO₂. Both of these methods are energy-intensive; for example, in amine-based post-combustion capture,

Table 2.2 Design criteria and supporting literature for choosing PEI-infused mesoporous silica as the CO₂ sorbent and a regeneration temperature of $\approx 110^\circ\text{C}$

Requirement for a sorbent	How PEI+silica meets it	Reference
High CO ₂ capacity at low partial pressure	Branched or linear PEI offers a substantial amine concentration, enabling a working capacity of 1.5 mmol g^{-1} - 2 mmol g^{-1} even at 400 ppm CO ₂ , which surpasses the performance of many MOFs and zeolites.	Early DAC proof-of-concept on nano-silica [157].
Fast mass-transfer kinetics	The utilization of mesoporous or fibrous silica serves to decrease the length of diffusion pathways, facilitating rapid reaction with CO ₂ due to the presence of amine in the form of a liquid film.	KCC-1 fibrous silica cut diffusion resistance vs. MCM-41 while boosting uptake by $\sim 25\%$ [122].
Regeneration with low-grade heat	The thermal decomposition of carbamate and bicarbonate compounds formed on PEI occurs between 90°C and 120°C , enabling CO ₂ desorption using lower-grade heat sources such as waste steam or 100°C hot water. This contrasts with aqueous amine systems that require higher temperatures, typically in the 120°C - 180°C range, for efficient desorption.	Multi-cycle steam TSA at 110°C showed $\leq 10\%$ capacity loss in 20 cycles [115].
Stability and oxidative tolerance	The neutral oxide surface of silica provides an inert matrix, physically anchoring PEI without introducing catalytic degradation. Maintaining regeneration temperatures at $\leq 110^\circ\text{C}$ and oxygen levels at $\leq 3 \text{ vol } \%$ minimizes oxidative imide formation.	Spectroscopic studies identify a sharp rise in PEI oxidation $\geq 120^\circ\text{C}$ in air [132].
Scalability & cost	Silica, whether in fumed or gel form, is available at an industrial cost of less than $\$3 \text{ kg}^{-1}$, while PEI is priced at $\$4 \text{ kg}^{-1}$ - $\$6 \text{ kg}^{-1}$ in bulk. Both substances are non-toxic, commercially accessible, and are already in use in direct air capture pilot projects at scales of over one kilotonn.	Cost and pilot data summarised in recent regeneration review [4].

regenerating the solvent with steam can consume a substantial portion of a power plant's energy output [80]. This energy is frequently derived from burning additional fuel or utilizing grid electricity, which increases CO₂ emissions and diminishes the net environmental benefits of CO₂ capture. In contrast, solar-driven regeneration harnesses energy directly from sunlight, significantly decreasing reliance on fossil fuels and related emissions. Research indicates that integrating solar heat into a capture process can substantially decrease the parasitic energy load; for instance, substituting solar thermal energy for steam in a CO₂ scrubber reduced the net efficiency penalty from over 10% to approximately 6.9% [80]. Solar-based CO₂ desorption essentially shifts a significant portion of the energy demand to a clean, external source, thereby reducing the carbon footprint of the capture cycle.

A key advantage of solar photothermal regeneration lies in its potential for enhanced energy efficiency and targeted application. Conventional heating strategies often involve increasing the temperature of the entire sorbent bed or solvent volume. In contrast, photothermal techniques enable the localization of heat at the micro or nanoscale. For example, the introduction of light-absorbing nanoparticles into a CO₂-rich amine solution, followed by irradiation, can generate localized hot spots, facilitating the formation of vapor bubbles that strip CO₂ without requiring uniform heating of the bulk solvent [92]. This selective heating minimizes energy waste compared to methods that heat an entire material column. Overall, solar-based regeneration offers a cleaner operational profile, producing virtually no direct emissions during operation, and promotes greater lifecycle sustainability. By leveraging sunlight to drive CO₂ release, the process avoids the combustion of additional fuel or reliance on grid electricity, thereby aligning carbon capture with renewable energy goals [92]. Although practical challenges remain, the environmental benefits are clear: photothermal or photo-assisted CO₂ desorption can substantially reduce the energy intensity and greenhouse gas emissions associated with carbon capture when compared to conventional thermal or pressure-swing approaches [92]. In the long term, integrating carbon capture with abundant solar energy provides a pathway towards more sustainable and potentially carbon-negative operations.

- *Potential integration with carbon capture technologies:* Solar-assisted CO₂ capture can be developed through experimental methodologies that employ light to facilitate or enhance CO₂ release from sorbent materials. Generally, these approaches fall into two categories: photothermal regeneration, wherein sunlight is converted into heat within the adsorbent/absorbent system to accelerate CO₂ desorption. In both scenarios, the objective is to utilize photons as a substitute for, or supplement to, traditional thermal energy inputs. This is sometimes referred to as light-induced swing adsorption (LISA),

analogous to pressure or temperature swing methods, where changes in light exposure modulate CO₂ binding affinity [102, 79, 78].

Photothermal methods utilize materials that efficiently absorb light and convert it into heat, increasing the local temperature of the CO₂-loaded sorbent. A seminal experiment employed a nanofluid composed of carbon nanoparticles in a monoethanolamine solution [92]. Upon illumination, the nanoparticles heated up, generating minute vapor bubbles within the liquid, thereby facilitating CO₂ desorption in situ. Notably, this process occurred without the necessity of heating the bulk solvent to its boiling point; the CO₂ was expelled around the heated nanoparticle surfaces [92]. This localized photothermal boiling resulted in a regeneration rate of approximately 3.6 mol CO₂ per MJ of incident light in initial experiments, and subsequent optimizations led to improved efficiency. For instance, the addition of co-solvents to modulate fluid properties resulted in an enhancement of over 200% in CO₂ release efficiency compared to the baseline process [92]. Photothermal regeneration has also been demonstrated in continuous-flow packed-bed architectures. For example, a composite packed bed of graphite–TiO₂ microparticles was recently developed to facilitate CO₂ desorption under simulated solar light [21, 20]. The study [21] demonstrated continuous flow operation, achieving an average regeneration efficiency of 64% for CO₂ release, driven solely by light input without any additional heating. Collectively, these results highlight the promise of integrating photothermal functionality into capture media so that illumination produces a rapid, localized temperature rise that directly drives CO₂ release.

Recent work increasingly targets multifunctional materials that combine sorption capacity with strong photothermal response, reducing reliance on external heaters. For instance, an azo-functionalized cobalt MOF acted as an intrinsic nano-heater, exhibiting an estimated photothermal conversion efficiency of $\approx 20.3\%$ under near-infrared light, resulting in a temperature increase of around 53 °C in less than 3 minutes of irradiation, while maintaining a high CO₂ capacity [28]. Such designs illustrate a pathway to “internally heated” sorbents, where sunlight can supply the desorption driving force within the material itself.

Concurrently, investigations are focusing on photoactive sorbents that exploit light-induced alterations in chemical structure to enable CO₂ capture and release. Metal-organic frameworks incorporating photosensitive ligands or guest molecules represent a significant class of such materials. Upon illumination, these MOFs undergo reversible modifications that modulate either the pore size or the CO₂ adsorption affinity, facilitating CO₂ desorption via irradiation with specific wavelengths, thereby circumventing

thermal activation. For example, a Cu-azobenzene MOF demonstrated notable photo-switching behavior, exhibiting a $\approx 51\%$ reduction in CO_2 uptake under UV light at 273 K relative to dark conditions, indicating substantial CO_2 liberation upon UV exposure at low temperatures [102]. This light-triggered desorption is also fully reversible. More broadly, Luo et al. [28] reported a MOF, functionalized with diarylethene ligands, that achieved approximately 75% CO_2 desorption capacity under UV light exposure [28]. Furthermore, a related framework incorporating azobenzene derivative ligands exhibited approximately 78% reversible CO_2 capture/release performance upon UV irradiation. Importantly, cyclability and tolerance to realistic environments remain central requirements for deployment: for example, PCN-250 was reported to release appreciable CO_2 under UV illumination while retaining structural integrity over repeated cycles, including under humid conditions [79]. Together, these studies suggest that solar-assisted regeneration can be realized either through photothermal heating (light-to-heat conversion) or true photo-switching (light-modulated affinity), with ongoing research focused on improving swing magnitude, optical/thermal efficiency, and long-term stability under practical operating conditions.

2.5 Problem statement and need for solar-assisted CO_2 capture research

2.5.1 Limitation of conventional capture methods

Traditional CO_2 capture technologies, such as chemical absorption with amine solvents and cyclic adsorption processes, are inherently limited. These limitations include high energy demands and regeneration costs, as amine scrubbing, a benchmark post-combustion capture method, requires considerable heat input to strip CO_2 from the solvent, resulting in significant energy penalties and operational costs [23]. Similarly, adsorption-based methods like PSA necessitate substantial electricity for gas pressurization or vacuum, while TSA relies on thermal inputs, making both energy-intensive. Furthermore, these processes exhibit operational complexity and maintenance issues, as they involve multiple stages and often use corrosive or degradable materials. Amine solvent systems, for example, face solvent degradation and equipment corrosion, along with challenges like foaming and solvent losses, complicating operation and increasing maintenance requirements. Scalability also presents a challenge, as scaling up conventional capture to handle large emission sources or dilute streams is difficult due to the massive throughput and energy requirements. Large industrial CO_2 sources would require very high sorbent/solvent circulation rates and enormous energy

for regeneration, posing significant engineering and logistical challenges [23]. In practice, the need for robust materials that can withstand repeated cycles without significant performance loss is another concern, as current absorbents/adsorbents tend to degrade over time, which can further increase costs and reduce long-term efficiency [23]. These limitations underscore the need for alternative capture approaches that are more energy-efficient, simpler to operate, and easier to scale.

2.5.2 Gaps in Understanding and Development of Solar-Assisted CO₂ Capture Technologies

Solar-assisted CO₂ capture technologies have emerged as a potentially advantageous strategy for overcoming the inherent limitations of conventional methodologies. These systems aim to harness solar energy, either through photothermal conversion or light-induced chemical mechanisms, to facilitate CO₂ capture and subsequent release, thereby minimizing the reliance on external energy inputs. For example, specifically engineered sorbent materials can convert sunlight into thermal energy to promote CO₂ desorption, or modulate their binding affinity upon irradiation, enabling controlled CO₂ release. This concept offers a compelling route to reduce the dependence on fossil-derived heat or electricity for carbon capture processes [155]. However, the development of solar-driven CO₂ capture remains in its nascent stages, and several critical knowledge gaps and challenges must be addressed:

- *Low technology readiness*: The majority of solar-assisted capture technologies are in preliminary phases of development, specifically at the laboratory or prototype level, which impedes their immediate commercial deployment. A significant number of photo-responsive sorbents have yet to undergo testing within realistic direct air capture settings, thus their actual viability is yet to be determined [155]. Present photothermal regeneration systems also necessitate marked enhancements in efficiency before they can effectively substitute conventional steam-driven systems [155]. In aggregate, the technology readiness level of these methodologies is currently low, highlighting the imperative for extensive research and development efforts to facilitate progression towards pilot and industrial implementation stages.
- *Limited scalability*: The scalability of solar-driven CO₂ capture technologies is constrained by materials-related and design-based challenges. The integration of photochromic compounds or specialized nanoparticles in advanced sorbents can be either expensive or limited to laboratory-scale synthesis, thereby impeding large-scale production and increasing costs [106]. Furthermore, the implementation of practical solar

capture units necessitates the integration of solar collectors or light delivery systems suitable for processing vast gas volumes, which presents a non-trivial engineering problem. Scaling these technologies to handle meaningful CO₂ flows remains contingent upon breakthroughs in both material science and system design.

- *Insufficient kinetic and mechanistic understanding:* A significant knowledge gap persists regarding the kinetic and mechanistic performance of these novel systems when subjected to real-world operating conditions. Key areas requiring further investigation include the fundamental adsorption and desorption rates under light stimulation, the efficiency of light-to-thermal energy conversion in packed sorbent beds, and the mechanisms governing CO₂ binding and release in photo-switchable materials. For example, empirical data from photothermal systems often reveal regeneration efficiencies that fall short of expectations, potentially stemming from incomplete heat delivery or suboptimal light absorption [155]. Likewise, the observed differences in CO₂ uptake between light and dark states in photoswitchable adsorbents can be marginal, necessitating further research into the underlying molecular mechanisms. Enhancing reaction kinetics and pinpointing the rate-limiting steps are therefore essential to facilitate the design of more effective solar-driven capture processes.
- *Integration barrier:* The integration of solar-assisted CO₂ capture into continuous industrial operations is fraught with challenges. A primary concern is the intermittency of solar availability, which contrasts with the around-the-clock operational requirements of many capture processes. This necessitates sophisticated designs to ensure consistent CO₂ removal. Another significant integration barrier lies in the physical design of reactors to effectively accommodate light irradiation. For instance, the limited penetration depth of UV light, required by some photo-switchable sorbents, mandates the use of thin sorbent layers [106], which drastically reduces volumetric efficiency and may require a fundamental re-engineering of contactors, moving away from conventional packed columns. Furthermore, coupling solar thermal collectors to amine scrubbers presents non-trivial engineering problems; research indicates that indirect integration is often more practical than direct solvent heating due to control and temperature-matching considerations. Therefore, the development of viable integration schemes that allow solar energy to augment CO₂ capture without disrupting existing industrial processes remains a significant challenge [155].
- *Material stability:* The long-term operational stability of photo-assisted capture materials represents a critical concern. The limited cycling of many materials in laboratory conditions raises questions about their capacity to withstand extended periods of

sunlight exposure, adsorption, and desorption processes. Potential photochemical fatigue or irreversible structural changes could diminish performance, underscoring the importance of ensuring high fatigue resistance and sustained CO₂ capacity over extended durations. Demonstrating stability under real-world conditions is thus essential. Robustness and durability, therefore, constitute key research gaps, as any viable solar-driven system will necessitate materials that retain effectiveness after prolonged use in practical environments [106].

2.6 Why investigate metallic substrates for light-assisted CO₂ capture?

Although a substantial corpus of research on light-assisted CO₂ capture centers on porous adsorbents and photoresponsive frameworks, these systems encounter significant scale-up challenges pertaining to light delivery, mechanical durability, and reactor integration. Specifically, the shallow penetration depth of UV/visible light compels the use of thin sorbent layers, thereby curtailing volumetric productivity and precluding conventional packed-column configurations. Concurrently, existing capture technologies are constrained by high regeneration energy requirements and operational complexity, prompting the exploration of alternative materials and architectures that facilitate simplified regeneration while maintaining resilience across repeated cycles.

In this regard, metals provide a compelling and complementary material class for light-assisted regeneration for three main reasons:

- Meshes, foams, monoliths, coated plates, and other metallic substrates are thermally stable, mechanically robust, and already produced in large quantities with precise geometry. For continuous-flow capture hardware, where pressure drop, heat management, and long-term cycling stability are crucial design constraints, this makes them appealing. Metallic structures can be used as self-supporting beds or structured reactors, providing useful illumination pathways without the need for delicate thin films, in contrast to some photochromic or nanoparticle-based sorbents that might be costly or challenging to scale.
- They couple strongly to light through photothermal and photoelectronic pathways - Metals absorb electromagnetic radiation through their conduction electrons, enabling incident light to be transformed into (i) localized heating and/or (ii) non-equilibrium electronic excitations (“hot” carriers). These two pathways are the same as the two

desorption routes discussed in Section 2.7. This makes metallic substrates a natural place to study how light changes the effective desorption kinetics.

- Their CO₂ binding can be tuned systematically by electronic structure and composition
 - A central hypothesis motivating this thesis is that CO₂ adsorption on transition-metal surfaces can be modulated by changes in surface electronic structure, including transient charge redistribution under illumination and compositional tuning through alloying. This provides a physically interpretable pathway to engineer “just-strong-enough” binding: sufficiently robust to sequester CO₂, yet sufficiently feeble (in the presence of light) to facilitate regeneration at a lower thermal cost. Metals are the best link between molecular-scale mechanisms and reactor-scale performance because you can calculate adsorption energetics and charge transfer from first principles and then test the results in the lab.

Taken together, metallic substrates offer an investigation route that directly targets the key bottleneck identified earlier, reducing regeneration energy while maintaining operational simplicity and scalability. Accordingly, the next section (Section 2.7) introduces the theoretical basis for light-driven CO₂ desorption from metallic surfaces, focusing on photochemical (electron-transfer) and photothermal mechanisms.

2.7 Theory of Photo-Desorption of CO₂ from Metallic Surfaces

The desorption of CO₂ from a metal surface exposed to light can occur through two main mechanisms: *photochemical* (*photo-induced electronic*) and *photothermal* mechanisms. In photochemical desorption, often referred to as *photon-stimulated desorption* (PSD), incident photons (i.e. the light quanta) trigger electronic excitations that reduce the strength of the bond between the adsorbate and the surface. This process imparts kinetic energy to the CO₂ molecule, enabling its release. Alternatively, the photothermal mechanism involves the conversion of absorbed light energy into heat, leading to an increase in the local surface temperature and subsequent thermal activation of CO₂ desorption. These mechanisms may function independently or synergistically. The following sections will provide a detailed analysis of each mechanism, utilizing quantum-level theory to explicate the underlying processes, and incorporating relevant models and equations (for activation energies, desorption rates, and transition probabilities).

2.7.1 Photo-Induced Electron Transfer Mechanism (Photochemical Desorption)

Within the photochemical mechanism, the interaction of incident photons with the metal-adsorbate system results in the generation of excited electronic states, which, in turn, weakens or cleaves the metal-CO₂ bond. The high electronic density of states in metals facilitates photon (typically in the UV or visible range) absorption, promoting electrons from occupied states below the Fermi level to unoccupied states above it. These energized “hot” electrons (or the corresponding holes left behind) can then be transferred to the adsorbate, in this case, the CO₂ molecule, or otherwise interact with it. A conventional description posits that hot electrons scatter into an unoccupied orbital of the adsorbed CO₂, leading to the transient formation of a negative-ion state of the molecule (CO₂⁻). This temporary charging of the adsorbate exerts substantial effects on bonding: the occupation of an anti-bonding orbital following electron addition to CO₂ can induce a transformation from a linear CO₂ configuration to a bent anion, which exhibits a diminished binding affinity for the surface relative to the neutral CO₂ species. As a result, electronic excitation can lead to the weakening or inversion of the metal-CO₂ bond into a repulsive interaction.

Non-adiabatic, Franck–Condon Excitation

Given the disparity in time scales between electronic transitions and nuclear motion, excitation can be modeled as a vertical transition (an application of the *Franck–Condon* principle) on the system’s potential energy surface (PES). The adsorbate’s center-of-mass position is effectively static during the photon-induced electronic transition. Figure 2.3 illustrates this concept, depicting potential energy surfaces for adsorbed CO₂ on the metal. The ground-state PES (blue curve) features a potential well, representing chemisorbed or physisorbed CO₂ bound with a defined adsorption energy. Photo-excitation induces a vertical transition to an excited-state PES (red curve), which is more repulsive and indicative of a state with an altered charge distribution (e.g. an antibonding or negative-ion state). Post-excitation (denoted by the vertical arrow $h\nu$ in Figure 2.3), the CO₂ molecule occupies a higher-energy surface. If this excited PES is repulsive, the molecule accelerates away from the surface, converting electronic energy into kinetic energy. This is characteristic of *Menzel-Gomer-Redhead* (MGR) photodesorption, where the excited state lacks a bound minimum, leading to immediate desorption. From a quantum mechanical perspective, the likelihood of a photon-induced electronic transition occurring within a given time frame can be quantified using Fermi’s

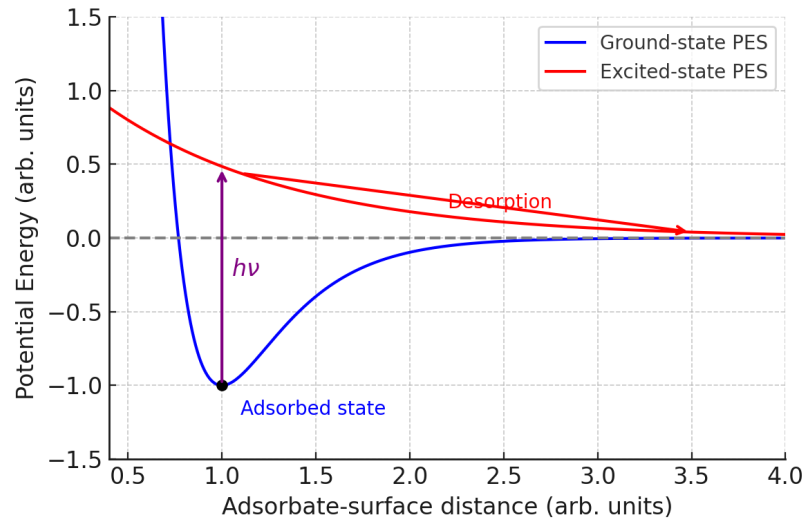


Fig. 2.3 Schematic potential energy surfaces for photodesorption of an adsorbed molecule.

Golden Rule, which (for an initial state $|i\rangle$ and final state $|f\rangle$) is given by:

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle \Psi_f | \hat{H}' | \Psi_i \rangle|^2 \rho(E_f), \quad (2.3)$$

where $\hat{H}'$ represents the Hamiltonian for the interaction between light and matter, and $\rho(E_f)$ signifies the density of final states at the transition energy. This reinforces that the transition rate (and thus photodesorption yield) is contingent on both the square of the electronic coupling matrix element connecting initial and excited states, and the accessibility of final states. Within a metal, the high density of electronic states, denoted as $\rho(E)$, implies a multitude of available final states for an excited electron. However, it also suggests that the excited electron can readily dissipate energy through scattering into alternative states. Consequently, non-adiabatic effects are intrinsic, potentially leading the system to undergo multiple electronic transitions (excitation and rapid de-excitation) throughout the desorption process.

The Menzel-Gomer-Redhead model

The Menzel-Gomer-Redhead (MGR) model, introduced in 1964, represents one of the first theoretical frameworks for explaining the photodesorption of neutral species from metallic surfaces and captures the core principles of this process. Within the MGR framework, also known as the “negative ion” model in surface photochemistry, the adsorbate initially resides in its electronic ground state ($M + A$), characterized by an equilibrium bond length at the surface. The absorption of a photon triggers an immediate electronic transition to a

metastable excited state of the system, typically involving either an antibonding neutral state or an ionic state (where charge has transferred between metal (M) and adsorbate (A)) of the adsorbate. A key feature of this model is the displacement of the excited-state potential energy surface relative to the ground-state PES (as in Figure 2.3). This displacement leads to two possible scenarios:

1. When the system persists in the excited state for an extended period (adiabatic desorption), the molecule is able to move along the repulsive potential energy surface and subsequently detach from the surface as a neutral (CO_2) molecule. Its translational energy is converted from the difference in potential energy. This process effectively involves the photon providing a near-direct impulse to the molecule through the force exerted by the excited state.
2. Alternatively, if the electron undergoes rapid non-adiabatic de-excitation back to the ground state while the molecule is in close proximity to the surface, the molecule returns to the ground-state PES but with increased vibrational energy (because it was set in motion on the excited surface). This additional energy may elevate the molecule to a highly excited vibrational state within the ground potential; should this energy exceed the desorption threshold (the adsorption energy), the molecule can still escape from the surface while in the ground state. Conversely, it will be recaptured into the bound state (energy dissipation to the lattice will eventually remove the excess energy).

It is worth noting that alongside the MGR mechanism, alternative pathways, including the *Antoniewicz* model, can occur. In the *Antoniewicz* model, photon excitation leads to an ionic state ($M^+ + A^-$ or $M^- + A^+$) characterized by an initial attractive potential for the adsorbate, contrasting the repulsive potential in the MGR model. The adsorbate experiences a momentary attraction (due to image-charge attraction of the ionic adsorbate) toward the surface, gaining inward kinetic energy, followed by de-excitation. If appropriately timed, the acquired kinetic energy can propel the molecule outward on the ground state, enabling it to overcome the adsorption well. Both the MGR and *Antoniewicz* models represent specific instances of *Desorption Induced by Electronic Transitions* (DIET). Advanced theoretical approaches employ time-dependent quantum wave-packet simulations on multiple potential energy surfaces to comprehensively elucidate these non-adiabatic processes.

From a kinetic perspective, one can describe photodesorption in terms of a desorption rate or a cross-section per photon, details of which are in the appendix A. To conclude, it is important to note that on metal surfaces, electronic excitations exhibit short lifetimes (on the order of femtoseconds to picoseconds) due to rapid electron-electron and electron-phonon scattering processes within the metal. Consequently, adsorbates possess a limited timeframe

to respond to excited-state forces. If the molecule does not gain enough momentum in that time, it will relax with the surface and not desorb. Conversely, semiconductor or insulator surfaces, characterized by longer excited-state lifetimes, may exhibit behavior more akin to adiabatic motion on a well-defined excited potential energy surface. However, in the case of metals, the continuum of electronic states necessitates the consideration of non-adiabatic transitions and ultrafast dynamics in theoretical descriptions of photodesorption.

2.7.2 Photothermal Enhancement Mechanism (Local Heating and Plasmonic Effects)

An alternative mechanism for photon-induced desorption involves an indirect process mediated by thermal effects. In this scenario, the primary role of light is not to induce a specific electronic excitation within the adsorbate, but rather to deposit energy into the metal lattice as heat, consequently elevating the surface temperature, denoted as (T_{surf}). Effectively, the introduction of light reduces the activation energy barrier by supplying thermal energy. It is important to note that this mechanism does not necessitate a specific electronic transition within the molecule beyond those inherent in thermally activated processes. This indirect mechanism is particularly relevant under conditions such as continuous-wave or long-pulse irradiation, high laser fluences that induce significant heating, and in systems incorporating plasmonic metal nanostructures, which efficiently convert light into thermal energy.

Thermal desorption basics

In the absence of light, the rate of thermally induced desorption is governed by the Arrhenius equation. Specifically, for a first-order desorption process, the rate equation can be expressed using the Polanyi–Wigner form:

$$r(\Theta) = -\frac{d\Theta}{dt} = \nu\Theta^n \exp\left(-\frac{E_{des}}{k_B T_{surf}}\right) \quad (2.4)$$

Here, Θ represents the surface coverage (which may influence the order n of desorption), ν is the pre-exponential factor (attempt frequency for desorption), and E_{des} denotes the activation energy required for desorption (which for an adsorbed molecule is approximately the binding energy to the surface). Notably, the rate exhibits exponential sensitivity to temperature T : even a modest elevation in local temperature can substantially enhance the desorption rate. This is because the Boltzmann population of molecules possessing energy exceeding E_{des} increases sharply with increasing temperature. As illustrated in Figure 2.4, a comparison of Boltzmann energy distributions at lower and higher temperatures reveals this principle. The

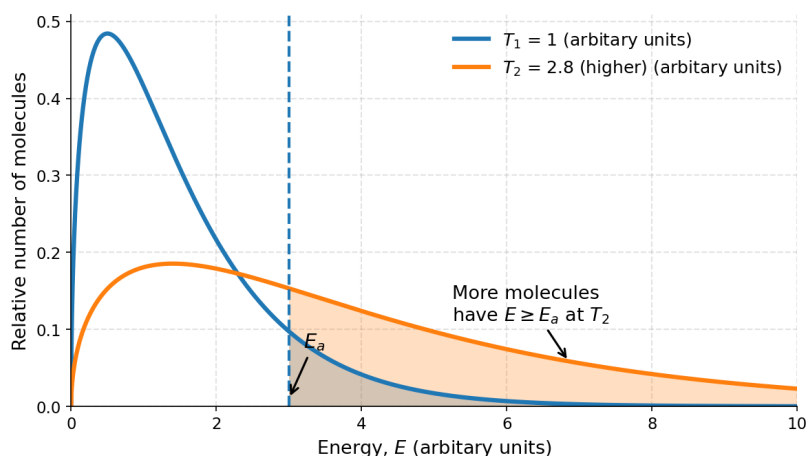


Fig. 2.4 Thermal activation and the role of temperature in desorption. The plot shows a schematic Boltzmann distribution of molecular energy at two temperatures.

shaded region to the right of E_{des} indicates the proportion of molecules with sufficient energy to undergo desorption. At elevated temperatures, this fraction becomes considerably larger, thereby increasing the likelihood of desorption.

The absorption of light by a metal surface leads to a portion of the incident energy being converted into lattice vibrations (phonons), thereby increasing the temperature of the material. This process can occur through several pathways. In a planar metal surface, interband or intraband absorption results in the excitation of electrons, which subsequently thermalize with the lattice (within picoseconds) via electron-phonon scattering, dissipating energy as heat. Notably, nanostructured metal surfaces, particularly those that support *localized surface plasmon resonances* (LSPR), can exhibit highly efficient photothermal conversion. This involves the non-radiative decay of collective oscillations of conduction electrons (plasmon) into energetic electrons, which subsequently thermalize, producing heat. Essentially, the metal nanoparticle functions as a nano-heater. Due to its small volume, the local temperature of a nanoparticle (or nanostructure) can significantly increase upon absorption of even a modest amount of energy, and this heat remains localized near the surface where adsorbates are situated.

When incident light is tuned to the plasmon resonance of the metal (e.g., the plasmon band of a gold nanoparticle at ~ 520 nm), the absorption cross-section is substantially enhanced, leading to the conversion of nearly all photon energy into thermal energy via Landau damping of the plasmon within an ultrashort duration. This engenders high local temperatures at specific hotspots, a photothermal effect leveraged in applications such as plasmonic nanoparticles for photothermal cancer therapy, owing to their ability to generate intense local heat. In the context of CO_2 desorption, plasmonic photothermal heating can

facilitate desorption *by lowering the effective barrier*. The CO₂ molecules in the heated region experience increased thermal energy, thus diminishing the additional energy required for escape. From the Arrhenius perspective, light does not directly alter E_{des} but increases T , thereby increasing the factor $\exp(-\frac{E_{des}}{k_B T_{surf}})$. This can be formulated as an apparent reduction of the required activation energy due to the thermal excitation. Under purely photothermal illumination, the desorption barrier E_{des} is not altered; illumination raises the local surface temperature (T_{surf}), which increases the Arrhenius rate. Any genuine reduction in the barrier arises only from photo-induced electronic effects (e.g., transient population of antibonding states), not from heating per se.

In essence, ***both mechanisms typically function in conjunction***: photons generate hot carriers, instigating electronic bond weakening, and subsequently convert into thermal energy, thereby increasing the local temperature. Consequently, a thorough analysis and modeling of photodesorption necessitates a multifaceted approach. Such an approach should integrate quantum mechanics, to account for rapid electronic events, with statistical mechanics, for the slower thermal effects, to comprehensively elucidate the light-mediated removal of CO₂ from metal surfaces. Therefore, the subsequent sections of this chapter will transition from a qualitative examination of mechanisms to the theoretical frameworks required to quantitatively analyze the mechanisms discussed in Section 2.7. Section 2.8 will delineate the core quantum mechanical principles relevant to adsorbate-surface interactions. Section 2.9 will revisit the Schrödinger equation and its associated approximations for extended systems. Section 2.10 will introduce DFT, the first-principles method employed throughout this thesis to compute adsorption energies, ground-state structures, and other electronic properties pertinent to CO₂ adsorption on transition-metal substrates. Finally, Section 2.11 will introduce the "breakthrough curve" experimental methodology employed to ascertain the adsorption capacity of different materials within this study.

2.8 THEORETICAL PARTS

Within the physical domain, any observable effect is attributable to one of the four fundamental forces: electromagnetism, the strong nuclear force, the weak nuclear force, and gravitation. However, in the context of materials science, electromagnetic interactions are of primary relevance, thereby allowing for the exclusion of the other forces from consideration. The diverse phenomena observed in materials under varying conditions can be attributed to electromagnetic interactions between their subatomic particles. First-principles methods consider nuclei and electrons as fundamental particles, elucidating events at the subatomic level. Consequently, the system can be represented using quantum mechanics, which involves

complex partial differential equations. First-principles calculations rely solely on the atomic numbers of the constituent atoms for simulations, without the need for external parameters. Accurate descriptions of these interactions enable the evaluation of all experimentally relevant properties and phenomena for any material, hence their designation as first-principles methods. A range of techniques can be applied to address specific problems. First-principles methodologies employ electrons, nuclei, and their interactions as essential elements, operating without the need for empirical data and providing a robust characterization of interatomic interactions in varied conditions. Density functional theory, which emphasizes electron density, represents a significant advancement, enabling the application of ab initio methods to increasingly complex systems. Consequently, electromagnetic properties and bond formation/breakage can be evaluated using these first-principles methods. This approach has been employed to compute lattice constants and crystal structures in ground-state energy configurations, as well as to determine atomic forces and various structural and electronic properties.

Basics of quantum theory

Quantum theory can be used to describe matter at the fundamental level if we ignore relativistic effects. The main characteristic of this theory is the multi-body wavefunction:

$$\Psi(r_1, r_2, \dots, t)$$

Here, $r_1, r_2, \dots$, etc., corresponds to position vector (x,y,z) of all elementary particles in the system (like protons, electrons, neutrons). The wavefunction takes on a complex estimation, of the form $a + bi$ and advances in time, t . The physical importance of the wavefunction is that, $\{\Psi^*(r_1, r_2, \dots, t) \Psi(r_1, r_2, \dots, t)\}$ is proportional to the joint probability of particle one is at r_1 , and particle 2 is at r_2 , etc, all at the time t ($\rho(r_1, r_2, \dots; t)$).

Here $*$ denotes the complex conjugate, i.e., $a - bi$. Therefore, the quantity $\Psi^*\Psi$ is always positive and real, $a^2 + b^2$.

$$\rho(r_1, r_2, \dots; t) \propto \Psi^*(r_1, r_2, \dots, t) \Psi(r_1, r_2, \dots, t) \quad (2.5)$$

In contrast to Newtonian mechanics, where particles are considered to have definite positions at any given time, quantum mechanics employs the wavefunction to describe the evolution of probabilistic states. This implies a fundamental limit to the precision with which particle positions can be known, suggesting that predicting probabilities is the most accurate assessment achievable due to inherent randomness at the quantum level.

This concept might seem unusual because we are unaccustomed to such behavior on a macroscopic scale. Indeed, for larger objects, these probability distributions are narrowly focused

relative to the object's size. Consequently, from a macroscopic measurement perspective, we can typically determine an object's location in space with precision. However, for small objects, such as atoms and electrons, these distributions become significant.

2.9 Schrödinger equation

Atoms, the fundamental constituents of materials, are composed of electrons and nuclei. The total energy of a material is essentially the sum of the kinetic energies of its subatomic particles and the interactions among them. These interactions are Coulombic, encompassing nucleus-electron, nucleus-nucleus, and electron-electron forces. The potential established by the nuclei of different atoms governs electronic states. Solving the time-independent Schrödinger equation yields the system's ground state total energy. This equation, a linear partial differential equation, elucidates the wave function or state function of a quantum-mechanical system.

The general time-dependend wave equation of Schrödinger is expressed as [85]:

$$\hat{H}\Psi(r_i, r_I, t) = E\Psi(r_i, r_I, t) \quad (2.6)$$

Here, $\hat{H}$, Ψ , and E are the Hamiltonian operator, wave function, and system energy, respectively. The variables r_I , and r_i are the coordinates corresponding to nucleus and electron, respectively. In the aforementioned equation, all components, including electrons, nuclei, and time variables, actively contribute through wave functions. This system is exceedingly complex and can only be evaluated for single-electron systems (hydrogen-like). Without critical assumptions, the equation lacks feasibility. The subsequent assumptions are adopted to facilitate this method.

1. Neglecting gravity, relativity, and time
2. Skip nucei and spin
3. Neglecting about the excited states

By applying the aforementioned approximations, the resultant equation is simplified, yielding what is known as the time-independent electronic wave equation, is given as:

$$\hat{H}(r)\Psi(r) = E\Psi(r) \quad (2.7)$$

where $\hat{H}(r)$, $\Psi(r)$, and E are the Hamiltonian energy operator, electronic wave function, and the total electronic energy of the system respectively and it is given as:

Energy operator: Hamiltonian,

$$\hat{H} = E_i^{kin} + U_{Ii} + U_{ij} \quad (2.8)$$

In equation (2.8) the first term is kinetic energies of n electrons, and can be written in an atomic unit by

$$E_i^{kin} = -\frac{\hbar^2}{2m} \sum_i^n \nabla_i^2 = -\frac{1}{2} \sum_i^n \nabla_i^2 \quad (2.9)$$

where ∇^2 is the Laplacian operator given as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad (2.10)$$

the second term is attractive potential energies of n electrons due to the nuclei, and is given as

$$U_{Ii} = -\sum_I^N \sum_i^n \frac{Z_I}{|r_{Ii}|} \quad (2.11)$$

where n and N are the number of electrons and nuclei in the system, and Z_I are the charges of the nuclei. To consider the complete interaction from all electrons to all nuclei double sum is being incorporated. The third term, denotes the repulsive potential energies of n electrons between each other, since it is double counted therefore to give that correction it is given with the usual correction factor of $1/2$:

$$U_{ij} = \frac{1}{2} \sum_{i \neq j}^n \frac{1}{|r_{ij}|} \quad (2.12)$$

Adding all these together, the Hamiltonian operator, $\hat{H}$, is therefore given by

$$\hat{H} = -\frac{1}{2} \sum_i^n \nabla_i^2 - \sum_I^N \sum_i^n \frac{Z_I}{|r_{Ii}|} + \frac{1}{2} \sum_{i \neq j}^n \frac{1}{|r_{ij}|} \quad (2.13)$$

Despite the simple looking, Schrödinger wave equation, solving it and evaluating a property out of that is very complicated. It works perfectly for simple systems such as hydrogen, or helium. Therefore for considering a many-body effect, various levels of approximations like the Hartree method, Hartree-Fock method, etc., have been given without losing the parameter-free nature of the first-principles methods. The major advancement at last happened when Hohenberg and Kohn [57] in 1964 introduced two hypothesis relating electron density and

energy functionals, and Kohn and Sham [69] in 1965 came up with an extraordinary method based on these theorems called the *density functional theory* (DFT).

2.10 Density Functional Theory

DFT, developed by Hohenberg, Kohn, and Sham, offers a correlative method to the Hartree-Fock approach for evaluating electronic structure. This theory has experienced significant advancements over the past few decades. Rather than calculating the multielectron, multidimensional wavefunction, DFT concentrates on calculating only the electron density $\rho(r)$, which is defined as the number of electrons per unit volume.

2.10.1 Hohenberg and Kohn Theorems

The theorems by Hohenberg and Kohn [57] form the basis of DFT, demonstrating that the ground state wavefunction and energy of a poly-electronic system are uniquely determined by a functional of the electron density. In mathematical terms,

$$E_0[\rho(r)]$$

Here, the brackets indicate the presence of a *functional*. A functional can be defined mathematically as an operation that relies on the complete behavior of a function, not merely its value at a particular point. Essentially, it is a function whose argument is another function.

I Theorem - Electron density as central player

The first theorem posits that a unique external potential, $U_{ext}(\equiv U_{li})$, is exclusively determined by the ground-state electron density. Therefore, different external potentials will invariably lead to different electron densities. If we focus solely on the ground-state properties of a system, knowing the electronic density at a given external potential is sufficient to determine the total energy or other properties.

II Theorem - Search for the ground-state energy

The second theorem established a method for determining the minimum energy state of a system, demonstrating that the ground state can be identified through the variational principle. Specifically, for a given external potential U_{ext} , minimizing the system's energy with respect to electron density leads to the lowest point in the energy well, as described by the *variational principle*. Furthermore, the electron density that achieves this energy

minimization corresponds to the ground-state electron density, denoted as ρ_0 . Kohn and Hohenberg's second theorem serves as the basis for computing the ground state energy. In applying the variational method, electron densities that integrate to the total number of electrons (N) are considered within the defined spatial domain. Thus, for a system of N electrons, the following formulation is applicable:

$$\int \rho(r) dr = N$$

To obtain ground state energy a new functional G is minimised.

$$\delta \{E_v[\rho] - \mu [\int \rho(r) dr - N]\} = \delta G = 0 \quad (2.14)$$

Here μ is the Lagrange multiplier. The functional minimisation leads to an Euler Lagrange equation

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho(r)} = U(r) + \frac{\delta F^{HK}[\rho(r)]}{\delta \rho(r)} \quad (2.15)$$

Here $U(r)$ is the external potential due to nuclei. The $F^{HK}[\rho]$ is known as 'universal functional' since it can be used for any system and is independent of any external potential.

2.10.2 Kohn-Sham System

The Kohn-Sham method, a formulation of DFT, focuses on identifying accurate approximations for the *universal* functional. It delineates a collection of energy components that, when summed, yield the *universal* functional. Each component originates from a distinct physical phenomenon, with some being estimated effortlessly. However, those components that are not easily evaluated are subjected to approximation techniques.

The cornerstone of the Kohn-Sham (KS) method is the creation of a theoretical auxiliary system (known as *Kohn-Sham* system), meticulously designed to mimic the behavior of a real many-electron system. This framework comprises a set of particles with properties analogous to electrons in the original system, except that the electron-electron repulsive interaction is neglected within this construct. These particles are posited to move within an external potential, known as the Kohn-Sham potential, which is characterized to ensure that the system's ground-state electron density matches the density of the electronic system under investigation. Given the absence of inter-particle interactions, the ground-state wavefunction Ψ_{KS} of the Kohn-Sham system can be explicitly written in terms of simple single-particle wavefunctions. A key constraint lies in ensuring that the complete wavefunction adheres to anti-symmetry, a condition that can be satisfied by expressing single-orbital wavefunctions

$\phi_i(r_i)$ as a *Slater determinant*, as follows:

$$\Psi_{KS}(r_1, \dots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(r_1) & \cdots & \phi_1(r_N) \\ \vdots & \ddots & \vdots \\ \phi_N(r_1) & \cdots & \phi_N(r_N) \end{vmatrix} \quad (2.16)$$

In DFT, Kohn and Sham use their fictitious system (i.e. *Kohn-Sham* system) to determine the ground state energy functional, which can be written as [69]:

$$E[\rho(r)] = \int U(r)\rho(r)dr + E_{kin}[\rho(r)] + E_H[\rho(r)] + E_{XC}[\rho(r)] \quad (2.17)$$

The first term on the RHS gives the interaction of the electrons with external potentials; here, is their interactions with the nuclei:

$$\int U(r)\rho(r)dr = - \int \sum_{k=1}^M \frac{\rho(r)}{|r - R_k|} dr \quad (2.18)$$

The second term gives the kinetic energy. It is assumed to be identical to that which would be attained for an equivalent system of noninteracting electrons:

$$E_{kin}[\rho(r)] = \sum_{i=1}^N \int \Phi_i^*(r) \left(-\frac{\nabla^2}{2}\right) \Phi_i(r) dr \quad (2.19)$$

The third term, the Hartree term, is given by the electron-electron repulsive interactions between an electron at r_1 and the mean electron density at r_2 in a mean-field approximation:

$$E_H[\rho(r)] = \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2 \quad (2.20)$$

And the last term the exchange-correlation functional is not known exactly. It includes correlation and exchange effects, as well as the difference between the true kinetic energy and the noninteracting kinetic energy assumption.

As we know, we can obtain the energy expression as an expectation value of $\hat{H}$:

$$E = \int \Psi^* \hat{H} \Psi dr \quad (2.21)$$

Now applying the variational principle with a Langrage multiplier λ with normality constraint on energy equation with respect to electron density, the energy equations returns the Kohn-

Sham wave equation as:

$$0 = \frac{\delta}{\delta \rho(r)} \{E[\rho(r)] - \lambda [\int \rho(r) dr]\} \rightarrow \frac{\delta E[\rho(r)]}{\delta \rho(r)} = \lambda \quad (2.22)$$

$$[-\frac{1}{2}\nabla^2 + U_{eff}(r)]\phi_i(r) = \epsilon_i\phi_i(r) \rightarrow \hat{H}_{KS}\phi_i(r) = \epsilon_i(r)\phi_i(r) \quad (2.23)$$

2.10.3 Exchange-Correlation Functional

DFT simplifies the complex quantum mechanical problem of determining the ground-state of a many-electron system by reducing it to a self-consistent, one-electron form via the Kohn-Sham equations (2.17). While formally exact, this method necessitates approximations for the exchange-correlation energy as a functional of density to enable practical calculations. Consequently, the accuracy of a DFT calculation hinges on how well the approximated exchange-correlation energy functional reproduces the exact value. Several approximations are available for E_{xc} , with the *local density approximation* (LDA) [88] being the most basic. It is given by:

$$E_{xc}^{LDA}[\rho(r)] = \int \rho(r) \epsilon_{xc}(\rho(r)) dr \quad (2.24)$$

According to the LDA, the exchange-correlation energy is exclusively dependent on the local electron density and can be approximated through a basic function of electron density, ρ . In this context, $\epsilon_{xc}(\rho)$ denotes the exchange-correlation energy per particle, typically obtained from homogeneous electron gas simulations and frequently adapted to simpler formats. The exchange-correlation energy is divided into exchange and correlation elements in a linear manner, as below:

$$E_{xc} = E_x + E_c \quad (2.25)$$

so that independent expressions for E_x and E_c are derived to obtain accurate and compatible formulations for both contributions, incorporating corrections that account for non-local effects. The phrase “local” indicates the absence of any $\rho(r)$ derivative in the E_{xc} expression (given by (2.24)), suggesting that the LDA approximation is valid only when the electronic density changes gradually with position. While the exchange contribution can be computed analytically, the correlation energy lacks an analytical expression and is typically calculated using Monte Carlo simulations [141] based on the energy of the homogeneous electron gas. The resulting data is then fitted to an analytical function and incorporated into the exchange component.

As the LDA’s approximation of energy based on a constant local density is inaccurate when density changes rapidly, such as in molecules. To improve accuracy, the gradient

of the electron density can be considered, which is known as the Generalized Gradient Approximation (GGA) [101]. Symbolically this can be written as

$$E_{xc}^{GGA}[\rho(r)] = \int \rho(r) \epsilon_{xc}^{GGA}[\rho(r), \nabla \rho(r)] dr \quad (2.26)$$

In contrast to the LDA, a straightforward simple functional form that accurately represents GGA data does not exist. Consequently, the function $E_{xc}^{GGA}[\rho(r)]$ is frequently approximated using a carefully selected form, fitted to meet various physical constraints. Thus, the general form of GGA is an expression dependent on the LDA, incorporating an additional enhancement factor $F(s)$ that modifies the LDA energy.

$$E_{xc}^{GGA}[\rho(r), s] = \int \epsilon_{xc}^{LDA}[\rho(r)] F(s) dr \quad (2.27)$$

Here, the s depends on both electron density and its gradient [76]:

$$s = C \frac{|\nabla \rho(r)|}{\rho^{\frac{4}{3}}(r)} \quad (2.28)$$

For all my calculation evaluating structural and electronic properties of my materials, I have used potentials constructed assuming a GGA for the exchange-correlation functional.

2.10.4 Pseudopotential

Core electrons, primarily those occupying closed shells, are localized near the nucleus [154]. When atoms form bonds to create a solid, these core electrons remain tightly bound within their deep potential well, undergoing minimal alteration under typical conditions, and primarily oscillating due to the intense Coulombic potential of the nuclei. Consequently, their contribution to bonding is negligible during molecule or crystal formation. In contrast, valence electrons, situated outside the core region, largely dictate a system's physical properties, engaging in bonding, ionization, electrical conduction in metals, and other atomic interactions.

From a computational standpoint, it is sufficient to consider solely the active valence electrons, while treating core electrons as fixed entities that exert a screened potential on the valence electrons; this approach is known as the *frozen core approximation*. Due to the orthogonality requirement, valence electron wavefunctions demonstrate rapid oscillations in the core region. The computational expense of representing these functions using plane waves is considerable because of the resulting large basis set. Therefore, the pseudopotential approximation is applied, which replaces the core electrons and the strong Coulomb potential with a weaker

pseudopotential acting on pseudo-wavefunctions. In principle, pseudo-wavefunctions should not have nodes inside the core regions, thereby requiring only a small basis set, and the frozen-core approximation enables precisely this condition. As a result, we can "soften" both the wave functions of the valence electrons and their potentials with ions, a procedure specifically termed as *pseudization*. Following this simplification, the Kohn-Sham equation (2.23) can be expressed using the pseudopotential and pseudized wave functions, leading to an altered charge density:

$$\left[-\frac{1}{2}\nabla^2 + U_{PP}(r)\right]\phi_i^{PP}(r) = \epsilon_i\phi_i^{PP}(r) \quad (2.29)$$

$$\rho(r) = \sum_i |\phi_i^{PP}(r)|^2 \quad (2.30)$$

There are various pseudopotentials available to choose from, I have used projector-augmented wave (PAW) pseudopotentials in my calculations.

PAW Potentials

The Projector Augmented Wave (PAW) method, an all-electron (AE) potential employing the frozen-core approximation, was initially introduced by Bloch [13] and subsequently refined by Kresse and Joubert [71]. It aims to combine the efficiency of pseudopotentials (PP) with the accuracy of all-electron potentials. This approach employs distinct representations for both the core and valence regions of the wave functions.

Due to the orthogonality constraint, DFT wave functions exhibit sharp features near the core regions, where all states are non-zero. Conversely, only valence states are non-zero, leading to smoother wave functions in the interstitial regions. Accurately representing the oscillatory behavior in the core regions necessitates a comprehensive set of plane waves. One approach to mitigate this issue involves the utilization of pseudopotentials, wherein the combined system of cores and core electrons is represented by a smoother, more computationally tractable potential. The PAW method addresses this issue by transforming rapidly oscillating wave functions into smoother wave functions, thereby enhancing computational efficiency. This approach facilitates the calculation of AE properties from these smooth wave functions. As a generalization of both the PP and linear augmented plane-wave (LAPW, The LAPW technique involves a spatial division into atom-centered augmentation spheres, within which wave functions are treated as atom-like partial waves, and an interstitial region beyond these spheres, where envelope functions are specified. These partial waves and envelope functions are then matched at the sphere boundaries) methods, PAW enables DFT calculations to be performed with greater computational efficiency.

As discussed earlier, wavefunctions are smooth in the bonding region but show rapid oscillations near the nuclei. To address this problem, we seek a linear transformation $\hat{\mathcal{T}}$ which converts auxiliary smooth wave function $|\tilde{\psi}_n\rangle$ to the true all-electron KS single-particle wave function $|\psi_n\rangle$

$$|\psi_n\rangle = \hat{\mathcal{T}} |\tilde{\psi}_n\rangle \quad (2.31)$$

where n is the quantum state label, having a k index, a band index, and a spin index. This alteration yields the transformed KS equations,

$$\hat{\mathcal{T}}^* \hat{H} \hat{\mathcal{T}} |\tilde{\psi}_n\rangle = \epsilon_n \hat{\mathcal{T}}^* \hat{\mathcal{T}} |\tilde{\psi}_n\rangle \quad (2.32)$$

and this needs to be solved instead of the usual KS equation. Now suitable defining $\hat{\mathcal{T}}$, such that the auxiliary wave functions obtained from solving (2.32) becomes smooth. Since the true wave functions are already smooth at an absolute minimum distance from the core, $\hat{\mathcal{T}}$ should only alter the wave function close to the nuclei. Therefore,

$$\hat{\mathcal{T}} = 1 + \sum_a \hat{\mathcal{T}}^a \quad (2.33)$$

where a is the atom index, and the atom-centered transformation, $\hat{\mathcal{T}}^a$, has does not affect a certain atom-specific augmentation region $|r - R^a| < r_c^a$. The cut-off radii, r_c^a should be chosen such that there is no overlap of the augmentation spheres. Inside this augmentation spheres, we expand the true wave function in the partial waves ϕ_i^a , and for each of these partial waves, we elucidate a auxiliary smooth partial wave $\tilde{\phi}_i^a$, and require that

$$|\phi_i^a\rangle = (1 + \hat{\mathcal{T}}^a) |\tilde{\phi}_i^a\rangle \quad \Leftrightarrow \quad \hat{\mathcal{T}}^a |\tilde{\phi}_i^a\rangle = |\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle \quad (2.34)$$

for all i, a . The (2.34) completely defines $\hat{\mathcal{T}}$, if ϕ and $\tilde{\phi}$ are given. We must need the partial wave and its smooth counterpart to be identical outside the augmentation sphere, therefore

$$\forall a, \quad \phi_i^a(r) = \tilde{\phi}_i^a(r), \quad \text{for } r > r_c^a \quad (2.35)$$

where $\phi_i^a(r) = \langle r | \phi_i^a \rangle$ and likewise for $\tilde{\phi}_i^a$. If the smooth partial waves form an absolute set inside the augmentation sphere, we can formally dilate the smooth all electron wave functions as

$$|\tilde{\psi}_n\rangle = \sum_i P_{ni}^a |\tilde{\phi}_i^a\rangle, \quad \text{for } |r - R^a| < r_c^a \quad (2.36)$$

where P_{ni}^a are some, expansion coefficients. Since $|\phi_i^a\rangle = \hat{\mathcal{T}} |\tilde{\phi}_n\rangle$ we see that the expansion

$$|\psi_n\rangle = \hat{\mathcal{T}} |\tilde{\psi}_n\rangle = \sum_i P_{ni}^a |\phi_i^a\rangle, \quad \text{for } |r - R^a| < r_c^a \quad (2.37)$$

has identical expansion coefficients, P_{ni}^a . As it is essential that $\hat{\mathcal{T}}$ to be linear, the coefficients P_{ni}^a must be linear functionals of $|\tilde{\psi}_n\rangle$, i.e.

$$P_{ni}^a = \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle = \int dr \tilde{p}_i^{a*}(r - R^a) \tilde{\psi}_n(r) \quad (2.38)$$

where $|\tilde{p}_i^a\rangle$ are some fixed functions termed as smooth projector functions. Due to no overlapping between the augmentation spheres, we anticipate the one center expansion of the smooth all electron wave function, $|\tilde{\psi}_n\rangle = \sum_i |\tilde{\phi}_i^a\rangle \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle$ to reduce to $|\tilde{\psi}_n\rangle$ itself inside the augmentation sphere defined by a . Thus, the smooth projector functions must satisfy

$$\sum_i |\tilde{\phi}_i^a\rangle \langle \tilde{p}_i^a| = 1 \quad (2.39)$$

inside each augmentation sphere. This also implies that

$$\langle \tilde{p}_{i_1}^a | \tilde{\phi}_{i_2}^a \rangle = \delta_{i_1, i_2}, \quad \text{for } |r - R^a| < r_c^a \quad (2.40)$$

i.e. the projector functions ought to be orthonormal to the smooth partial waves inside the augmentation sphere. There are no constraints on $\tilde{p}_i^a$ outside the augmentation spheres, so for our ease, we might as well characterize them as local functions, i.e., $\tilde{p}_i^a(r) = 0$ for $r > r_c^a$. One should note that the completeness relation (2.39) is equivalent to the requirement that $\tilde{p}_i^a$ should produce the accurate expansion coefficients of (2.36)-(2.37), while (2.40) is merely the implication of this restriction. Using the completeness relation (2.39), we see that

$$\hat{\mathcal{T}}^a = \sum_i \hat{\mathcal{T}}^a |\tilde{\phi}_i^a\rangle \langle \tilde{p}_i^a| = \sum_i (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle) \langle \tilde{p}_i^a|, \quad (2.41)$$

where the first equality is true in all of space, while other equality is due to (2.34). Thus we can conclude that

$$\hat{\mathcal{T}} = 1 + \sum_a \sum_i (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle) \langle \tilde{p}_i^a|. \quad (2.42)$$

To summarize, we obtain the all electron KS wave function $\psi_n(r) = \langle r | \psi_n \rangle$ from the transformation

$$\psi_n(r) = \tilde{\psi}_n(r) + \sum_a \sum_i (\phi_i^a(r) - \tilde{\phi}_i^a(r)) \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle, \quad (2.43)$$

where the smooth auxillary wave function $\tilde{\psi}_n(r)$ is obtained by solving the eigenvalue equation (2.32). The transformation (2.43) is expressed in terms of the three components :

1. the partial waves $\phi_i^a(r)$,
2. the smooth partial waves $\tilde{\phi}_i^a(r)$,
3. the smooth projector functions $\tilde{p}_i^a(r)$.

So this transformation has solved our trouble of original KS wave functions, that they exhibit rapid oscillations in some fragments of space, and smooth behavior in other parts of space. By the decomposition (2.43), we have separated the original wave functions into auxiliary wave functions which are smooth everywhere and a contribution which contains rapid oscillations but only contributes in specific, small, areas of space. Because of the above reasons and accuracy of calculation, I have used the PAW method for my calculations.

To summarize the whole section, I have presented a flow chart in Fig. 2.5 describing the general working principle of DFT.

2.10.5 Bader Charge Analysis

In the context of DFT computations applied to materials and surfaces, the analysis of the spatial distribution and magnitude of electronic charge is crucial for elucidating chemical bonding, adsorption processes, and surface interactions. A widely utilized method for quantitative charge partitioning is Bader charge analysis, which was pioneered by Richard Bader and his research team. This approach is rooted in the quantum theory of atoms in molecules (QATIM) [7]. Bader charge analysis partitions the 3-D electronic charge densities obtained from DFT calculations into distinct atomic regions, based on the topology of electron density ρ . The core principle is to define atomic boundaries within a molecule or crystal by analyzing the gradient field of the electron density. Specifically, the division of space into atomic volumes, known as Bader volumes, is accomplished by locating zero-flux surfaces, which are surfaces through which the gradient of the electron density exhibits zero normal flux [53]. Mathematically, a Bader volume Ω_i for atom i is defined as follows:

$$\nabla\rho(r)\cdot n(r) = 0, \forall r \in \delta\Omega_i \quad (2.44)$$

where $n(r)$ is the unit normal vector at the boundary surface $\delta\Omega_i$. The integral of the electronic charge density within these Bader volumes directly yields atomic charges:

$$Q_i = Z_i - \int_{\Omega_i} \rho(r) dr \quad (2.45)$$

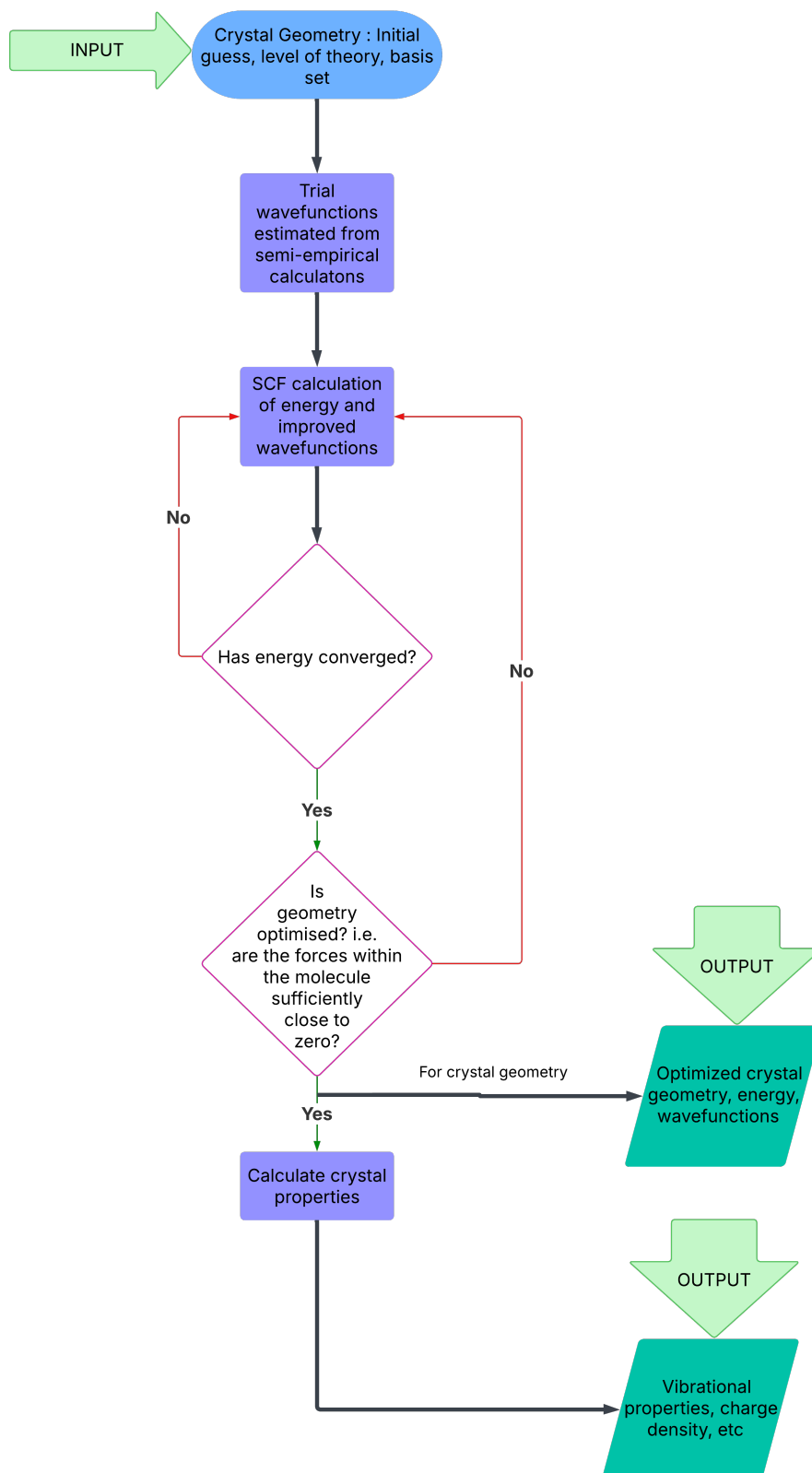


Fig. 2.5 shows a flow chart for the steps involved in geometry optimization.

Here, Z_i signifies the nuclear charge of atom i , and the integral quantifies the cumulative electron charge attributed to the corresponding atomic volume. The net atomic charge is then the difference between the nuclear charge and the Bader charge. Consequently, the resulting Bader charges serve as indicators of effective atomic charges, offering valuable insights into localized electron accumulation or depletion phenomena associated with chemical bonds and interactions.

Bader charge analysis is especially useful when examining interactions at surfaces and interfaces. In adsorption studies, this method allows researchers to quantitatively determine charge transfer between adsorbates and the metal substrate, leading to a better understanding of adsorption strength and activation mechanisms [91, 144, 113]. By calculating Bader charges, one can identify electron donor or acceptor species and explain how the electronic structure of the metal affects adsorption behavior and reactivity [144, 113]. Implementation of Bader charge analysis are widely available via computational packages such as Vienna Ab initio Simulation Package (VASP), Quantum ESPRESSO, and GPAW, which generate charge density files processed by tools like Henkelman's Bader analysis software. This accessibility has established Bader charges as a reliably adopted tool in computational studies of materials, catalysts, and surfaces, complementing other electronic structure analyses, such as density of states (DOS) or projected density of states (pDOS) [37]. In this dissertation, Bader charge analysis is utilized as a primary method for quantifying electron transfer phenomena within metal-CO₂ adsorption systems. Specifically, it serves to substantiate and provide interpretation for DFT predictions regarding charge redistribution during CO₂ adsorption and photo-induced desorption processes, thereby reinforcing the correlation between computational findings and empirical observations.

2.11 Breakthrough Curve Analysis in CO₂ Adsorption for Capture Applications

The performance of a sorbent for CO₂ capture is commonly evaluated using dynamic adsorption tests in a fixed-bed column, commonly referred to as "breakthrough-curve" experiments. These experiments involve the continuous flow of a CO₂ (often diluted in an inert carrier like N₂) containing gas mixture through a packed bed of adsorbent material at a controlled rate. Real-time monitoring of the outlet CO₂ concentration allows for the generation of a breakthrough curve, which plots the ratio of outlet to inlet CO₂ concentration (C_{out}/C_{in}) as a function of time. Initially, the fresh sorbent bed facilitates near-complete CO₂ capture, resulting in a minimal outlet concentration. However, as the sorbent approaches

saturation, CO₂ begins to “break through” and emerge at the outlet, eventually reaching the inlet concentration upon full saturation of the bed. The concentration of each gas is monitored at the column’s exit using a gas detector, such as a mass spectrometer (MS), a thermal conductivity detector (TCD), or a non-dispersive infrared (NDIR) gas analyzer. The resulting S-shaped breakthrough curve provides a basis for determining key performance metrics related to the sorbent’s CO₂ capture capabilities.

Subsequent to the experiment’s conclusion, whether dictated by a predetermined cycle time or the attainment of sample saturation, the concentration profile is integrated to quantify the CO₂ adsorbed, thereby yielding the adsorption capacity. Provided that the detection apparatus can independently measure the concentrations of multiple gaseous species without cross-interference, both the breakthrough and equilibrium adsorption capacities for each species can be quantitatively determined via the following relationships:

$$q = \frac{(F_{in} \cdot t) - V_{dead} - \int_0^t F_{out} dt}{m} \quad (2.46)$$

where, F_{in} is inlet flowrate of gas, t is adsorption time, V_{dead} is the dead volume of the system, F_{out} is the outlet concentration of the gas, m is the dry mass of the adsorbent [96]. In breakthrough experiments, it is important to accurately quantify the dead volume (V_{dead}) of the experimental setup; therefore, the integral should be determined by comparing the signal from the sample column to that of a “blank” run, using an equivalent volume without any adsorbent [108].

2.11.1 Interpretation of Breakthrough Curves

The breakthrough curve generally exhibits an S-shaped profile, which reflects the adsorption dynamics within the fixed bed. Several key performance indicators can be derived from this curve:

- Breakthrough time (t_b): The breakthrough time (t_b) represents the duration until the outlet CO₂ concentration (C_{out}) reaches a small fraction of the inlet concentration (C_{in}). Typically, t_b is defined when $C_{out}/C_{in} = 0.05$. This time signifies when the adsorbent bed’s CO₂ removal efficiency begins to diminish. A prolonged breakthrough time suggests a greater working capacity under specific flow conditions.
- Saturation (or exhaustion) time (t_s): The saturation time (t_s) represents the point at which the outlet concentration approaches near-complete saturation, commonly defined as $C_{out}/C_{in} = 0.95$ or 0.99 . Reaching t_s signifies that the sorbent bed is essentially saturated, with no further capacity for CO₂ adsorption. The interval between t_b and

ts corresponds to the mass transfer zone (MTZ) traversing the fixed bed. A sharp breakthrough curve, characterized by a minimal difference between t_b and t_s , suggests a narrow MTZ and effective utilization of the adsorbent bed. Conversely, a gradual ‘S’ shaped curve indicates that a notable portion of the bed near the outlet remains unutilized at t_b . From a practical standpoint, a narrow MTZ is desirable, as it implies a reduced “unused bed length” at breakthrough and a greater degree of capacity utilization.

- **Working capacity / dynamic adsorption capacity:** Within the context of breakthrough experiments, working capacity, also known as dynamic adsorption capacity, represents the quantity of CO₂ adsorbed by the sorbent bed during the adsorption phase, typically up to the breakthrough point or a defined cutoff. It is expressed in mmol CO₂ per gram of sorbent (or mg/g) and determined by integrating the area above the outlet concentration curve until the specified endpoint. The total CO₂ captured up to time t can be mathematically expressed as:

$$q(t) = \frac{F C_{in}}{m} \int_0^t \left(1 - \frac{C_{out}(t')}{C_{in}}\right) dt' \quad (1)$$

where F is the molar flow rate of CO₂, m represents the mass of the adsorbent, and the integral signifies the fraction of CO₂ removed over time. Specifically, integrating up to t_b yields the *useful capacity* at breakthrough q_b , while integrating to t_s provides the *total capacity* q_s (often corresponding to the equilibrium capacity at that condition).

- **Shape and steepness:** The breakthrough profile’s curvature reveals insights into adsorption kinetics and axial dispersion phenomena. A steep breakthrough (nearly step function) indicates rapid adsorption kinetics and negligible axial dispersion, approaching an ideal plug-flow regime constrained by equilibrium. Conversely, a gradual S-shaped curve suggests significant mass transfer resistances (film diffusion, pore diffusion, or slower adsorption kinetics), resulting in a dispersed adsorption front. The mass transfer zone’s length (either spatially or temporally, as represented by the $(t_s) - (t_b)$ interval) depends on factors including the adsorption isotherm’s characteristics, diffusivity, and flow rate. Notably, strong isotherms (Type I, Langmuir) and high diffusion rates typically generate sharper curves, whereas slower diffusion or weaker isotherms (near linear) can produce more elongated curves.

3. Computational investigation of CO₂ interaction on pure metals

3.1 Introduction

This chapter details a first-principles investigation into CO₂ adsorption on low-index surfaces of pure metals, incorporating explicit surface charge (neutral, electron-rich, hole-rich) control to simulate charge states relevant to photoinduced surface phenomena. Employing plane-wave Kohn–Sham DFT, adsorption energies, optimized geometric configurations, Bader charge distributions, and relevant electronic descriptors under conditions of consistent kinetic-energy cutoffs and Γ -centered k-point meshes were calculated, thereby ensuring numerically converged energetic parameters for comprehensive comparative screening across various metals. Subsequently, structure-property dependencies are quantified using mutual information (MI) to discern the most salient descriptors governing adsorption phenomena. An important performance criterion involves 'photoswitch-like' selectivity, wherein a single surface should exhibit robust CO₂ adsorption under one charge state while concurrently facilitating its facile desorption in an alternative charge state, thereby enabling demand-driven CO₂ capture and release via light-or field-induced charge modulation. Within this framework, we identify metals that exhibit an optimal balance between adsorption and desorption characteristics under charge control, proposing them as candidates for subsequent experimental investigations. This computational approach focuses on CO₂ adsorption on pristine metal surfaces, modeling excess surface charge as a theoretical proxy for photo-induced charging phenomena; comprehensive methodological particulars and validation strategies are detailed in §3.2.

3.1.1 Note on previously published content

This chapter is adapted from a previously published peer-reviewed article:

Sahu T, O'Brien PG, Ghuman KK. Harvesting surface charges on metals for energy-

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My contribution (**Tanay Sahu**): Writing – original draft, visualization, validation, methodology, investigation, Formal analysis, data curation.

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Paul G O’Brien: Writing – review & editing, supervision, funding acquisition.

Kulbir Kaur Ghuman: Writing – review & editing, supervision, resources, project administration, funding acquisition, conceptualization.

3.2 Methodology

3.2.1 Computational framework

All first-principles calculations were conducted utilizing Kohn–Sham DFT, implemented within the Quantum Espresso (QE) [42] plane-wave code. The projector-augmented wave (PAW) method [13] was employed to describe core electrons, while valence electrons were expanded using a plane-wave (PW) basis set. The Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation (GGA) [101] was selected for the exchange-correlation functional. Spin polarization was incorporated for systems involving ferromagnetic substrates. Electronic states were expanded up to a kinetic-energy cutoff of approximately 61 Ry(830 eV) and sampled using Γ -centered Monkhorst–Pack k-point meshes [89], specifically $2 \times 2 \times 1$, ensuring convergence of total energy to within ≤ 10 meV per adsorbate. Partial occupancies were addressed through metallic smearing (Methfessel-Paxton [86]) in the vicinity of the Fermi level. Geometry optimizations were performed using conjugate-gradient method with a force threshold of $0.1 \text{ eV } \text{\AA}^{-1}$ and an energy convergence criterion of 10^{-2} eV . PBE, PAW, QE, and Monkhorst–Pack are standard, widely validated choices for transition-metal surfaces. To validate our simulation parameters, the lattice constants for Zn and Pt were determined using a $3 \times 3 \times 3$ supercell, while maintaining the other parameters as previously described. The calculated lattice parameters for both Zn ($a = 2.66 \text{ \AA}$, $c = 4.94 \text{ \AA}$) and Pt ($a = 2.77 \text{ \AA}$) [113] were in good agreement with previously reported literature values (Zn : $a = 2.665 \text{ \AA}$, $c = 4.952 \text{ \AA}$ [82, 64, 66]; and Pt : $a = 2.775 \text{ \AA}$ [72]). This methodology was ultimately adopted due to its ability to preserve adsorption-energy trends while introducing minimal perturbations to chemisorption geometries.

3.2.2 Surface models

Low-index facets, characteristic of prevalent crystallographic terminations, were generated for face-centered cubic (fcc) (Cu(111), Pt (111), Ni (111), Al-alpha (110), Fe-gamma (110), and Co-alpha (111)), body-centered cubic (bcc) (V (110) and Fe-alpha (110)), and hexagonal close-packed (hcp) (Co-epsilon (0001), Zn (0001), and Al-beta (0001)) metals. These models consisted of four atomic layers, with a 10 Å vacuum spacing incorporated to mitigate unphysical interactions between periodic slab images [81]. Dipole corrections were enabled along the surface normal for asymmetric slabs to remove artificial fields across the vacuum. Additionally, a range of potential adsorption sites for CO₂ on the metal surfaces were investigated. The identification of these potential adsorption sites was achieved utilizing the “pymatgen adsorption module,” [95] which systematically generates diverse adsorption configurations based on geometric considerations. Figure 3.1 visually depicts the identified adsorption sites across various materials. Adsorption energies were determined using the following equation:

$$E_{ads} = E_{adsorbate+slab} - (E_{adsorbate} + E_{slab}) \quad (3.1)$$

where, $E_{adsorbate+slab}$ denotes the total energy of the adsorbate-surface system (whether neutral or charged), E_{slab} corresponds to the energy of the pristine surface, and $E_{adsorbate}$ represents the energy of the isolated CO₂ molecule in the gas phase. Visualization of all structures were done using either the Xcrysden package [70] or virtual nano lab (VNL) [124].

3.2.3 Modeling excess charges

To investigate the influence of surface charge on CO₂ binding, and specifically how light-induced charges facilitate CO₂ desorption, serving as a model for light-excited carrier accumulation at metal surfaces, DFT calculations were performed wherein an extra electron and a hole were introduced. Specifically, neutral, positively charged, and negatively charged slabs of the previously mentioned metal surfaces were considered. These slab models maintained periodicity parallel to the surface and were interfaced with a semi-infinite effective screening medium (ESM) [97], which served to simulate a vacuum in both directions perpendicular to the surface.

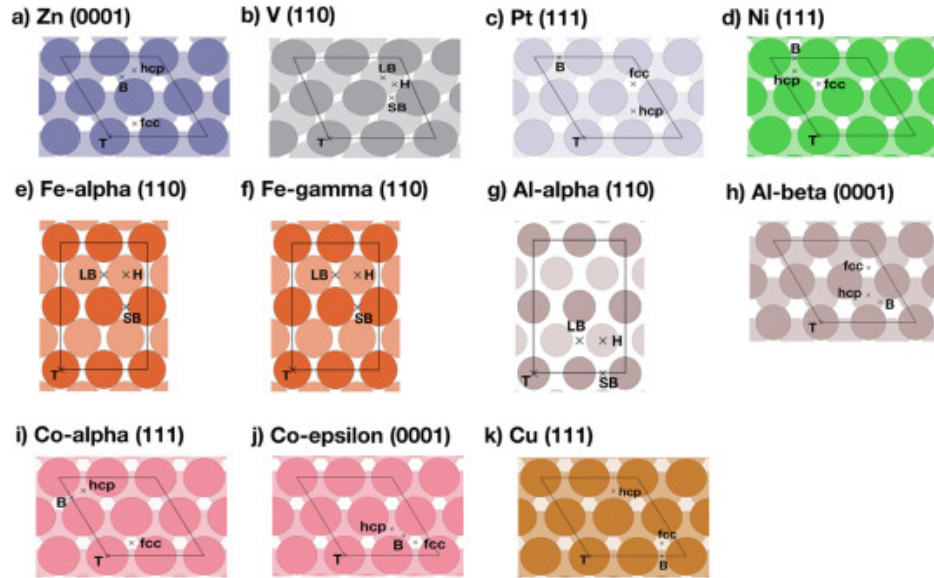


Fig. 3.1 A visual representation of adsorption sites of CO_2 on various metals (dark color balls represent the surface atoms, and light color balls represent the subsurface atoms). Adsorption sites are represented by T (top), B (bridge), fcc (hollow), hcp, SB (short bridge), LB (long bridge), and H (hollow) [113].

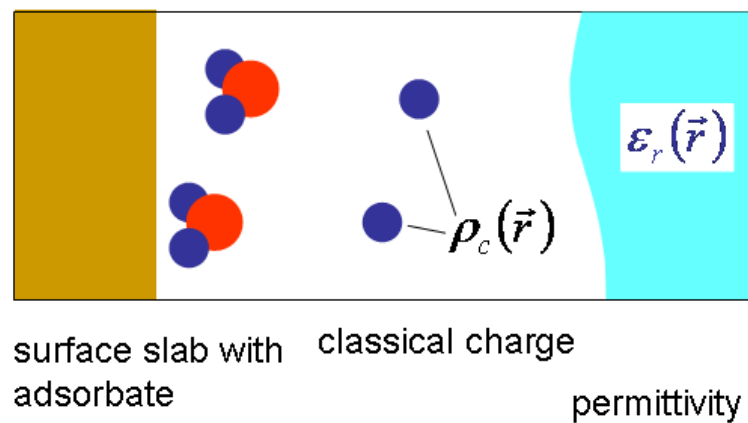


Fig. 3.2 Schematic showing ESM formulation [97].

Effective Screening Medium

The Effective Screening Medium (ESM)[97] method employs a slab model, maintaining periodicity in the directions parallel to the surface, a common approach in first-principles calculations. This method describes the screening effect by integrating local relative permittivity $\epsilon_r(r)$ and classical charge $\rho_c(r)$ within the slab model (refer Figure 3.2). For example, to model an STM tip, a region of infinite relative permittivity is introduced, designated as the ESM region, depicted by the blue area in the aforementioned figure (Figure 3.2). Conversely, to simulate the solution, an ESM region with $\epsilon_r(r) = 78.4$ is employed to replicate the screening effects of water, alongside classical charges representing electrolyte ions.

Crucially, the relevant physical effect of $\epsilon_r(r)$ can be incorporated as a boundary condition for the Poisson equation, thereby circumventing the need for explicit treatment of the entire spatial domain. This approach enables the use of an infinitely thick ESM region, effectively creating an isolated slab model, which is paramount for accurately describing systems dominated by long-range Coulomb interactions. The classical charge distribution $\rho_c(r)$ can be represented through effective point charges or, more conveniently, by a continuum model like the Poisson-Boltzmann equation, which relates it to the electrostatic potential $V(r)$ based on the Maxwell-Boltzmann distribution.

Basic formulation of ESM[97]

The total energy expression for the ESM method is given as Equation 3.2:

$$E_{tot}[\rho_e, V] = T[\rho_e] + E_{ex}[\rho_e] - \int dr \frac{\epsilon_r(r)}{8\pi} |\nabla V(r)|^2 + \int dr [\rho_e(r) + \rho_1(r) + \rho_c(r)] V(r) \quad (3.2)$$

This equation diverges from the standard slab formalism through the incorporation of $\epsilon_r(r)$ and $\rho_c(r)$. For methodological expediency, the electrostatic potential is employed as the variational parameter. Consequently, this equation can be re-expressed as shown in Equation 3.3:

$$E_{tot}[\rho_e, V] = T[\rho_e] + E_{ex}[\rho_e] - \frac{1}{2} \int dr dr' [\rho_e(r) + \rho_1(r) + \rho_c(r)] G(r, r') [\rho_e(r') + \rho_1(r') + \rho_c(r')] \quad (3.3)$$

when the Green's function for the Poisson (Equation 3.4):

$$\vec{\nabla} \cdot [\epsilon_r(r) \vec{\nabla}] G(r, r') = -4\pi \delta(r - r') \quad (3.4)$$

is introduced. The Kohn-Sham equation, derived by varying the total energy with the Kohn-Sham orbital, is not affected by the ESM, but the Poisson equation, derived from electrostatic

potential variation, is affected as shown in Equation 3.5:

$$V(r) = \int dr' G(r,r') [\rho_e(r) + \rho_1(r) + \rho_c(r)] \equiv \int dr' G(r,r') \rho_{tot}(r') \quad (3.5)$$

3.3 Results

The DFT calculations shed light on the following observations:

3.3.1 Structure of adsorbed CO₂ molecule

The results from the DFT simulations elucidate the state of adsorbed CO₂, which can be categorized into three distinct scenarios. *Case 1*: CO₂ adsorbs molecularly onto the surface, retaining its fundamental chemical structure, albeit with modifications to the C-O bond lengths and O-C-O bond angle. This molecular adsorption is accompanied by a degree of charge transfer from the metal surface to the adsorbed CO₂ molecule, resulting in CO₂^{δ-}. *Case 2*: CO₂ dissociates into CO and O when it is adsorbed on the surface of the metal. This outcome signifies highly active metal sites conducive to CO₂ reduction, rather than molecular adsorption. *Case 3*: CO₂ does not attach to the surface of the metal, suggesting suboptimal efficacy of these metallic sites for applications such as CO₂ capture or catalytic CO₂ reduction reactions. The cases of molecularly adsorbed, dissociated, and non-interacting CO₂ are represented by green, red and blue color respectively in Table 3.1.

The adsorption behavior of CO₂ on certain metal surfaces is contingent upon the surface charge. For instance, on V and Fe(gamma), CO₂ undergoes dissociation when the surface is neutral or negatively charged, yet exhibits molecular adsorption across most sites when the metal surface is electron-deficient (positively charged). It is noteworthy that across the comprehensive range of metal surfaces examined, a robust correlation between the CO₂ adsorption state and the surface charge is not consistently apparent. For example, CO₂ tends to dissociate on Zn when negatively charged, whereas an inverse trend is evident for Al(alpha), where dissociation is favored under positively charged surface conditions. In the context of *Case 1* it is worth mentioning, increased bending of the CO₂ geometry correlates with a reduction in the energy level of its in-plane orbitals (2π_u orbital). This decrease, particularly in the 2π_u orbital energy, critically enhances the electrophilic nature of the carbon atom [3]. This can be observed from Table 3.2, which represents the Bader Charge transfer indicating a reduction in charge on the carbon atom within adsorbed CO₂ as compared to that of the carbon atom of isolated CO₂.

3.3.2 Adsorption energy of CO₂

Table 3.1 summarizes the results from the adsorption energy analysis for each metal surface. These findings indicate that, across most investigated metal sites, the adsorption energy is generally lower (more favorable) when the surface is neutral, and conversely, it tends to increase (become less favorable) when the surface carries either a positive or negative charge. This pattern suggests a preferential adsorption of CO₂ onto neutral metal surfaces. For instance, the adsorption energies for the studied Fe surfaces consistently exhibit negative values in their neutral state, yet transition to positive values when the Fe surface is charged, whether positively or negatively. Nevertheless, certain metals, such as Al (beta and alpha), do not conform to this observed trend. The CO₂ adsorption is enhanced on aluminium in the presence of excess electrons, which has been observed in experimental studies [34]. This phenomenon may be attributable to the inherent absence of d-electrons in aluminum. Conversely, transition metals, characterized by broad sp-electron states and localized d-states, exhibit variations in adsorbate-surface interactions predominantly influenced by differences in their d-state characteristics, a principle widely recognized in scholarly literature [114]. Additionally, CO₂ adsorption exhibited varying favorability across various metallic substrates. Specifically, negative adsorption energies were consistently recorded for all sites on V and Al, signifying that CO₂ adsorbs readily on their surfaces irrespective of their charge state. Conversely, Ni surfaces, under both charged and neutral conditions, exhibited significantly positive adsorption energies across all sites, thereby suggesting that Ni possesses minimal activity for CO₂ adsorption.

Clearly, analysis of adsorption energy reveals that the influence of surface charge on CO₂ adsorption energy varies across different metallic substrates. For instance, metals such as Co, Fe, V, and Zn exhibit significantly lower binding strengths (relatively higher adsorption energy) for CO₂ when a surface charge is present, compared to their uncharged state, across the majority of their adsorption sites. Conversely, metals including Al, Pt, and Cu do not display a distinct trend, with only a limited number of sites demonstrating lower CO₂ binding strength (relatively higher adsorption energy) under charged conditions relative to neutral ones.

Table 3.1 Adsorption energies of CO₂ molecules on neutral, positive, and negative surfaces. The green color indicates CO₂ is molecularly adsorbed, the blue color indicates CO₂ is not interacting, and the red color indicates CO₂ is dissociating on the metal surfaces [113].

Metal	Adsorption Energy (eV)			Metal	Adsorption Energy (eV)		
Cu	Neutral	Positive	Negative	Fe (alpha)	Neutral	Positive	Negative

Site T	0.17	1.23	2.06	Site T	-2.10	0.18	0.20
Site B	0.08	0.24	0.14	Site H	-2.28	0.17	0.26
Site hcp	0.07	0.28	-0.07	Site SB	-2.30	0.22	0.21
Site fcc	0.08	0.16	0.38	Site LB	-2.24	0.28	0.24
Zn				Fe (gamma)			
Site T	0.04	0.29	0.16	Site T	-2.26	0.06	0.24
Site hcp	0.06	0.21	-0.01	Site H	-2.20	0.14	0.18
Site B	0.05	0.21	0.14	Site SB	-2.24	0.10	0.24
Site fcc	0.03	0.00	0.10	Site LB	-2.36	0.12	0.22
Pt				Co (alpha)			
Site T	0.39	0.19	0.06	Site T	-5.29	0.09	-4.86
Site B	0.06	-0.07	0.07	Site B	-5.29	0.16	0.11
Site hcp	0.04	-0.06	0.09	Site hcp	-5.13	0.13	10.20
Site fcc	0.03	0.23	-0.01	Site fcc	-5.13	0.09	10.27
V				Co (epsilon)			
Site T	-0.24	-0.07	-0.11	Site T	-5.25	0.10	0.17
Site LB	-0.31	-0.07	-0.14	Site B	-5.09	0.23	-1.95
Site SB	-0.33	-0.07	-0.12	Site fcc	-5.08	0.27	0.34
Site H	-0.28	~0	-0.18	Site hcp	-4.96	-0.07	0.32
Al (alpha)				Ni			
Site T	0.08	-0.06		Site T	17.08	18.99	19.21
Site SB	0.04	0.02	0.02	Site B	17.02	19.01	18.99
Site LB	0.01	0.07	0.02	Site hcp	16.96	19.01	19.13
Site H	0.05	0.23	0.02				
Al (beta)							
Site T	-0.41	-1.12	0.17				
Site B	-0.05	-0.42	-0.04				
Site hcp	-0.27	-0.43	-0.07				
Site fcc	-0.26	-0.44	-0.04				

3.3.3 Bader charge of CO₂

The structural analysis outcome has been validated through Bader charge analysis. The Bader charge, representing the electron density localized on an atom, is instrumental in understanding the chemical bonding and electronic structure of a system. It serves to elucidate an atom's electron-donating or electron-accepting characteristics, thus providing crucial insights into the distribution of electrons among atoms and the mechanisms of chemical bond formation [130, 116, 53]. The net Bader charge of the CO₂ molecule and the metal slab was determined by subtracting the individual atomic Bader charges from the total number of valence electrons defined within the pseudopotential. This predominant charge transfer mechanism on metallic surfaces is hypothesized to activate CO₂, leading to the formation of CO₂^{δ-} and CO₂⁻ species through partial and complete electron transfer, respectively. This finding is substantiated by our bader charge analysis, which reveals that charge is transferred to CO₂, leading to the formation of CO₂^{δ-}. Based on the Bader charge on CO₂, it appears that negatively charged surfaces transfer the maximum amount of charge to CO₂, followed by neutral surfaces and positively charged surfaces. Refer Table 3.2.

Table 3.2 Bader charges on each atom of CO₂ in the charged and uncharged condition of metal surfaces [113].

Metal	Metal				Metal	Metal					
	Site T	C	Neutral	Positive	Negative		Site T	C	Neutral	Positive	Negative
Zn	Site T	C	4.000	1.534	1.710	Co_alpha	Site T	C	1.700	1.736	4.000
		O	-2.074	-0.435	-1.067			O	-0.823	-0.680	-2.348
		O	-2.035	-1.438	-2.600			O	-1.873	-1.755	-3.068
		CO2	-0.109	-0.340	-1.956			CO2	-0.997	-0.699	-1.416
	Site hcp	C	2.528	1.546	3.114	Site B	Site B	C	1.841	1.727	1.694
		O	-1.457	-0.449	-2.079			O	-0.825	-0.657	-0.882
		O	-1.912	-1.441	-2.066			O	-1.861	-1.752	-2.240
		CO2	-0.842	-0.344	-1.031			CO2	-0.845	-0.682	-1.428
	Site B	C	4.000	1.532	1.710	Site hcp	Site hcp	C	1.688	4.000	1.655
		O	-2.548	-0.448	-1.067			O	-0.642	-2.518	-0.953
		O	-2.040	-1.423	-2.600			O	-1.908	-1.773	-2.259
		CO2	-0.588	-0.339	-1.956			CO2	-0.863	-0.290	-1.557
V	Site fcc	C	4.000	2.410	1.795	Site fcc	Site fcc	C	1.700	2.136	1.967
		O	-2.704	-1.021	-1.137			O	-0.823	-0.795	-0.855
		O	-1.962	-1.798	-2.705			O	-1.873	-1.796	-2.514
		CO2	-0.666	-0.409	-2.047			CO2	-0.997	-0.455	-1.402
	Site T	C	1.408	2.023	1.462	Co_epsilon	Site T	C	1.787	1.980	3.998
		O	-0.939	-1.614	-1.291			O	-0.827	-0.782	-2.080
		O	-1.862	-1.516	-2.607			O	-1.888	-1.737	-2.768
		CO2	-1.393	-1.107	-2.436			CO2	-0.929	-0.540	-0.849

Pt	Site2 LB	C	1.539	2.058	1.571	Al_alpha	Site B	C	1.716	2.489	2.709
		O	-1.074	-1.622	-1.257			O	-0.840	-1.002	-1.563
		O	-1.847	-1.541	-2.620			O	-1.871	-1.693	-2.535
		CO ₂	-1.381	-1.105	-2.307			CO ₂	-0.995	-0.206	-1.389
	Site SB	C	1.437	2.018	1.719		Site fcc	C	1.701	4.000	3.475
		O	-1.121	-1.592	-1.107			O	-0.855	-2.480	-2.148
		O	-1.879	-1.535	-2.583			O	-1.866	-1.774	-2.712
		CO ₂	-1.564	-1.109	-1.971			CO ₂	-1.020	-0.254	-1.386
	Site H	C	1.453	1.134	1.474		Site hcp	C	1.767	4.000	2.978
		O	-1.125	-1.786	-1.277			O	-0.632	-2.075	-1.711
Pt		O	-1.863	-0.596	-2.587	Al_alpha		O	-1.947	-1.894	-2.645
		CO ₂	-1.536	-1.249	-2.389			CO ₂	-0.811	0.032	-1.379
	Site T	C	1.818	0.667	4.000		Site T	C	1.423	0.560	
		O	-1.768	-0.857	-2.415			O	-1.303	-2.196	
		O	-0.090	0.229	-2.523			O	-1.892	-1.893	
		CO ₂	-0.039	0.039	-0.938			CO ₂	-1.772	-3.530	
	Site B	C	2.200	4.000	4.000		Site SB	C	2.269	0.687	1.405
		O	-0.755	-1.919	-2.279			O	-1.831	-2.106	-1.888
		O	-1.953	-1.938	-2.605			O	-1.863	-2.408	-2.419
		CO ₂	-0.508	0.143	-0.884			CO ₂	-1.425	-3.827	-2.902
	Site hcp	C	4.000	4.000	4.000		Site LB	C	2.015	-1.524	1.707
		O	-2.509	-1.932	-2.415			O	-1.961	-2.164	-1.896

Cu		O	-1.981	-1.928	-2.523		O	-1.897	-2.092	-2.394
		CO ₂	-0.490	0.140	-0.938		CO ₂	-1.844	-5.780	-2.584
	Site fcc	C	4.000	-0.122	2.944	Site H	C	4.000	-0.256	1.750
		O	-2.499	-0.100	-1.673		O	-3.317	-2.165	-1.920
		O	-1.905	0.259	-2.399		O	-1.948	-2.038	-2.388
		CO ₂	-0.404	0.037	-1.129		CO ₂	-1.265	-4.459	-2.557
	Site T	C	1.723	2.415	1.706	Al_beta	C	-3.879	-1.182	-1.866
		O	-0.842	-1.514	-0.863		O	-2.079	-1.995	-1.097
		O	-1.877	-1.812	-1.811		O	-2.592	-2.041	-1.290
		CO ₂	-0.996	-0.912	-0.968		CO ₂	-8.549	-5.218	-4.253
	Site B	C	2.761	1.493	2.148	Site B	C	1.151	1.863	0.461
		O	-1.597	-1.013	-0.923		O	-1.312	-1.999	-1.370
		O	-1.942	-1.920	-1.947		O	-1.934	-1.936	-2.681
		CO ₂	-0.778	-1.441	-0.722		CO ₂	-2.096	-2.073	-3.590
	Site hcp	C	4.000	2.145	4.000	Site hcp	C	2.457	4.000	1.383
		O	-2.382	-1.663	-2.459		O	-2.226	-2.203	-1.978
		O	-2.104	-1.673	-2.085		O	-1.952	-1.934	-2.611
		CO ₂	-0.486	-1.190	-0.544		CO ₂	-1.720	-0.137	-3.207
	Site fcc	C	2.773	1.468	1.839	Site fcc	C	1.322	1.877	-0.239
		O	-1.618	-1.019	-0.788		O	-1.461	-2.476	-1.528
		O	-1.959	-1.927	-1.945		O	-1.928	-1.869	-2.701
		CO ₂	-0.805	-1.478	-0.894		CO ₂	-2.067	-2.468	-4.468

Fe_alpha	Site T	C	1.715	1.844	4.000	Ni	Site T	C	4.000	4.000	4.000				
		O	-0.976	-0.929	-2.057			O	-2.091	-2.038	-2.058				
		O	-1.819	-1.768	-2.706			O	-2.007	-1.845	-2.731				
		CO ₂	-1.080	-0.854	-0.763			CO ₂	-0.099	0.117	-0.789				
	Site H	C	1.875	1.825	4.000	Site B	C	4.000	4.000	4.000					
		O	-0.944	-0.913	-2.082		O	-2.064	-1.996	-2.102					
		O	-1.868	-1.740	-2.735		O	-1.979	-1.907	-2.697					
		CO ₂	-0.938	-0.828	-0.817		CO ₂	-0.043	0.098	-0.799					
	Site SB	C	1.801	1.849	4.000	Site hcp	C	4.000	4.000	4.000					
		O	-0.884	-0.921	-2.099		O	-2.057	-2.095	-2.116					
		O	-1.817	-1.770	-2.756		O	-2.019	-1.823	-2.717					
		CO ₂	-0.900	-0.842	-0.855		CO ₂	-0.076	0.083	-0.833					
Fe_gamma	Site LB	C	1.719	1.854	4.000										
		O	-1.018	-0.921	-2.051										
		O	-1.801	-1.770	-2.812										
		CO ₂	-1.100	-0.837	-0.863										
	Site T	C	1.680	2.960	1.683										
		O	-1.059	-1.739	-0.820										
		O	-1.847	-1.865	-2.280										
		CO ₂	-1.226	-0.644	-1.417										
	Site H	C	1.869	2.919	1.451										
		O	-0.953	-1.636	-0.968										

	O	-1.891	-1.886	-2.185	
	CO ₂	-0.976	-0.603	-1.701	
Site SB	C	1.773	2.960	3.999	
	O	-0.893	-1.739	-2.089	
	O	-1.809	-1.865	-2.729	
	CO ₂	-0.928	-0.644	-0.819	
Site LB	C	1.724	2.177	1.729	
	O	-1.021	-0.945	-0.852	
	O	-1.798	-1.784	-2.401	
	CO ₂	-1.095	-0.552	-1.524	

3.3.4 D-band analysis

The interfacial interaction between catalyst surfaces and CO₂ molecules is pivotal in governing the efficacy and consequences of heterogeneous adsorption and desorption phenomena. According to Sabatier's principle, achieving optimal catalytic performance necessitates a finely tuned adsorption strength for CO₂ molecules on the catalyst surface, avoiding both excessively strong and unduly weak binding [73]. Consequently, numerous computational investigations have been undertaken to explore diverse metal catalysts, aiming to discern the optimal attributes requisite for highly efficient CO₂ adsorption and subsequent desorption processes. Achieving efficient adsorption and desorption of reactants, intermediates, and products on catalytic surfaces necessitates precise modulation of the adsorption affinity of metal-based catalysts. A common approach to infer this affinity involves calculating the d-band center value (d_{bc}). Specifically, an upward shift of the d-band center relative to the Fermi energy ($\Delta E_{dbc} = d_{bc} - F_e$, ' F_e ' being the Fermi energy), characterized by a reduced absolute energy difference from the Fermi level, implies a less stabilized d-band center. This phenomenon leads to an increased bond strength by decreasing the occupancy of antibonding orbitals between the reactants and the catalyst surface [93, 127]. The data on ΔE_{dbc} in Figure 3.3 reveals that V exhibits the lowest value, indicative of its significant reactivity towards CO₂ molecule compared to other metals. This observation is corroborated by Table 3.1, which demonstrates V's efficacy in dissociating CO₂ across most conditions. Conversely, Ni shows minimal interaction with CO₂ despite its low ΔE_{dbc} an outcome consistent with prior research [143]. This discrepancy suggests that while the d-band center model generally correlates with adsorbate-metal interaction strength [41, 51], other factors such as electron transfer dynamics and specific orbital overlaps might be more dominant for certain metal-adsorbate systems [74].

3.3.5 Mutual information

To quantify the interdependencies among various parameters, including the d-band center relative to the Fermi energy, Bader charge, and CO₂ adsorption energy, mutual information (MI) from probability and information theory was utilized. In this context, an MI value of zero signifies statistical independence between two random variables, whereas higher values denote a more pronounced relationship. The calculation of MI is predicated on non-parametric approaches that involve estimating entropy from k-nearest neighbor distances. Mathematically, MI is defined as:

$$I(X;Y) = D_{KL}(P_{(XY)} \parallel P_X \otimes P_Y) \quad (3.6)$$

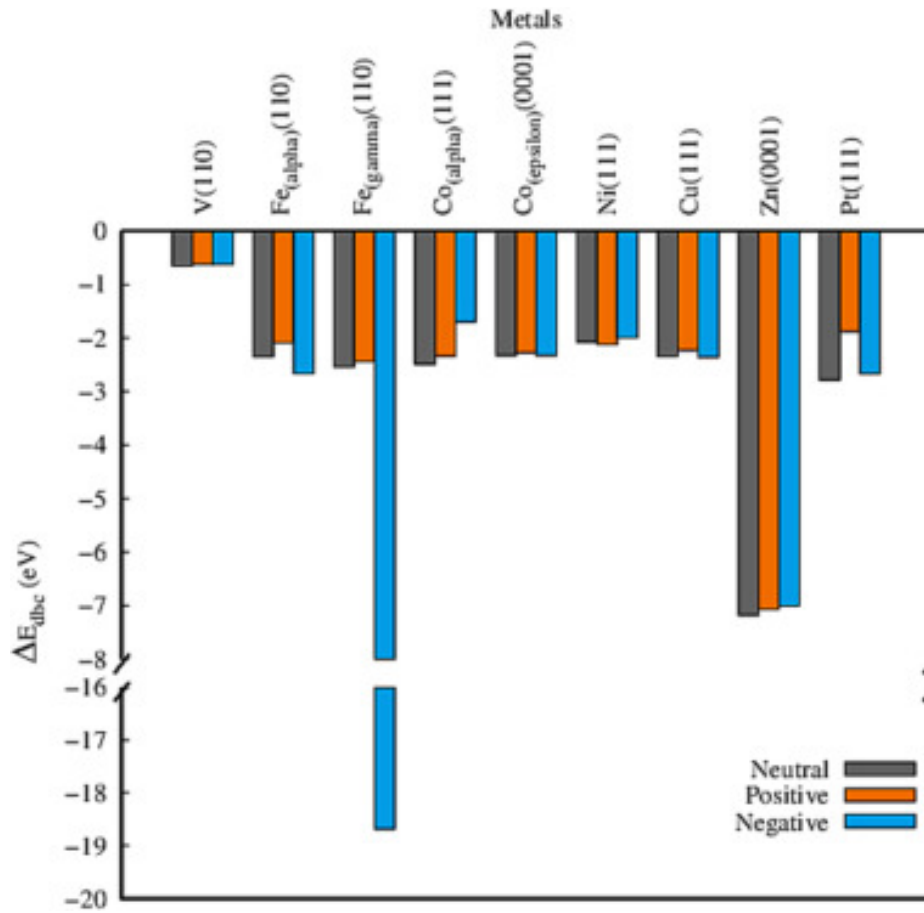


Fig. 3.3 D-band center value with respect to Fermi energy of different metals in charged and uncharged conditions [113].

where (X, Y) are a pair of random variables with values over the space $x \times y$. $P_{(X,Y)}$ is their joint distribution, and P_X & P_Y are marginal distribution. D_{KL} is the Kullback-Leibler divergence, $P_X \otimes P_Y$ is the outer product distribution which assigns probability $P_X(x) \cdot P_Y(y)$ to each (X, Y) .

Figure 3.4 (a), (b), and (c) illustrates the mutual information values for neutral, positively, and negatively charged surfaces, respectively. Key dependencies observed include: the adsorption energy of the CO_2 molecule correlates with both the Bader charge of carbon and the CO_2 bond angle under neutral surface conditions. The dependency between the average CO_2 bond length and the Bader charge on the carbon atom is highest for the neutral surface, followed by the positively charged surface, and lowest for the negatively charged surface. Furthermore, the dependency between the Bader charge on the carbon atom and its bond angle is maximal for the neutral surface and minimal for the positively charged surface. Conversely, the dependency between the d-band center and the Bader charge of the CO_2 molecule is most

prominent for the positively charged surface, subsequently for the negatively charged surface, and negligible for the neutral surface. The relationship between the average CO₂ bond length and the O-C-O bond angle is maximal for the negatively charged surface, followed by the neutral surface, and minimal for the positively charged surface. Finally, the dependency of the CO₂ molecule's adsorption energy on the Bader charge of the entire CO₂ molecule is observed exclusively for the positively charged surface.

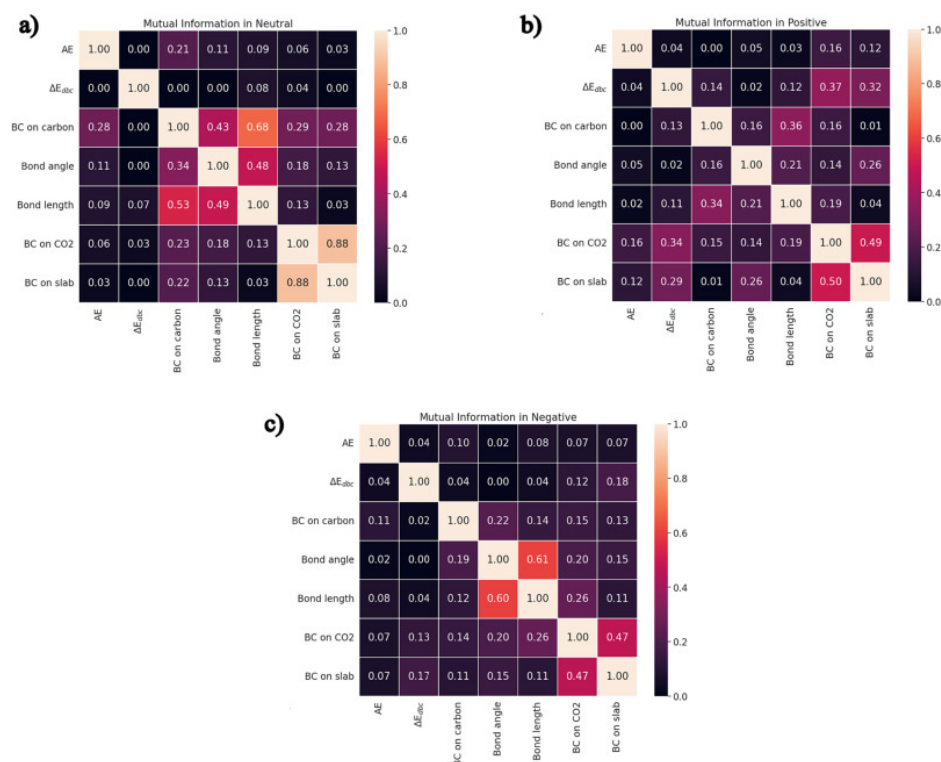


Fig. 3.4 Heatmap representing mutual information values between different factors in the presence and absence of charge. AE = adsorption energy of CO₂, BC = Bader charge [113].

3.4 Summary

The analysis focused on the adsorption energy of CO₂, specifically concentrating on its molecular adsorption. Sites where CO₂ dissociation occurred were intentionally excluded, as the primary objective was to investigate the adsorption and desorption mechanisms of molecular CO₂. It is imperative that an effective adsorbent not only exhibits strong adsorption capabilities but also facilitates the facile desorption of CO₂. Consequently, metals characterized by strong adsorption but weak desorption are considered inadequate for efficient CO₂ capture. An optimal metal surface for CO₂ capture should display a "photoswitch-like"

behavior, enabling both adsorption and desorption of CO₂ in response to varying surface charge conditions. Therefore, an ideal metal surface for CO₂ capture must demonstrate both lower and higher adsorption energies when its surface charges are modulated across neutral, positive, and negative states. Based on these considerations, Fe, V, and Ni exhibited low suitability; Fe and V predominantly induce CO₂ dissociation at most active sites, whereas Ni displays negligible interaction.

Furthermore, CO₂ adsorption occurs on neutral surfaces, with Pt demonstrating the highest activity in this state. Conversely, metals such as Cu and Al(alpha) exhibit effective CO₂ adsorption in an electron-rich state, while Co(epsilon) and Fe(gamma) become active in an electron-deficient state. Notably, a negatively charged Cu surface surpasses Pt in CO₂ adsorption activity. Regarding CO₂ desorption, Cu, Zn, and Al(alpha) perform more effectively in an electron-deficient state, whereas other surfaces desorb CO₂ in an electron-rich state. In summary, Cu (100% adsorption in electron-rich conditions and 50% desorption in electron-deficient conditions), Zn (75% adsorption and desorption in neutral and electron-deficient conditions, respectively), Co(alpha), and Al(beta) (50% adsorption and desorption efficiency in neutral and electron-rich conditions, respectively) are identified as metals exhibiting balanced adsorption and desorption efficiencies.

3.5 Limitations

3.5.1 Methodological Limitations

The PBE-GGA functional, while standard for transition-metal surface calculations, is known to systematically underestimate adsorption energies and can inadequately represent strongly correlated d-electron systems [99]. Higher-level treatments such as hybrid functionals or DFT+U would improve accuracy but were computationally prohibitive for the screening scope of this study. The four-layer slab models with a $2 \times 2 \times 1$ k-point mesh represent a balance between fidelity and cost; thicker slabs and denser k-grids could refine subsurface relaxation effects and the adsorption energy landscape, particularly for metals with complex Fermi surfaces.

The ESM charge model serves as a theoretical proxy for photo-induced carrier accumulation but does not capture the transient, non-equilibrium nature of photoexcitation, including hot-carrier thermalization, electron-hole recombination, or spatially inhomogeneous carrier distributions under real illumination. The integer charge approximation may therefore over or underestimate experimentally achievable surface charge densities. Additionally, the analysis is restricted to ideal, defect-free low-index facets; real surfaces with step edges,

vacancies, and co-adsorbed species (e.g., H₂O, N₂) would exhibit modified CO₂ binding thermodynamics not captured here.

3.5.2 Limitations of the d-band Center Model and Alternative Descriptors

The d-band center model (ΔE_{dbc}) predicts adsorbate binding strength from the position of the metal d-band relative to the Fermi level, and performs well under neutral conditions. However, it fails in several cases examined here. Most notably, Ni exhibits negligible CO₂ adsorption despite a low ΔE_{dbc} , consistent with prior work. The model’s core assumption of structureless d-band coupling does not account for orbital symmetry specificity, spin-polarization, or the anisotropic charge redistribution induced by surface charging. Furthermore, under charged conditions, the Fermi level itself shifts, introducing a systematic ambiguity into ΔE_{dbc} comparisons across charge states. This is corroborated quantitatively by the mutual information analysis in §3.3.5, which shows that ΔE_{dbc} carries low mutual information with CO₂ adsorption energy for both charged surface conditions.

Several alternative descriptors are better suited to charge-modulated systems. The surface work function (ϕ) directly reflects the net electrostatic environment at the metal-vacuum interface and is inherently sensitive to surface charge density and adsorbate induced dipoles, making it a more physically transparent descriptor for field or photo-assisted capture. Charge transfer descriptors, specifically the net Bader charge transferred to CO₂ (Δq_{CO_2}), as reported in Table 3.2, exhibit higher mutual information with adsorption energetics and encode both molecular activation and electrostatic coupling in a single, charge-state-resolved quantity. Surface energy (γ) offers a complementary measure of facet reactivity arising from atomic coordination. Collectively, a multi-descriptor framework combining ϕ , Δq_{CO_2} , and the O-C-O bond angle is expected to yield more robust and transferable predictions than ΔE_{dbc} alone, and represents a productive direction for future screening.

3.5.3 Computational Resource and Hardware Limitations

All calculations were performed on the Graham and Cedar clusters of the Digital Research Alliance of Canada (formerly Compute Canada), using Intel Broadwell nodes (32 cores, 128 GB RAM) managed via SLURM. Charged ESM slab calculations were significantly more expensive than standard neutral runs: individual geometry optimizations required 8-48 hours of wall-clock time (longer for spin-polarized systems such as Fe and Co), consumed 32-64 GB of RAM per job, and were parallelized across 16-32 MPI tasks. The 168-hour SLURM wall-time cap necessitated job chaining for several slow converging magnetic systems,

requiring manual restart verification to ensure continuity. The total campaign exceeded 350 individual DFT jobs, consuming a substantial portion of the available core-hour allocation. This precluded several scientifically desirable extensions: expansion to 3×3 supercells to reduce lateral adsorbate interactions; nudged elastic band (NEB) calculations for dissociation pathways (≈ 10 -20 additional single-points per path); inclusion of van der Waals dispersion corrections (DFT-D3); and screening of additional metals (e.g., Ag, Au, Pd, Rh). The geometry optimization force threshold of $0.1 \text{ eV } \text{\AA}^{-1}$, while standard for high-throughput screening, is less stringent than would be required for transition-state searches or zero-point energy corrections. Future work would benefit from GPU-accelerated DFT implementations and automated workflow frameworks (e.g., AiiDA) to enable broader and higher-resolution exploration of the charge-modulated material space identified here.

3.6 Conclusion

This chapter, drawing on first-principles calculations, elucidates how surface charge influences the interaction of CO_2 with pure transition-metal surfaces, thereby presenting a feasible approach for controlling low-energy adsorption-desorption dynamics. Across the low-index facets investigated, it was observed that the adsorption state of CO_2 and its binding strength are highly sensitive to both the specific metal and the presence of excess electrons or holes at the surface. Under neutral conditions, Fe and V exhibit significant reactivity, often leading to CO_2 dissociation, whereas Ni remains largely inert. In contrast, Cu, Zn, Al, Co, and Pt exhibit intermediate behaviors where CO_2 adsorption can be either promoted or suppressed through charge manipulation. Mutual information analysis indicated that singular electronic descriptors, such as the d-band center, are insufficient on their own to predict CO_2 binding or activation across the diverse chemical compositions and charge states examined. Instead, the observed energetics are more comprehensively explained by charge redistribution on the adsorbate and the accompanying structural changes, particularly on neutral and positively charged surfaces. These findings suggest that electrostatic tuning, whether achieved photochemically (via photo-induced carriers), electrostatically (through interfacial fields), or chemically (work-function engineering), can be strategically employed to realize "photoswitch-like" surfaces capable of adsorbing CO_2 under one charge state and desorbing it under another, thereby reducing the thermal penalties associated with regeneration.

Building on these insights, it is anticipated that the deliberate manipulation of surface charge will significantly enhance both adsorption and desorption steps, thereby facilitating energy-efficient cycling in practical systems. This understanding suggests two immediate

avenues for further exploration. Firstly, alloying presents a rational pathway to independently optimize and integrate the electronic structure, carrier lifetimes, and surface geometry; specifically, combinatorial investigation within the Cu-Zn-Co-Al material space offers a promising strategy to balance capacity, kinetics, and switchability while leveraging favorable optical and thermophysical properties. Secondly, while the simulations presented in the chapter focused on isolated CO₂ to elucidate the fundamental metal-adsorbate interactions, the core principle of utilizing light to modify surface electronic structure and interfacial charge is readily applicable to liquid media. Thus, we anticipate extending these identical design rules to plasmonic and non-plasmonic nanofluids, where wavelength-selective illumination could precisely modulate the charge at the nanoparticle-electrolyte interface, consequently influencing CO₂ binding thermodynamics and interfacial kinetics without inducing bulk heating. Collectively, these advancements are poised to transform the mechanistic understanding, specifically, the charge-mediated control over CO₂ binding on metallic surfaces, into practical design principles for developing light and field-assisted capture media suitable for both solid surfaces and nanoparticulate fluids.

4. Design and calibration of a photothermal breakthrough apparatus

4.1 Introduction

This chapter elucidates the design, commissioning, and calibration of a photothermal breakthrough apparatus developed for the precise quantification of light-assisted CO₂ adsorption and desorption within well-controlled laboratory settings. The experimental setup integrates a windowed fixed-bed reactor with capabilities for precise gas delivery (CO₂/N₂ blending via mass-flow controllers), continuous in-line concentration measurement (NDIR), multi-point temperature sensing throughout the bed (axial and radial thermocouples), and an illumination module (solar-simulator LED source) offering steady irradiance options. The design of the apparatus prioritized several key considerations: ensuring optical access while minimizing heat losses, effectively mitigating and quantifying axial and radial thermal gradients during illumination, and facilitating reproducible transitions between purely thermal and light-assisted operational modes. The calibration protocols, detailed in this chapter, consist of verifications of flow rates and gas compositions, assessments of analyzer linearity and drift, thermocouple mapping and lag correction, calibration of irradiance and power at the bed plane (with spectral characterizations for source matching), and a comprehensive uncertainty values (within breakthrough time, working capacity, regeneration time, and specific energy input) meticulously propagated to key figures of merit. To validate the system's performance prior to evaluating metallic materials, the apparatus is benchmarked against polyethyleneimine-infused silica, a well-characterized CO₂ sorbent. This process establishes baseline adsorption capacities and characterizes both its thermal and light-assistive responses. The chapter concludes by outlining protocols specifically designed for operations involving gas-phase CO₂ and high-irradiance conditions, alongside a concise comparison of dark versus illuminated regeneration strategies. This comparison serves to contextualize and motivate the subsequent chapters, which focus on pure metals and prospective alloy candidates.

4.1.1 Note on previously published content

This chapter have been adapted from a previously published peer-reviewed article:

Sahu T, Eke V, O'Brien PG, Ghuman KK. Solar-driven photothermal desorption of CO₂ from PEI-infused silica gel. *Applied Thermal Engineering*. 2025 Nov.

My contribution (**Tanay Sahu**): Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Co-author contributions:

Victor Eke: Writing – review & editing, Methodology, Investigation.

Paul G O'Brien: Writing – review & editing, Writing – original draft, Supervision, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Kulbir Kaur Ghuman: Writing – review & editing, Writing – original draft, Supervision, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization..

4.2 Methodology

4.2.1 Preparation of adsorbent

The selection of polyethyleneimine (PEI)-infused mesoporous silica as a sorbent is predicated on its proven efficacy as a solid amine system, enabling efficient capture at ambient pressures [157] and subsequent complete desorption using low-grade thermal energy [122, 115]. Furthermore, the intrinsic oxidative stability of silica, coupled with the commercial accessibility, cost-effectiveness, and industrial scalability of both PEI and silica gel, collectively establish PEI-modified silica as a technically and economically feasible material for scalable CO₂ capture applications. These combined characteristics render PEI-infused silica a highly advantageous material for robust and large-scale CO₂ separation processes. Refer Table 2.2 for further details.

Silica gel (pore size 60 Å, 70-230 mesh) and PEI solution (linear, average molecular weight 1300) were obtained from Sigma-Aldrich and utilized without further pretreatment. The synthesis of Si-PEI adsorbents was accomplished through a wet infiltration method, consistent with established protocols documented in the literature [117]. For the preparation of adsorbents containing 30 wt% PEI [142], 12 g of PEI was initially dissolved in 224 g of methanol, maintained under continuous agitation (stirring) for 10 minutes. Subsequently, 28 g of silica gel was introduced, ensuring a methanol-to-silica ratio of 8:1. The resultant

mixture was subjected to stirring for 8 h at ambient temperature, followed by a drying process at 80 °C for 12 h, yielding approximately 40 g of the final product. The chosen sample size (amount) was calibrated to occupy the majority of an adsorbent bed, which possessed a volume of 240 cm³. This preparation ensures consistent PEI distribution within the silica matrix, which is critical for maximizing CO₂ adsorption capacity and minimizing diffusional limitations during breakthrough experiments. For visual representation of the preparation process refer Figure 4.1.

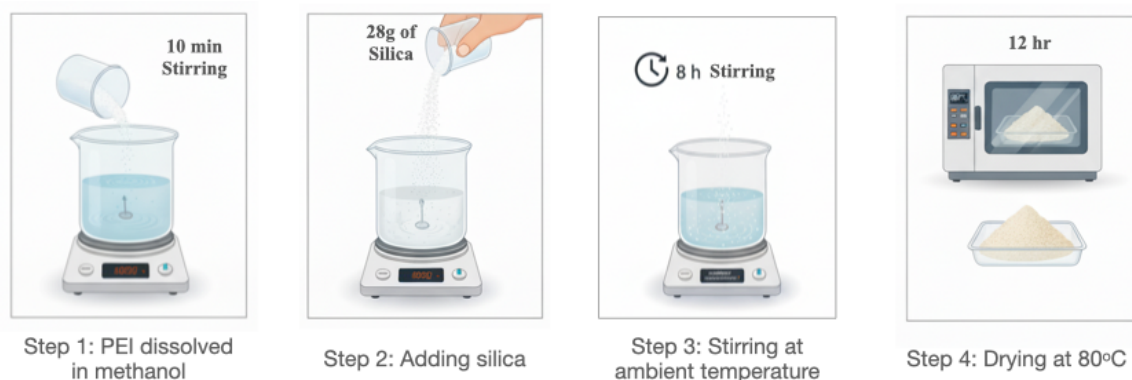


Fig. 4.1 Schematic illustration of Si-PEI adsorbent synthesis.

4.2.2 Characterization

The surface morphological characteristics of the adsorbents were determined via scanning electron microscopy (SEM) utilizing a Tescan VEGA 3 LMH instrument. The SEM operated in high vacuum (5×10^{-2} Pa), employing a secondary electron detector. Imaging was performed across an accelerating voltage range of 200V to 30kV, as indicated in the image metadata. For SEM analysis, samples were meticulously prepared by mounting them on aluminum stubs using carbon adhesive, followed by the application of a thin, conductive coating of either carbon or gold via sputter coating to mitigate potential charging artifacts. Both low and high magnifications were utilized during imaging to facilitate the examination of macro and micro-scale surface features of the materials. Elemental analysis was conducted using Energy Dispersive X-ray (EDX) spectroscopy, an integral component of the SEM system. A Bruker Quantax 100 EDS system, featuring an XFlash 410 silicon drift detector and an XFlash MIN SVE signal processing unit, was employed for this purpose. This methodology facilitated the determination of elemental distribution and quantitative assessment of atomic percentages on the sample surfaces, both preceding and following experimental treatments. Both elemental mapping and point-based quantification approaches

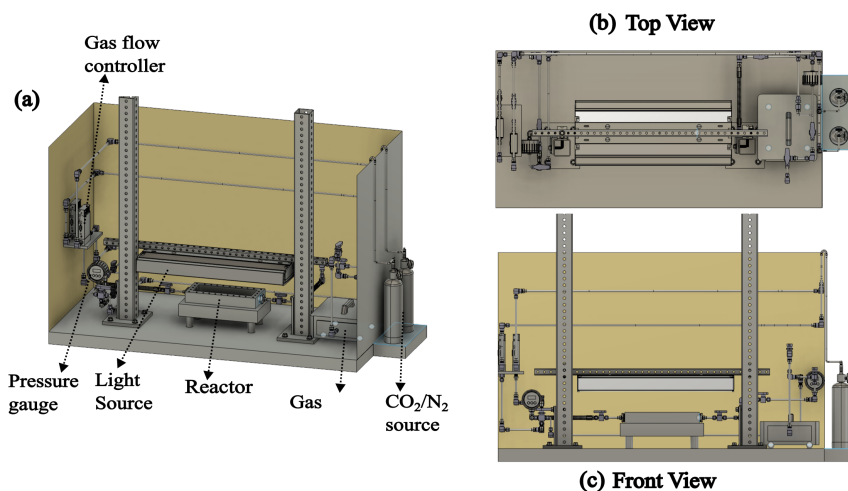


Fig. 4.2 Experimental setup for CO₂ adsorption and desorption tests. 3D Autodesk fusion views of the custom-built setup from (a) oblique, (b) top, and (c) front views [112].

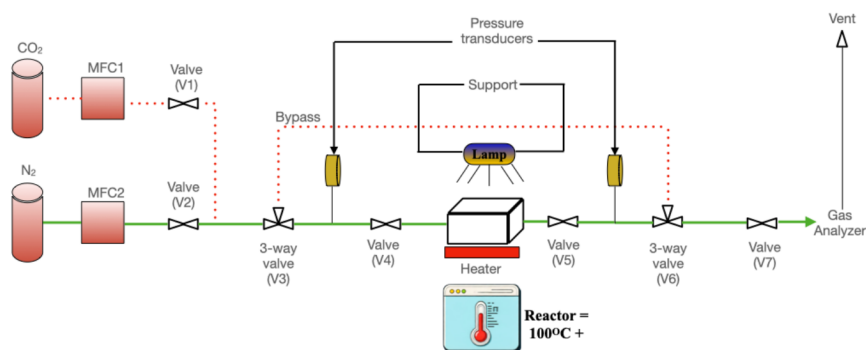
were utilized to acquire a comprehensive understanding of the material's composition. X-ray diffraction (XRD) analysis was conducted utilizing a Bruker D8 Advance diffractometer, equipped with Cu K α radiation and a LYNXEYE XE-T detector. The instrument operated in a $\theta - 2\theta$ coupled scan mode, employing a goniometer with a radius of 272 mm, to scan a 2θ angular range from 10° to 70° , with a step size of 0.02° . Samples, prepared in powdered form, were uniformly distributed on zero-background holders to ensure representative data acquisition.

4.2.3 CO₂ adsorption and desorption measurements

Description of adsorbent bed with PEI-infused silica

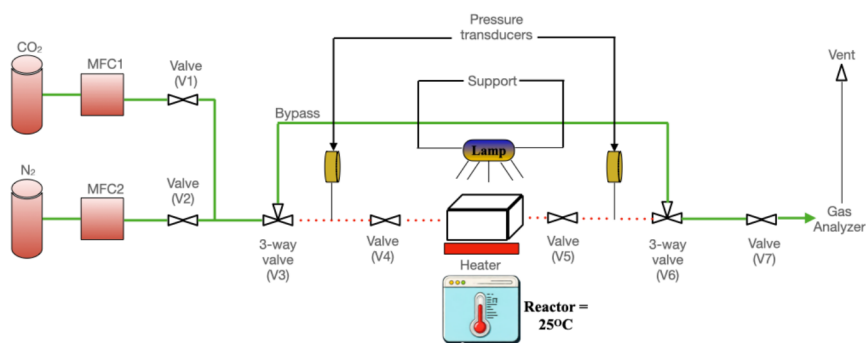
A custom-built adsorption bed was employed to assess the adsorption capacity of PEI-infused silica gel and its subsequent desorption mechanisms, utilizing both thermal and light-assisted methodologies. This adsorbent bed comprised a cuboidal aluminum chamber with internal dimensions precisely defined as 200 mm $\times$ 60 mm $\times$ 20 mm. To retain the adsorbent material, metallic mesh screens were strategically positioned at each extremity of the bed. Approximately 41 g of the PEI-infused silica gel was introduced into the central section of the chamber, situated between these mesh screens. The aluminum construction of the adsorbent bed afforded superior thermal conductivity, thereby ensuring a homogeneous temperature distribution throughout the adsorbent medium. Schematic of overall experimental setup is shown in Figure 4.2. It consist of CO₂/N₂ gas cylinders, mass-flow controller, pressure gauge, reactor, gas analyzer and a light source.

(i) Pre-cleaning phase

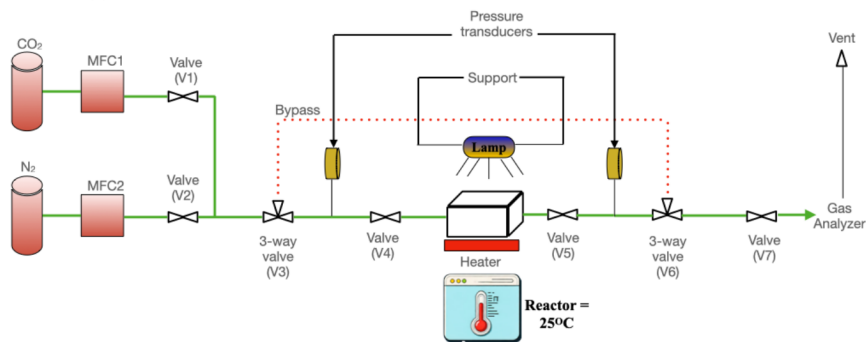


(ii) Adsorption phase

(a) First through bypass



(a) Second through reactor



(iii) Desorption phase

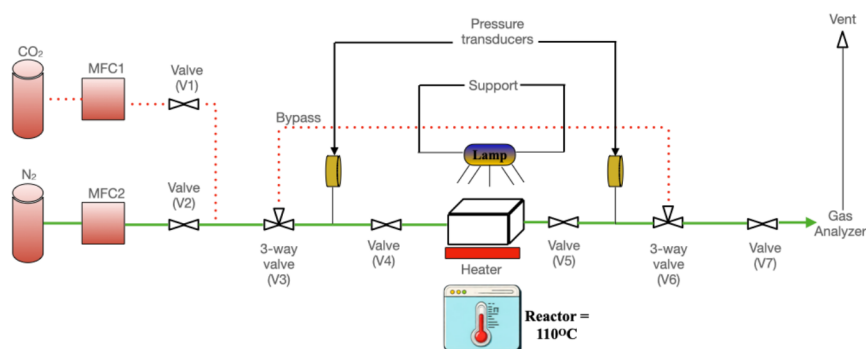


Fig. 4.3 Schematic of adsorption and desorption processes. (i) Pre-cleaning step, (ii) adsorption step, (iii) desorption step. Green color solid line indicate it is active and gas is flowing through it, red color dotted-line means it is inactive and no gas is flowing.

Adsorption and desorption process

Pre-cleaning phase :-

Prior to initiating the adsorption breakthrough experiments, the adsorbent material underwent a prerequisite preparatory treatment. Initially, the adsorbent was contained within the adsorption bed, with the inlet (V4 in Figure 4.3 (i)) and outlet (V5 in Figure 4.3 (i)) valves secured in a closed position. Subsequently, the integrated heating system (a PID Temperature Controller IPB-16S, by Inkbird) was activated to elevate the temperature within the adsorbent bed to 110 °C. Upon reaching and stabilizing the target temperature, the inlet and outlet valves were opened, and high-purity nitrogen (N₂) gas (provided by Linde Canada Inc.) was introduced into the system via the inlet valve at a precisely controlled flow rate of 100 SCCM, utilizing a mass flow controller (model 32907-59, Masterflex). This N₂ purge was sustained for 30 min at 110 °C under continuous flow to facilitate the removal of residual moisture or volatile impurities. Subsequent to this degassing phase, the heating system was deactivated, allowing the system to cool to the predetermined adsorption temperature, with the N₂ flow continuously maintained to prevent air ingress.

Throughout the adsorption and desorption experiments conducted in this study, both pressure and humidity were subjected to continuous monitoring. Pressure measurements were acquired utilizing a dedicated pressure sensor (LC10 series from Ralston Instruments), while humidity levels were concurrently recorded via a humidity sensor (HTM2500LF, TE Connectivity). Prior to the commencement of experiments, these sensing instruments underwent calibration to ensure the acquisition of precise and reliable data throughout the testing process.

Adsorption phase :-

During the adsorption phase, the flow of nitrogen was terminated, and a CO₂/N₂ gas mixture (9.9% CO₂ in N₂) was introduced at a total volumetric flow rate of 111 SCCM. Initially, this gas mixture was routed through a bypass line (as shown in Figure 4.3 (ii-a)) to allow for the stabilization of the CO₂ concentration reading. Upon achieving stabilization, the flow was redirected from the bypass line to the feed line supplying the adsorption bed, and the valves (V4 and V5 in Figure 4.3 (ii-b)) regulating the adsorption bed were subsequently opened, allowing the gas mixture to pass through the packed sorbent. Continuous monitoring of the outlet gas composition was performed using a non-dispersive infrared CO₂ sensor (model 906, Quantek Instruments) interfaced with a LabJack T7-Pro data acquisition system. The adsorption process was considered terminated upon the equilibration of the CO₂ concentration at the outlet with that at the inlet, thereby signifying the saturation of the adsorbent material.

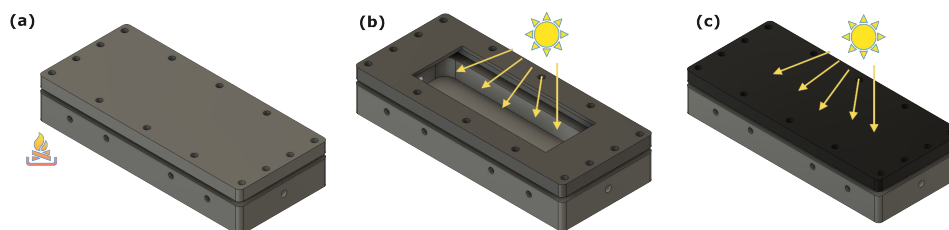


Fig. 4.4 Adsorption bed with different configurations wherein the lid is (a) an aluminum sheet without any modifications, (b) an aluminum sheet with a borosilicate window, and (c) an aluminum sheet coated with solar selective paint [112].

Table 4.1 Mass flow controller specifications (Cole-Parmer MC/MCW/MCV/MCP series) and usage in this work [112].

Item	Specification (Cole-Parmer MC/MCW/MCV/MCP series)	Notes for this work
Accuracy (at calibration, after tare)	$\pm(0.8\% \text{ of reading} + 0.2\% \text{ of full-scale})$	Used to bound flow error for each MFC [26].
High-accuracy option	$\pm(0.4\% \text{ of reading} + 0.2\% \text{ FS})$	If enabled; not assumed here [26].
Repeatability	$\pm 0.2\% \text{ FS}$	Relevant for run-to-run scatter [26].
Zero/span shift	0.02% FS per $^{\circ}\text{C}$ or per atm	Use lab T/P stability to argue this is negligible [26].
Turndown & response	200:1; $\approx 100 \text{ ms}$ typical	For context [26].
Gas selection	Built-in GAS SELECT TM /COMPOSER TM	Confirms gas-specific calibration was used (CO_2 , N_2) [26].

Desorption phase :-

Upon completion of the adsorption phase, desorption experiments were conducted systematically under three different conditions. For the first condition, designated as Case 1 (Figure 4.4 (a)), desorption was carried out in the absence of light (“dark” condition), utilizing a thermal heater to attain the predetermined target temperature (110°C). Conversely, light-assisted desorption experiments were executed under two distinct configurations: Case 2 involved the transmission of light through a transparent glass window directly onto the adsorbent bed (Figure 4.4 (b)), whereas Case 3 entailed applying illumination directly to the reactor top, which was coated with solar-selective paint (Thermalox 250 Selective Black) (Figure 4.4 (c)). In both light-assisted scenarios, an indoor LED lighting system (Model SolarSystem 550, California Lightworks, USA) served as the light source, elevating the adsorbent temperature to approximately 110°C . The average light intensity was quantified at 2.3 kW m^{-2} . This measurement was obtained using a calibrated digital optical power and energy meter, with its thermal power sensor precisely positioned at an equivalent distance from the light source as the adsorbent bed. Figure 4.5 illustrates a comparative analysis between the lamp spectrum and the AM1.5 G spectrum, following normalization to 1-sun conditions. A normalized mismatch factor (M) of 0.93 was calculated, thereby confirming that the LED array emitted a solar-representative spectrum. The intensities reported represent the averaged plane-of-array irradiance measured at the lid surface. Consequently, the AM1.5G-equivalent irradiance (G_{eq})

Table 4.2 Relative standard uncertainty budget for irradiance measurement (PM100D + S401C) [112].

Contributor	Rel. std. unc. (1σ)	Rationale
Meter calibration (S401C)	1.5%	Thorlabs thermal sensors: $\pm 3\%$ ($k=2$) at calibration wavelength $\Rightarrow \sim 1.5\%$ at 1σ .
Short-term repeatability	0.5%	Assessed stability of PM100D+S401C over repeated placements (conservative).
Spatial non-uniformity (lid plane)	2.0%	Assessed mapping uncertainty at the measurement plane (conservative; same spot and height).
Alignment/cosine	1.0%	A small residual tilt of the sensor is normal (a few degrees $\Rightarrow$ cosine error bound).
Spot-size/distance	2.0%	Beam divergence and standoff tolerance impacting irradiance at the lid plane.
Aperture/area	0.5%	Aperture diameter tolerance $\Rightarrow$ area uncertainty.
Spectral mismatch (M)	1.5%	From spectrum match/normalization used to compute M (conservative 1σ).
Combined (1σ)	3.74%	$u_r = 3.74\%$
Expanded ($k=2$)	7.5%	$U_r = 2u_r$

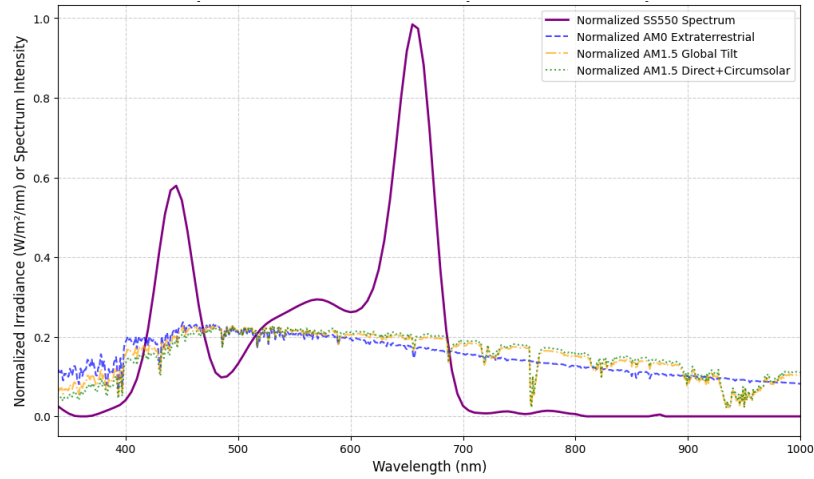


Fig. 4.5 Comparison of normalized SolarSystem 550 spectrum and standard AM1.5 spectrum [112].

was determined using the formula $G_{eq} = M \cdot G_{sim}$, resulting in an equivalent of approximately 2.14 suns. I have also provided a G_{eq} uncertainty budget in Table 4.2¹.

The desorption process commenced with the termination of the CO₂ supply, followed by the elevation of the temperature to 110 °C, which was sustained throughout the desorption phase. Initially, both the inlet and outlet valves of the adsorption bed were secured (off); however, upon achieving the target temperature of 110 °C, these valves (V4 and V5 in Figure 4.3 (iii)) were subsequently opened. Following this, the adsorption bed underwent purging with high-purity N₂ at a controlled flow rate of 100 SCCM. Continuous monitoring of the desorption process was achieved by tracking the CO₂ concentration at the reactor outlet. Des-

¹Instrument uncertainties are sourced directly from the manufacturer's datasheet and calibration certificate for the Thorlabs PM100D/S401C; lamp specifications are obtained from the California Lightworks SolarSystem 550 datasheet. Where a $k=2$ bound is stated, it is converted to relative 1σ by dividing by 2. Uncertainty model (relative 1σ). I combine contributors in quadrature:

$$u_r^2(G_{eq}) = u_r^2(E_{meas}) + u_r^2(M)$$

;

$$u_r^2(E_{meas}) = \sum u_r^2(contributor)$$

orption was considered complete once the CO₂ concentration returned to its baseline levels. The total quantities of adsorbed and desorbed CO₂ were subsequently quantified through the integration of the areas above and beneath their respective adsorption and desorption curves. Adsorption and desorption measurements for Cases 1 to 3, as well as control runs employing bare silica gel and a blank reactor, were systematically conducted in duplicate. All experiments were performed under consistent operational parameters and utilized identically prepared PEI-infused silica gel samples. The reported data (in Figure 4.8) for both the adsorption and desorption phases represent the arithmetic mean of the quantified CO₂ amounts. The error bars depicted in the corresponding plots denote the 95% confidence intervals (CIs) for the mean estimate, derived from the two replicates for each condition, thereby indicating experimental reproducibility and intrinsic variability.

Temperature-field metrics and definitions

The chosen regeneration temperature of 110 °C represents a considered compromise between two key factors: promoting the endothermic dissociation of PEI-CO₂ carbamates and bicarbonates, a process that achieves significant efficiency beyond approximately 90 °C, and mitigating the oxidative degradation of PEI [115, 132, 126]. Evidence from cyclical laboratory and pilot-scale investigations [4, 158] supports this operational temperature, showcasing complete capacity restoration and the preservation of amine stability when sorbents undergo regeneration within the 90 °C-120 °C temperature window [115, 132, 126, 4, 158]. Moreover, the regeneration temperature of 110 °C is readily achievable through the utilization of low-grade industrial waste heat or advanced flat-plate solar collectors (FPSCs), which are proficient in delivering fluid temperatures ranging from 100 °C to 120 °C under typical insolation conditions. Accordingly, the selection of 110 °C is strategically aimed at optimizing desorption efficiency, preserving sorbent stability, and facilitating the integration of practical, low-carbon thermal energy sources.

The assessment of bed heating uniformity and its direct correlation with desorption kinetics was conducted utilizing four strategically embedded temperature sensors and comprehensive analysis of the outlet CO₂ profile. Specifically, four T-type thermocouples (T1-T4) were positioned approximately equidistantly along the reactor's longitudinal axis: T1 at the gas inlet, T4 at the gas outlet, and T2-T3 integrated within the sorbent bed. From the acquired data, key metrics were extracted, including the instantaneous temperature distribution with corresponding statistical summaries, the synchronization lag relative to a predefined threshold, and the desorption time referenced against a baseline condition. These definitions are subsequently elaborated, with their respective values presented in Table 4.3.

Let $T_i(t_k)$ denote the temperature at sensor $i \in \{1, 2, 3, 4\}$ sampled at times t_k ($k \in \{1 \dots N\}$) over the desorption window $[t_0, t_N]$, where t_0 and t_N represent the times at which the desorption phase is initiated and completed, respectively. The instantaneous spread is then given by Equation (4.1):

$$\Delta T(t_k) = \max_i T_i(t_k) - \min_i T_i(t_k) \quad (4.1)$$

For summary statistics we use the instantaneous spread to determine and report the time-averaged temperature spread, the maximum temperature spread within the adsorption bed, and the 95th percentile for the temperature spread, which are described further with references to Equations 4.2 to 4.4 below.

The time-averaged temperature spread, $\Delta \bar{T}$, over the desorption phase is given by Equation (4.2):

$$\Delta \bar{T} = \frac{1}{N} \sum_{k=1}^N [\max_i T_i(t_k) - \min_i T_i(t_k)] \quad (4.2)$$

The maximum temperature spread within the adsorption bed during the desorption phase, ΔT_{max} , is given by Equation (4.3):

$$\Delta T_{max} = \max_k \Delta T(t_k) \quad (4.3)$$

The 95th percentile over all points in $[t_0, t_1]$ is given by Equation (4.4):

$$\Delta T_{95} = Q_{0.95} \{ \Delta T(t_k) \} \quad (4.4)$$

Thermal synchronization (90 °C): for each sensor i , defined as the lag between the time when the first and last bed sensors reach (90 °C), is given by Equation (4.7), smaller lag_{90} means more synchronous, uniform heating:

$$t_{90}^i = \inf \{ t > t_0 : T_i(t) > 90^\circ \text{C} \} \quad (4.5)$$

$$t_{90}^{max} = \max_i (t_{90}^i) \quad ; \quad t_{90}^{min} = \min_i (t_{90}^i) \quad (4.6)$$

$$lag_{90} = t_{90}^{max} - t_{90}^{min} \quad (4.7)$$

where superscripts min and max indicate the earliest and latest sensors to cross 90 °C, respectively.

To quantify differences in release kinetics, the desorption time was defined as the duration required for the smoothed CO₂ concentration at the reactor outlet to decrease below 0.05% following the initiation of desorption. This threshold approximates a “clean-bed” baseline,

Table 4.3 Metrics for evaluating temperature profiles in the adsorption bed along with desorption time. Desorption time is defined as the time required to reach 0.05% CO₂ threshold after start of desorption [112].

Case	ΔT_{max} (°C)	$\Delta \bar{T}$ (°C)	ΔT_{95} (°C)	t_{90}^{min} (sec)	t_{90}^{max} (sec)	lag_{90} (sec)	Adsorption (mmol/g)	Desorption (mmol/g)	Desorption time (sec)
Thermal (Case 1)	7.03	1.85	5.47	~22206	~22396	~190	0.60±0.008	0.23±0.009	~3892
Direct light (Case 2)	19.14	11.93	17.84	~23650	~24478	~828	0.59±0.002	0.28±0.020	~6025
Indirect light (Case 3)	9.18	3.48	7.90	~22650	~22650	~0	0.70±0.005	0.28±0.006	~3058

lies below the desorption tail across all cases, and furnishes a reproducible endpoint at the device level. Conducting a sensitivity analysis reveals that altering the cut-off concentration does not alter the trends observed from the results. From an analytical standpoint, the outlet CO₂ concentration in the terminal tail decays approximately exponentially. Thus, for example, shifting the endpoint from 0.05% to 0.10% shortens the desorption time by $\Delta t \approx \tau_{tail} \ln 2 \approx 0.693 \tau_{tail}$ across all cases, where τ_{tail} represents the time constant of the tail in the smoothed CO₂ trace. As both thresholds reside on the same exponential tail and values are comparable between cases, the estimates shift earlier by a similar amount, thereby preserving their relative ordering and altering the $\approx 22\%$ faster desorption in indirect mode only marginally.

Throughout the experiments, consistent operational parameters were maintained, with the inlet pressure held at approximately 1 atm and humidity at 0% during both the adsorption and desorption processes. These stable conditions were important to preclude any influence of moisture or pressure fluctuations on the observed CO₂ adsorption and desorption behavior. During the adsorption phase, a feed gas composition comprising 11 SCCM CO₂ and 100 SCCM yielded a corresponding CO₂ partial pressure (p_{CO_2}) of approximately 0.10 atm.

4.3 Results

Figure 4.6 illustrates the temperature profiles along with the adsorption/desorption breakthrough curves for various adsorbent bed configurations investigated in this study, consisting of the blank reactor, bare silica, Case 1, 2, and 3. The CO₂ concentration at the adsorbent bed outlet is shown by a purple line, with the cleaning, adsorption, and desorption phases clearly labeled and shaded in blue within each figure. The locations of the four thermocouples within the adsorbent bed are depicted in the inset of each corresponding figure. A more detailed discussion of the breakthrough curves and temperature profiles is provided with reference to Figure 4.6 and in Section 4.3.1 & 4.3.2, respectively.

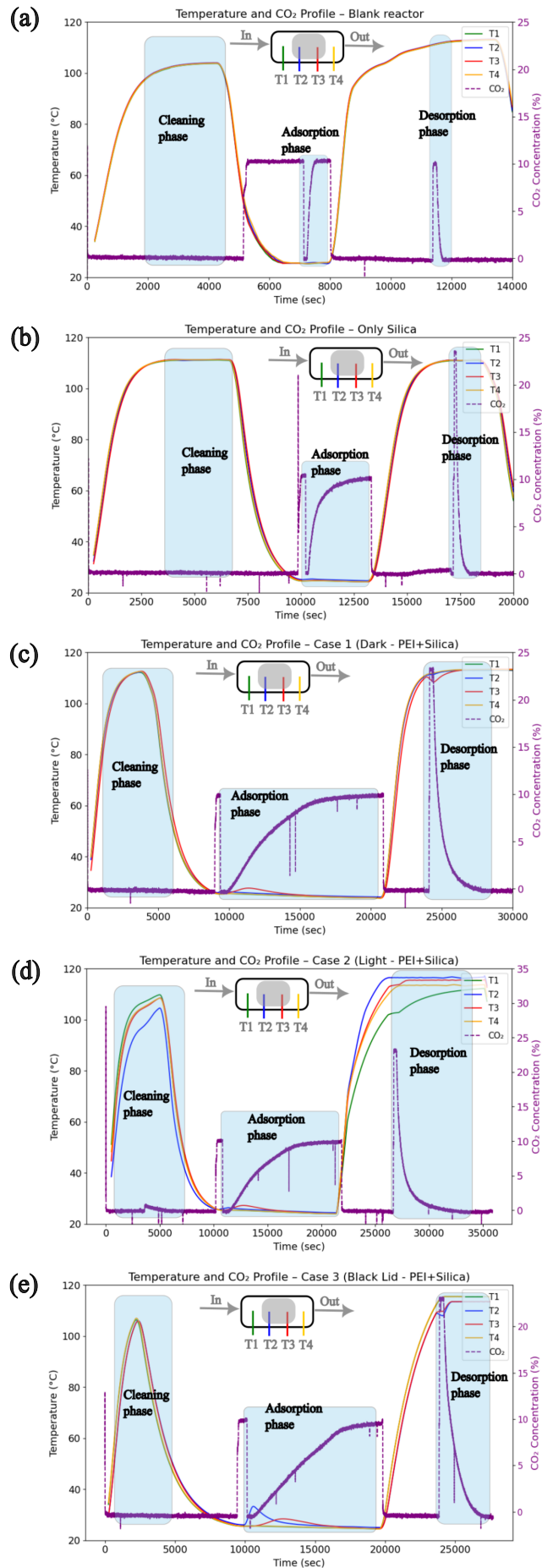


Fig. 4.6 Temperature profiles for different cases. (a) blank reactor, (b) only silica, (c) thermal (case 1), (d) direct light (case 2), (e) indirect light (case 3) [112].

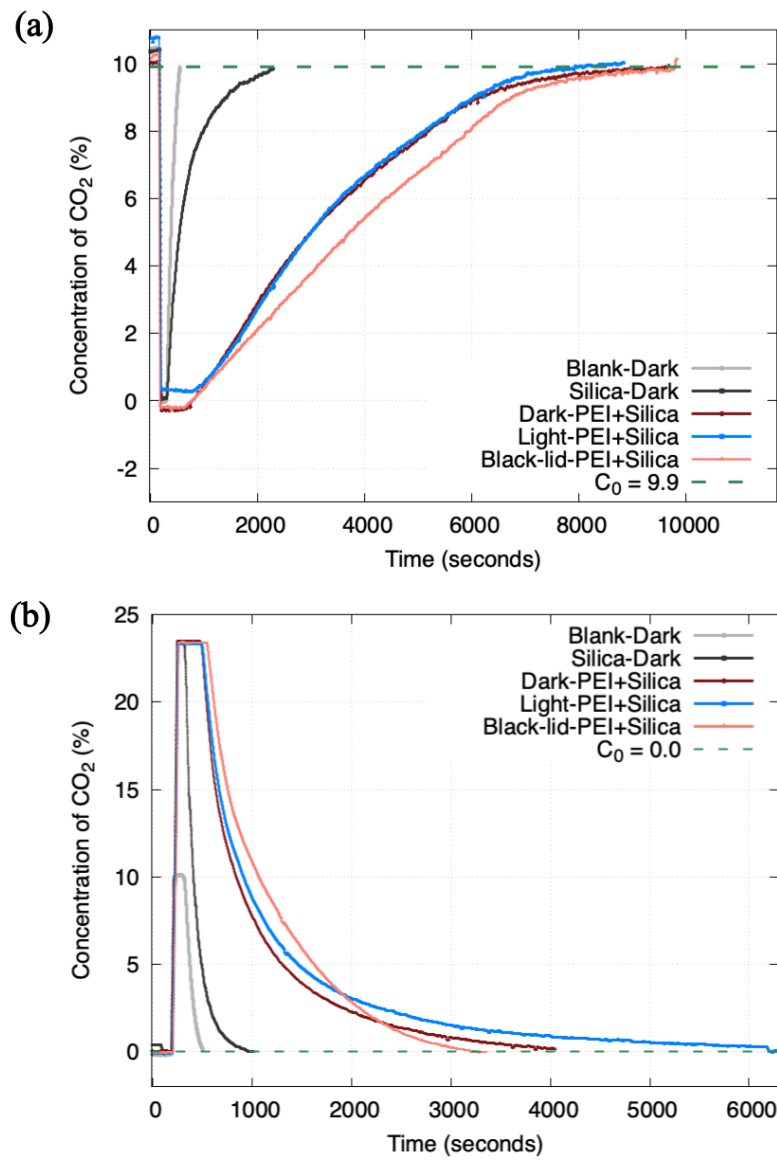


Fig. 4.7 CO₂ breakthrough curve. (a) Adsorption phase, (b) Desorption phase [112].

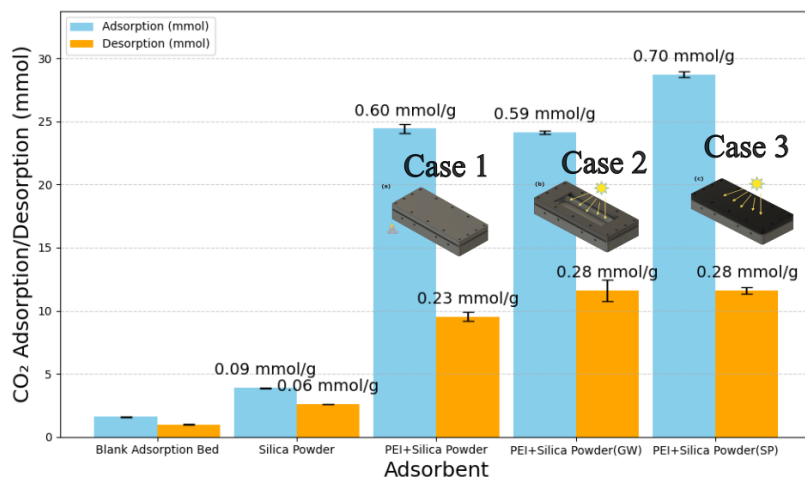


Fig. 4.8 Amount of CO₂ adsorbed (blue bars) and desorbed (orange bars) for an empty adsorption bed and different adsorbents. GW = Glass Window, SP = Solar Selective Paint. Cases 2 and 3 are compared according to the same run number (i.e. runs 3 and 4) and the data from Case 1 is from the first two runs for a sample [112].

Figure 4.7 presents the CO₂ breakthrough curves obtained under different experimental conditions, illustrating both the adsorption and desorption behaviors. The first plot (Figure 4.7a) depicts the adsorption phase, where the concentration of CO₂ in the output is monitored over time. The green dashed line represents the inlet CO₂ concentration, and the area between this line and the CO₂ concentration profiles is indicative of the amount of CO₂ adsorbed for each experiment. Since light is only introduced during the desorption phase, the adsorption profiles for Dark-PEI+Silica (Case 1) and Light-PEI+Silica (Cases 2 and 3) remain nearly identical, as expected.

The second plot (Figure 4.7b) depicts the desorption phase, where the CO₂ release is monitored over time. The area under the CO₂ concentration plots in Figure 4b represents the amount of CO₂ desorbed. For the case of the Dark-PEI+Silica (Case 1) sorbent, desorption was carried out using conventional heating at 110 °C, resulting in a gradual decrease in the effluent CO₂ concentration. When desorption was performed using solely light (Cases 2 and 3), the desorption curves showed broadly similar profiles, though slight differences are evident in the initial desorption rate and the duration of elevated CO₂ release. In particular, the Black-lid-PEI+Silica sample (Case 3) exhibits a more gradual tail, which may be attributed to slower, more uniform heating under indirect photothermal conditions. The effects of heating rates on the regeneration phase and the temperature profiles in the adsorbent bed for the different cases are discussed in Section 4.3.2.

4.3.1 Adsorption/desorption results

The amount of CO₂ adsorbed and desorbed during the breakthrough tests is presented in Figure 4.8². The results are shown for five different experimental conditions: “Blank Adsorption Bed,” “Silica Powder,” “PEI + Silica Powder (Case 1),” and “PEI + Silica Powder (using light - Cases 2 and 3)”. The “Blank Adsorption Bed” condition exhibits the lowest adsorption and desorption values, suggesting minimal CO₂ interaction with the inner walls and surfaces inherent in the experimental setup. The “Silica Powder” condition demonstrates a modest increase in both adsorption and desorption compared to the “Blank Adsorption Bed”, implying some interaction and adsorption between the CO₂ and the silica material, likely due to physisorption mechanisms driven by the surface area of the silica gel. Although the exact BET surface area of the silica used in this study was not measured, the material employed (silica gel, 60 Å pore size, 70–230 mesh) typically exhibits a surface area in the range of 480–540 m²/g [121]. The “PEI + Silica Powder” adsorbents exhibit significantly higher CO₂ adsorption capacities as compared to the reference cases wherein PEI is absent. This substantial increase in CO₂ uptake can be attributed to incorporating PEI, an amine-rich polymer known for its strong affinity towards CO₂ through chemisorption. The amine groups within PEI react with CO₂, forming carbamates and bicarbonates, thereby significantly enhancing the overall CO₂ capture capacity of the material. While the desorption values for “PEI + Silica Powder (Case 1)” were also higher than the baseline conditions, they were notably lower than the corresponding adsorption values, suggesting that a significant portion of the captured CO₂ remained bound to the material under the conditions employed during the desorption phase.

The “PEI + Silica Powder (using light - Cases 2 and 3)” configurations are pivotal to understanding the influence of light on the desorption process. As mentioned earlier, light is exclusively applied during the desorption phase for these cases, while the adsorption phase is conducted under the same conditions as the “PEI + Silica Powder” sample. Comparative analysis of the desorption data in Figure 4.8 for the ‘PEI + Silica Powder (using light - Cases 2 and 3)’ samples reveals a clear enhancement in CO₂ desorption when light is applied. For example, desorption under Case 1 (conventional heating) resulted in 0.23 mmol/g of CO₂ released, while Case 2 (direct light through a glass window) and Case 3 (indirect photothermal using a solar-absorptive coating) each yielded 0.28 mmol/g, corresponding to a ~22% increase in desorbed CO₂.

A direct comparison of desorption times with the PEI-silica literature is instructive. Sandhu et al. reported that over 80% of the adsorbed CO₂ was released within the first 3 minutes of

²A python script required to calculate the area under the curve in Figure 4.7 and obtain values mentioned in Figure 4.8 is mentioned in Appendix B.

steam injection at 110 °C in a packed bed of PEI-impregnated silica [115], while Al-Marri et al. demonstrated breakthrough-to-saturation adsorption times of under 72 seconds and majority desorption within approximately 5 minutes for PEI/mesoporous silica foam under thermal regeneration [2]. These times are substantially shorter than the ≈ 51 min (Case 3) and ≈ 65 min (Case 1) desorption durations observed in the present study, though the comparison is not strictly equivalent: the literature values involve either steam stripping, which disrupts CO₂-amine bonds more aggressively than an N₂ purge, or significantly smaller sorbent beds. Thakkar et al., using a protocol-set fixed-bed experiment with 420 ppm DAC-relevant CO₂ feeds and N₂ purge regeneration at 100-120 °C, employed adsorption and desorption durations of 250 and 180 min respectively [132], placing our cycle times well within the range of comparable N₂ purge thermal regeneration studies at higher CO₂ concentrations. Taken together, the present desorption times are consistent with N₂ purge TSA literature benchmarks, and the 22% reduction achieved by the indirect photothermal mode (Case 3 vs. Case 1) represents a meaningful improvement; however, achieving the sub-10 minute desorption times reported for steam-assisted regeneration would require either steam integration or a more aggressive photothermal heating rate than is feasible with the current solar-selective paint configuration.

These results show that for adsorption/desorption measurements carried out at equivalent cycle numbers (the third and fourth cycles were used to collect data for Cases 2 and 3 in Figure 4.8), the ratios of desorbed to adsorbed CO₂ for Case 2 and Case 3 were within experimental uncertainty, suggesting comparable regeneration efficiencies between the two photo-driven methods. Since the amount of CO₂ captured for the Case 3 is similar to the amount captured in Case 2 we suspect the dominant regeneration mechanism is likely photothermal rather than photochemical. While a photochemical contribution to the regeneration process for Case 2 cannot be completely ruled out, this contribution was not strong enough to increase the amount of CO₂ captured compared to Case 3. Future studies employing FTIR/XPS and controlled aging will aim to rigorously quantify chemical changes such as “amine leaching”³. This process can lead to a reduction in sorbent capacity and alterations in mass transport properties. The effects of heating the adsorbent by irradiating them directly (Case 2) and indirectly (Case 3) on the temperature profiles in the adsorbent bed and the duration of the regeneration phase are discussed further with reference to Table 4.3 in Section 4.3.2.

While further cycling of Case 2 was precluded by observed discoloration (Figure 4.10b), Case 3 underwent assessment for aging across nine cycles. The blue and orange bars in the Figure 4.9 correspond to the amount of CO₂ adsorbed and desorbed, respectively, with

³It refers to the physical loss or migration of PEI from the silica support, a phenomenon distinct from chemical aging.

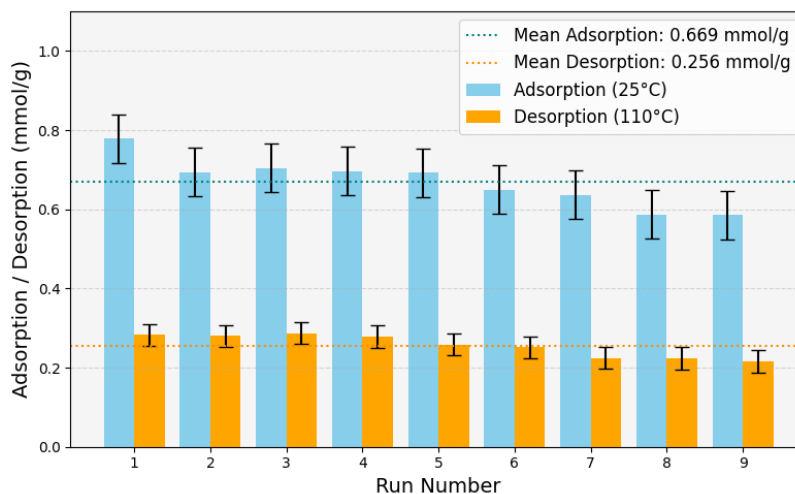


Fig. 4.9 Adsorption and desorption capacity of PEI-silica in the adsorption bed coated with solar selective paint over repeated runs [112].

error bars indicating the standard deviations across the measurements. The data shows the average CO_2 adsorption was 0.669 mmol/g across the cycles, while the mean amount of CO_2 desorbed was 0.256 mmol/g. These findings suggest that, although the system did not completely release all the captured CO_2 during the desorption phase in each cycle, it exhibited consistent desorption performance throughout the runs (crucially, the desorbed/adsorbed ratio remained largely unchanged at 0.383 ± 0.019 mmol/g (Table 4.4)). This indicates that while aging reduces the overall adsorption capacity, it does not compromise the proportion of captured CO_2 that can be released during the regeneration phase, affirming the efficacy of the photothermal approach in releasing adsorbed molecules.

4.3.2 Analysis of thermal profiles in the adsorption bed

Figure 4.6 (a-e) and Figure 4.11 illustrate temperature profiles at different bed locations during the adsorption and desorption phases. Although the adsorption phases and peak regeneration temperatures were similar across all experimental conditions, there were notable variations in heating uniformity. Over the desorption window, the mean temperature spread, $\Delta\bar{T}$, was 1.85 °C (Case 1: thermal), 11.93 °C (Case 2: direct illumination), and 3.48 °C (Case 3: indirect photothermal). In Case 2, the rapid heating of the at the top side of the adsorbent bed, which was surface exposed to incident radiation, relative to the bed's interior resulted in persistent axial (Figure 4.6d) and radial (Figure 4.11(a)) temperature gradients. Consequently, only a limited portion of the adsorbent bed achieved the effective desorption temperature window early in the process, leading to a slower progression of the desorption front. This

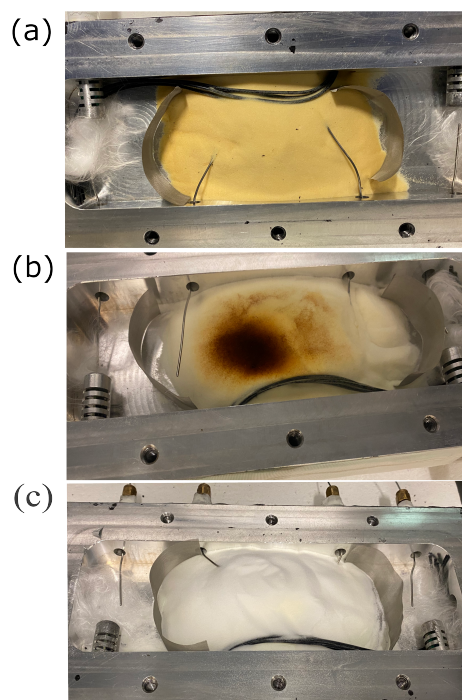


Fig. 4.10 Post-experiment PEI+silica sample condition. (a) when employing indirect light-assisted desorption (Case 3), (b) when employing direct light-assisted desorption (Case 2), and (c) pure silica gel [112].

Table 4.4 Adsorption/Desorption data over nine consecutive runs [112].

Cycle	Adsorbed CO ₂ (mmol/g)	Desorbed CO ₂ (mmol/g)	Ratio = $\frac{DesorbedCO_2}{AdsorbedCO_2}$
1	0.778	0.283	0.364
2	0.694	0.281	0.405
3	0.705	0.288	0.405
4	0.696	0.279	0.401
5	0.692	0.259	0.375
6	0.650	0.252	0.388
7	0.637	0.225	0.354
8	0.587	0.225	0.382
9	0.586	0.217	0.370
Mean $\pm$ SD	0.669 $\pm$ 0.061	0.257 $\pm$ 0.028	0.383 $\pm$ 0.019

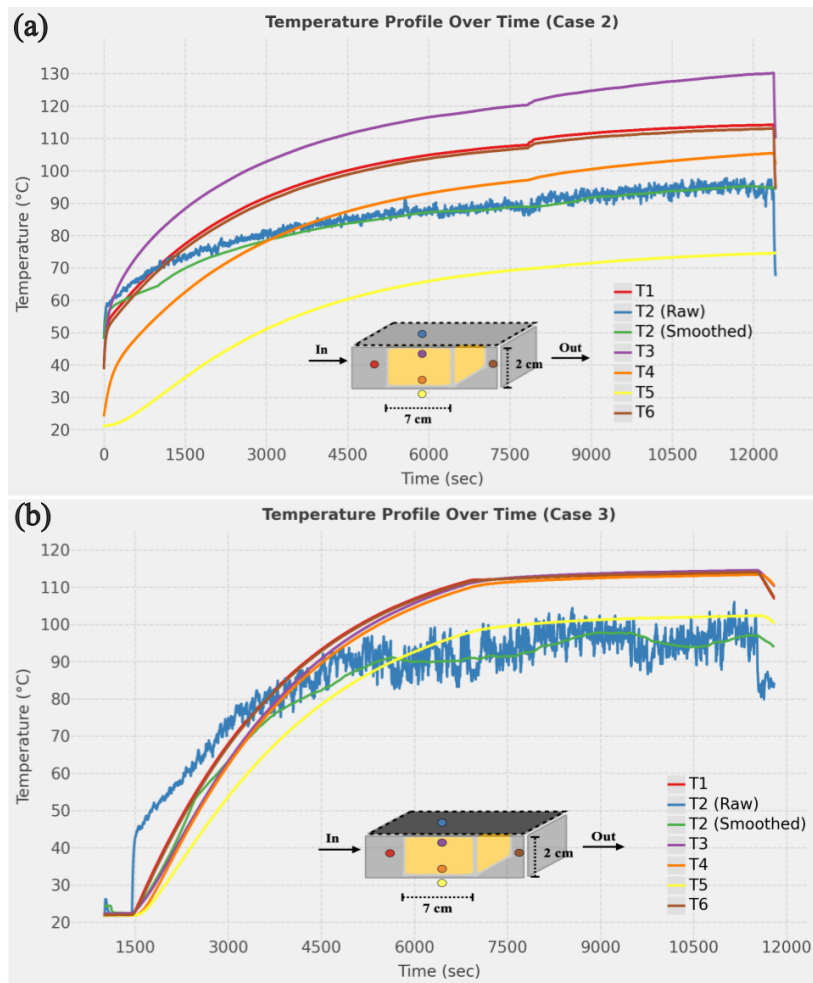


Fig. 4.11 Temperature profiles measured at six thermocouple locations (T1–T6) for (a) Case 2 and (b) Case 3. Inset schematic indicates sensor positions in the reactor [112].

observation aligns with transient CO₂ accumulation near the heated layer and the potential for re-adsorption in cooler regions; however, intra-bed gas composition was not directly measured. In contrast, Cases 1 and 3 exhibited more homogeneous temperature distributions, enabling the entire adsorbent bed to reach the operational temperature range more rapidly and undergo uniform desorption, resulting in reduced regeneration times (approximately 3896 s and 3058 s, respectively, compared to approximately 6024 s for Case 2).

In alignment with the thermal localization observed in Case 2, surface examinations indicated discoloration and localized alterations exclusively under direct illumination. Although diffusion measurements were not conducted, previous research suggests that thermal or oxidative densification of PEI on silica can impede amine accessibility and elevate transport resistance [151, 47, 54]. Consequently, this observation is presented as a materials-level interpretation rather than a direct measurement. Furthermore, given that Case 2 was operated under dry conditions, the formation of urea linkages is a plausible outcome. Dehydration of ammonium carbamates to urea is facilitated in dry CO₂ environments and significantly inhibited by the presence of even minimal amounts of water, a phenomenon documented for PEI/silica and analogous amine sorbents [54]. This finding offers a materials-level explanation for the observed discoloration and localized changes under direct illumination, despite the absence of direct urea assays in this study. Finally, the thermal synchronization metric mirrored the kinetics: the time for all sensors to reach 90 °C (lag_{90}) was ~ 0 s (Case 3), ~ 190 s (Case 1), and ~ 828 s (Case 2), matching the order of desorption times. I have also included a least-squares regression (desorption time versus lag_{90} or ΔT_{95}) with slope, R^2 , and 95% confidence intervals to substantiate the correlation between improved thermal uniformity and shorter desorption times (refer to Figure 4.12).

Importantly, the utilization of the solar-selective paint-coated surface in this setup led to accelerated desorption rates and more uniform thermal distribution (refer to Figures 4.6 and 4.11, for temperature profiles), which helped mitigate localized overheating of the adsorbent. Consistent with these profiles, Table 4.3 shows shorter desorption times for the coated configuration across otherwise matched conditions, underscoring that thermal uniformity and surface engineering are key levers in photothermal regeneration. Beyond kinetics, the coated approach (Case 3) maintained sorbent integrity over repeated cycles, indicating improved durability and positioning this indirect photothermal strategy as a promising, scalable option for light-assisted direct air capture.

However, some secondary factors may still influence the comparison. First, the observed increase in desorption for Case 2 over Case 1 could be influenced by temperature gradients within the adsorbent bed, with the silica gel near the top of the bed potentially being significantly hotter than the adsorbents closer to the middle of the adsorbent bed where the

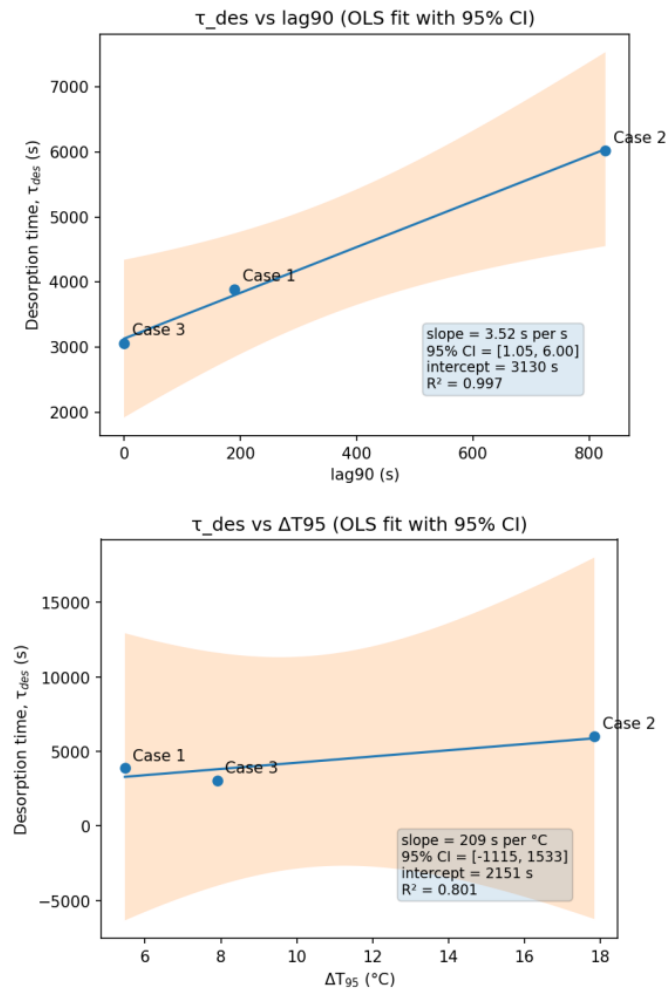


Fig. 4.12 Hotspot non-uniformity vs. desorption time. Larger lag90 $\Rightarrow$ a smaller fraction of the bed is actively desorbing at any instant $\Rightarrow$ slower front propagation $\Rightarrow$ longer desorption time. Because $n=3$ ($df = 1$), 95% confidence bands are necessarily wide ($t_{0.975,1} = 12.706$); we therefore report slope $\pm 95\%$ CI numerically and interpret the fit as supporting evidence rather than a precise predictive model [112].

thermocouples were located. Secondly, there may have been some CO₂ generated when the sample discoloured (see Figure 4.10b), while not ruled out, cannot be quantified with the present data.

The results presented in this work underscores the effectiveness of using light energy to drive CO₂ desorption from the PEI-modified silica gel, with the photothermal mechanism likely playing the dominant role. These results are highly significant and have major implications for replacing energy sources typically used for regenerating CO₂ adsorbents, such as electric power or heat derived from fossil fuels, with solar radiation. The intensity of the light incident onto the adsorption bed during the experiments, which was 2.3 kW m⁻² (equivalent to 2.3 times the standard AM1.5 solar spectrum intensity of 1 kW m⁻²), could be provided using flat plate solar collectors (FPSCs) with small concentration ratios. In practice, scalable FPSCs coupled with single-axis flat panel solar concentrators can readily achieve solar concentration factors greater than ten [123]. In contrast to more complex concentrating or evacuated-tube systems, FPSCs offer mechanical simplicity, require no tracking mechanisms, and are constructed from lightweight aluminum-polymer composites [146]. This simplicity translates to lower capital costs, typically 20–40% less per kW than evacuated tubes [146], making them a scalable heat source for distributed applications. Because our PEI-silica bed regenerates efficiently within the FPSC temperature range, the entire capture unit can be powered by cost-effective, lightweight solar-thermal hardware, enabling fully renewable and easily deployed solid-amine CO₂ capture.

4.3.3 Characterization

To better understand the underlying mechanisms responsible for these observed differences in performance and stability, a detailed characterization study was conducted on representative samples subjected to the various experimental conditions. The experimental investigation was carried out on a set of PEI-infused silica gel adsorbent samples subjected to different treatment conditions to evaluate their stability and performance in CO₂ adsorption–desorption cycles. The samples are defined as follows:

- Sample 1: Pristine PEI-infused silica gel before any experimental treatment.
- Sample 2: Post-experiment PEI-infused silica gel exposed to direct light through borosilicate glass (Case 2).
- Sample 3: Post-experiment PEI-infused silica gel exposed to direct light, exhibiting visible surface burning (Case 2).

- Sample 4: Post-experiment PEI-infused silica gel desorbed under Case 3 conditions, where the reactor was externally heated by light incident on a solar-absorptive coating (no direct illumination of the sample).
- Sample 5: Bare silica gel used as a control (without PEI infiltration).

These five samples were analyzed using SEM, EDX, and XRD to assess their structural, compositional, and functional integrity under varying operating conditions, and the results are shown in subsequent sections.

SEM

The surface morphology of the PEI-infused silica gel adsorbents was analyzed using SEM imaging at two different magnification levels before and after the experimental treatments. The lower magnification of $500\times$ was utilized to evaluate the overall particle structure (refer to Figure 4.13), while the higher magnification of $90,000\times$ allowed for the observation of more detailed surface features (refer to Figure 4.14). To mitigate the effects of surface charging during imaging, all samples were coated with a thin conductive layer.

Examination of the silica particles across all samples at low magnification (Figure 4.13) revealed their characteristic angular and irregular morphologies, with no observable indications of structural degradation, fusion, or collapse following the CO_2 adsorption–desorption cycles. This finding suggests that the infiltration of PEI and the application of light-assisted desorption did not induce significant damage to the bulk particle structure. The consistency in particle size and shape before and after the experimental treatments supports the structural resilience of the silica under the applied thermal and photonic conditions.

At the higher magnification level (Figure 4.14), the surface morphologies of the samples exhibit generally comparable characteristics. Although minor variations in surface roughness are observed, they are not substantial enough to enable definitive differentiation among the samples. Owing to the resolution limitations of conventional SEM imaging and the low atomic contrast of organic materials such as PEI, direct visual identification of PEI was not observed. As a result, any inferences regarding the presence or degradation of PEI based solely on surface texture remain speculative in nature.

EDX

The EDX atomic percentage analysis of the PEI-silica adsorbents reveals subtle variations in surface composition before and after experimental exposure, along with quantifiable uncertainties (refer to Figure 4.15). In the pre-experiment sample (Sample 1), the surface

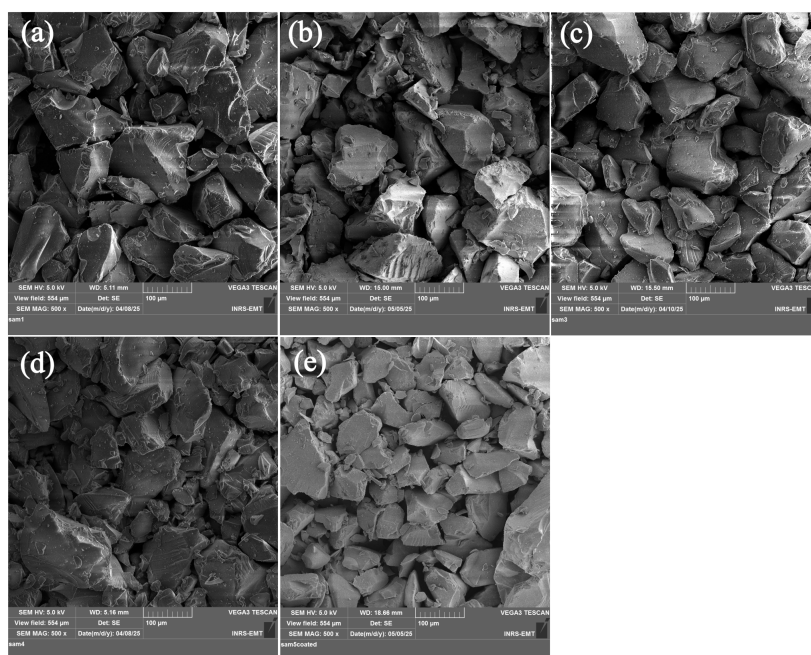


Fig. 4.13 SEM micrographs of the five adsorbent samples at low magnification ($500\times$): (a) Sample 1: pristine PEI-silica, (b) Sample 2: post-experiment with direct light exposure, (c) Sample 3: post-experiment with visible surface burning, (d) Sample 4: post-experiment with indirect light via solar absorptive coating, and (e) Sample 5: bare silica control. All samples exhibit the characteristic angular and irregular morphology of the silica support [112].

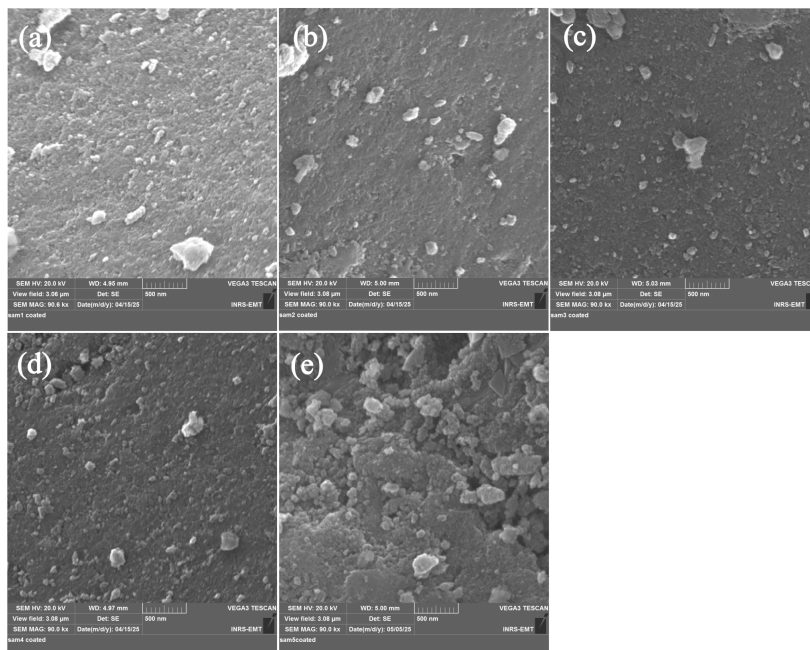


Fig. 4.14 High-magnification (90k $\times$) SEM micrographs of the same five samples: (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4, and (e) Sample 5. At this scale, no significant differences in surface texture or coating features are distinguishable among the samples. While minor roughness variations exist, the organic PEI layer is not directly observable due to the resolution limitations of SEM for low-atomic-number elements. All samples were sputter-coated with a thin conductive layer prior to imaging [112].

composition is characterized by 22.84 ± 1.78 at.% Si, 50.30 ± 6.09 at.% O, 19.08 ± 2.13 at.% C, and 7.70 ± 1.11 at.% N (1σ), with sulphur detected only in trace amounts (0.08 ± 0.04 at.%). These values indicate a robust deposition of PEI over the silica matrix (this is supported by the relatively high atomic percentages of carbon and nitrogen, both of which are signature elements of PEI and are not intrinsic to the silica gel. Their presence at such levels confirms that the surface is substantially covered by the organic amine-rich polymer). In Samples 2 and 3, the surface composition is characterized by slightly higher levels of the silica-based elements, Si at approximately 23.95–24.15 at.% and O at around 52.22–52.36 at.% - accompanied by lower organic content (C $\sim$ 16.95–16.98 at.% and N $\sim$ 6.64–6.66 at.%). Conversely, Sample 4 exhibits a modest shift, with a lower silica composition (23.61 at.% Si and 50.31 at.% O) but noticeably higher organic loading, as evidenced by increased carbon (18.66 at.%) and nitrogen (7.39 at.%) levels. The higher organic content in Sample 4 indicates a more effective retention, or possibly a re-equilibration, of the PEI coating following exposure, which may be critical for ensuring the availability of active amine functionalities necessary for CO₂ capture. Despite these shifts, the carbon-to-nitrogen ratio remains approximately constant (near 2.5), suggesting that, while some loss or reorganization

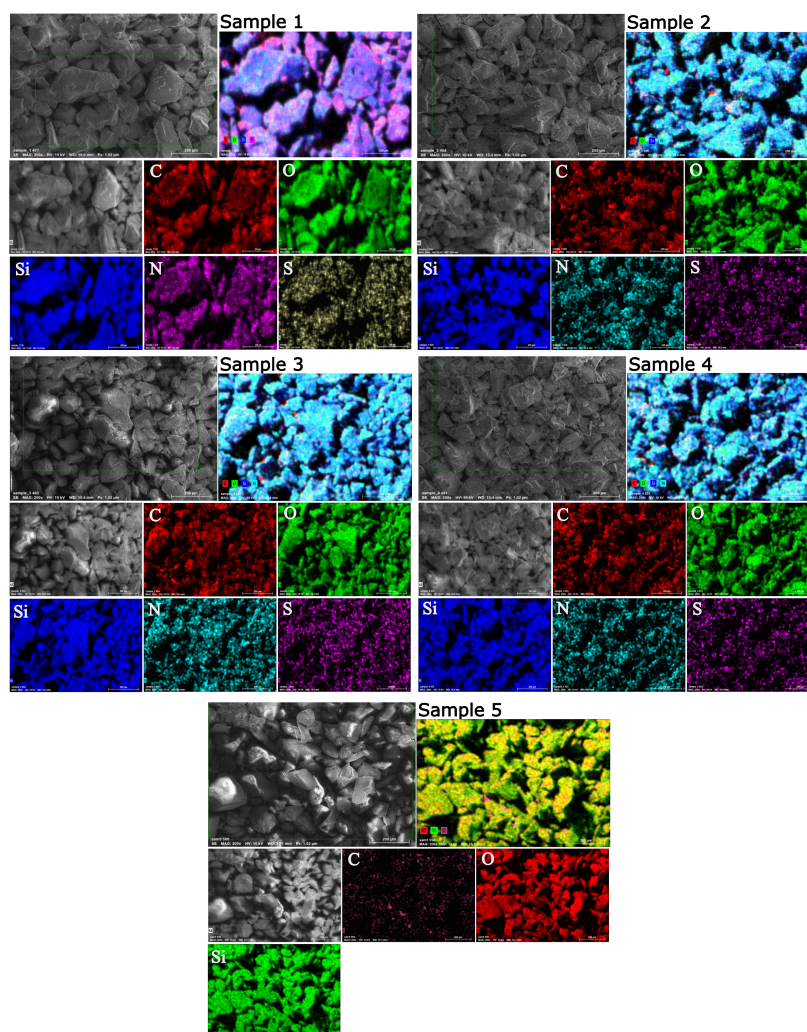


Fig. 4.15 Elemental mapping of five samples analyzed using EDX. Each row corresponds to a sample (top to bottom: Sample 1 to Sample 5), and each column represents an element (left to right: C, O, Si, N, and S). The presence and distribution of carbon and nitrogen in Samples 1-4 confirm PEI functionalization, while their absence in Sample 5 verifies the reference. Sample 3 shows localized signal depletion, indicating surface burning under direct light. Sample 4 retains a more uniform distribution due to indirect photothermal desorption [112].

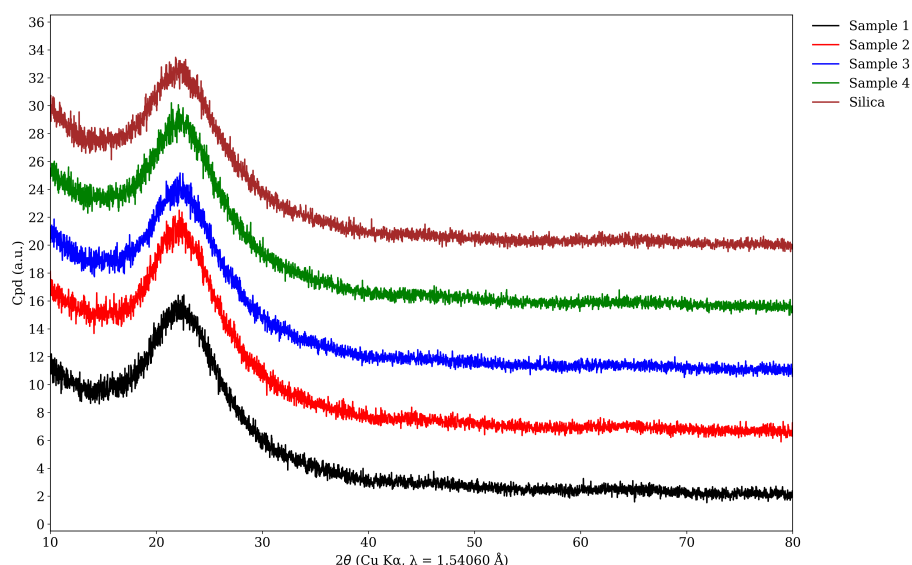


Fig. 4.16 XRD patterns of five samples: Sample 1 is the pre-experiment PEI-silica (black line). Sample 2 (red line) and Sample 3 (blue line) are the post-experiment PEI-silica exposed to direct light through borosilicate glass without and with discoloration, respectively. Sample 4 (green line) is the post-experiment PEI-silica used in the adsorption bed with a solar selective paint coated onto its top surface, and Sample 5 (brown line) is the bare silica gel [112].

of the PEI layer likely occurred (potentially through leaching or surface restructuring under operational conditions), the inherent amine functionality is largely retained. Sample 5 (pre-experiment bare silica) served as the reference and showed no detectable carbon or nitrogen, with Si and O levels at 67.74 at.% and 32.26 at.% respectively, confirming the absence of PEI in this sample. Notably, the uncertainties in the measurements, reflected in relative errors of about 4-11% for the silica and oxygen signals and higher values of 15-17% for nitrogen (with even greater relative errors for trace sulphur, up to 25-50%), underline the challenges associated with detecting lighter and low-abundance elements via EDX. These insights are critical when correlating the adsorbent's surface composition with its performance in CO₂ capture and other applications, where the availability of robust amine functionalities is paramount.

XRD

The XRD analysis of the PEI-infused silica gel adsorbents reveals that the bulk structure of the silica support remains predominantly amorphous across all five samples (refer to Figure 4.16). In each case, a broad diffraction hump typically centred between 22° and 23° 2θ is observed, characteristic of amorphous silica. This feature indicates that the short-range order of the silica network is retained, even after infiltration with PEI and subsequent

experimental treatments involving light-assisted desorption. Notably, the diffractograms of the pre-experiment sample (Sample 1) and the post-experiment samples (Samples 2-4) exhibit no new sharp reflections, suggesting the absence of crystallization or phase transformation. While PEI is known to be present in the samples, no distinct crystalline peaks corresponding to PEI are observed in the diffractograms.

The structural similarity among these samples implies that neither the infiltration process nor the applied stimuli (including direct or indirect light exposure) induces significant crystallization or decomposition into crystalline byproducts. Subtle variations in the baseline intensity or the width of the amorphous hump may reflect differences in PEI dispersion or minor surface-level reorganizations, but these are not indicative of any bulk structural change. As expected, the bare silica sample (Sample 5) also displays a comparable amorphous profile, further confirming that the observed features arise from the silica matrix itself.

The X-ray diffraction and energy-dispersive X-ray spectroscopy data collectively indicate that while the underlying amorphous silica structure and overall particle morphology are preserved, more nuanced surface-level chemical changes, such as potential degradation or redistribution of the PEI, are better assessed through compositional characterization rather than solely examining surface morphology.

4.4 Summary

This chapter details the development, operationalization, and validation of a windowed fixed-bed breakthrough apparatus specifically designed for controlled investigations into light-assisted CO₂ desorption. The system incorporates accurate CO₂/N₂ gas delivery, in-situ gas detection, multi-point thermometry, and a configurable illumination module, for which both plane-of-array irradiance and spectral properties were calibrated. The reliability of the reported performance metrics is underpinned by thorough measurement and analysis, encompassing rigorous flow and composition checks, assessment of analyzer linearity, precise placement of thermocouples, and lag correction. As a preliminary investigation preceding the study of metallic sorbents, PEI-infused silica was evaluated across three distinct regeneration modes: conventional thermal heating (Case 1), direct illumination through a transparent window (Case 2), and indirect photothermal heating facilitated by a solar-selective lid (Case 3). Quantitatively, light-assisted operation improved CO₂ desorption by ~22% relative to thermal baseline at a similar peak temperature. Moreover, results indicate the indirect photothermal approach significantly enhances desorption kinetics, achieving a complete desorption time of ~3058 s. This represents a substantial improvement over traditional thermal heating (~3892 s) and direct illumination (~6025 s), primarily attributed to enhanced

thermal homogeneity, efficient energy absorption, and uniform heat transfer throughout the sorbent bed. This minimizes localized overheating and adsorbent degradation often observed with direct illumination. Multi-cycle experiments revealed a decrease in capacity but a largely stable desorption-to-adsorption ratio, while subsequent material characterization indicated that indirect photothermal operation maintained superior sorbent structural integrity compared to direct illumination. Collectively, these findings serve to validate the experimental apparatus, quantitatively define the advantages of light-assisted desorption under precisely controlled conditions, and lay the groundwork for establishing benchmark protocols and data for subsequent investigations involving metal-surface adsorbents.

4.5 Limitations

4.5.1 Single Sorbent Validation

Validation was performed exclusively on PEI-infused silica gel. A more rigorous platform characterization would incorporate materials with contrasting adsorption mechanisms, such as zeolites (e.g., 13X) [14], MOFs [140], or activated carbons, to confirm that the reported thermal uniformity metrics and desorption time parameter τ_{des} are platform-dependent rather than sorbent-specific. Including a commercially benchmarked sorbent with a published isotherm would also provide an independent check on the accuracy of breakthrough curve integration and capacity quantification. Multi-sorbent validation is identified as a priority before broader material screening.

4.5.2 Dry Operating Conditions and Practical Impurities

All experiments were conducted under rigorously dry, high-purity CO₂/N₂ conditions. This departs substantially from realistic capture environments, where moisture and trace contaminants are unavoidable. Co-adsorbed water is known to shift the CO₂ binding mechanism in PEI sorbents from the carbamate dominant dry pathway toward bicarbonate formation, enhancing amine utilization but also introducing a latent heat penalty during desorption that would alter the energy balance of all three regeneration cases [115]. Moisture may further exacerbate the radial temperature non-uniformities already observed under direct illumination (Case 2) via selective evaporative cooling, while the boundary-heated indirect configuration (Case 3) is expected to be more resilient to this effect [47]. Beyond moisture, real flue gas streams contain SO₂, NO₂, and O₂ at ppm-level concentrations; these species react irreversibly with amine groups, forming stable sulfamates, nitrosamines, and oxidized

derivatives, causing capacity losses that would be undetectable over the nine cycles examined here [151, 54]. Future work should incorporate humidity controlled feeds and representative contaminant mixtures to delineate their impact on each regeneration modality.

4.5.3 Intra-Bed Gas Composition

The intra-bed CO₂ concentration profile was not measured directly; only the reactor outlet was monitored. The hypothesized re-adsorption of CO₂ in cooler bed regions during Case 2 therefore remains inferential. Multi-point bed sampling and CFD simulations of coupled heat and mass transfer are planned for future platform iterations.

4.5.4 Scale

Broadly, the gram-scale configuration (41 g, 240 cm³) is several orders of magnitude smaller than practical capture systems. The surface-area-to-volume advantage that underpins the indirect photothermal configuration diminishes at larger scales, and the $\approx 22\%$ desorption time improvement demonstrated here may not translate directly without redesigning the bed geometry or heat delivery system [123, 122, 146]. Scale-up modelling and techno-economic analysis are deferred to future work.

4.5.5 Cycling Stability and Mechanistic Attribution

The cycling assessment was limited to nine adsorption–desorption cycles for Case 3, with Case 2 precluded from extended cycling by visible surface discoloration. Slow degradation mechanisms, including urea bond formation under dry regeneration, oxidative amine loss, and PEI densification, may only become apparent over hundreds of cycles and would not be captured here [132, 54]. Furthermore, SEM, EDX, and XRD confirm preservation of bulk structure and elemental composition but cannot detect bond-level chemical changes such as amine-to-urea conversion or partial nitrogen oxidation; DRIFTS, solid-state ¹³C NMR, or XPS would be required for this [151]. Finally, the photothermal versus photochemical contribution to regeneration in Case 2 was inferred indirectly from the parity of desorption capacities between Cases 2 and 3, rather than established through direct mechanistic measurement. These outstanding questions apply equally to the metallic sorbent systems investigated in subsequent chapters.

4.6 Conclusion

The developed light-assisted breakthrough apparatus offers a meticulously calibrated framework, enabling the precise differentiation between illumination effects from purely thermal baselines during the CO₂ desorption process. At comparable peak temperatures, indirect light-driven regeneration, facilitated by a solar-selective lid, resulted in enhanced CO₂ desorption yields and promoted more rapid, homogeneous heating. In contrast, direct illumination led to the formation of undesirable radial and axial temperature gradients, slower propagation of the thermal front, and observable material degradation. These findings underscore two important operational considerations for achieving low-carbon regeneration: optimizing thermal-field distribution to mitigate in-bed temperature gradients and implementing spectrally tailored, uniformly distributed irradiance to prevent localized overheating. Acknowledging the inherent limitations of the current investigation, specifically, dry purge conditions, the absence of intra-bed gas-composition mapping, and reliance on ex-situ chemical diagnostics (rather than operando), several distinct avenues for future research are suggested. These include conducting humidified cycling experiments coupled with FTIR/XPS analyses to quantify amine leaching; incorporating advanced thermometry or sensing techniques to resolve through-thickness gradients; and performing comprehensive mass/energy balances to establish regeneration metrics on a per-mmol-CO₂ basis. At a systemic level, the operational temperature window (~ 110 °C) and irradiance requirements align seamlessly with the specifications of flat-plate solar thermal collectors, thereby facilitating a viable pathway towards entirely renewable sorbent regeneration. The rigorous protocols and performance benchmarks developed in this study will serve as a crucial foundation for subsequent chapters, extending the research scope from polymeric sorbents to advanced metallic and alloy materials. This study lays the foundational groundwork for future scale-up initiatives and field testing of light-assistive-based solid sorbent carbon capture systems, underscoring the continued need for optimizing energy efficiency, thermal management, and long-term operational stability. Moreover, this research represents a significant step forward in the development of integrated solar-driven carbon capture modules, providing a foundation for future implementations in which solar energy directly facilitates CO₂ desorption.

5. Experimental Validation of Computational Predictions

5.1 Introduction

This chapter presents an exploratory, measurement-oriented evaluation of three transition-metal candidates, namely, Cu, Al, and Ni, identified from the DFT screening in Chapter 3 for their contrasting electronic structures and predicted CO₂-surface interactions. The goal here is deliberately modest: to determine whether qualitative behaviors anticipated by computation are observable on bare metallic foams using the calibrated breakthrough apparatus from Chapter 4, and to obtain first trends on how external stimuli (light and, in a subset of tests, electrical bias) influence CO₂ desorption. These measurements are not intended to compete with high-surface-area sorbents; indeed, PEI-infused silica from Chapter 4 remains the performance benchmark and is used as a reference check for instrument response and data reduction. Rather, the foams serve as mechanistic testbeds that let us probe how external energy input (light) and electrostatic perturbations affect desorption kinetics on minimally porous, electronically active substrates. The experimental scope and control protocols replicate those employed in the calibration study, thereby enabling direct, equivalent comparisons. Cu, Al, and Ni foams are sectioned to identical geometries, cleaned via a standardized procedure, weighed, and affixed within the same adsorption bed. Each metal undergoes dark and illuminated desorption sequences under matched flow rates, gas compositions, and initial loadings; bracketing blank runs confirm analyzer stability, baseline drift correction, and integration fidelity. Illumination settings and temperature probe placements are held constant across metals, while replicate cycles assess the reproducibility of measurements. Because the geometric surface area of the foams is modest and not known a priori, the accessible interfacial area is first quantified via micro-CT and then used to normalize breakthrough curves. In addition to the thermal and light-assisted cycles (adsorption at 25 °C and desorption at 110 °C), a set of isothermal (adsorption and desorption at 25 °C) runs on Cu foam with

applied DC potentials is included. These voltage experiments are preliminary and limited in scope, but they provide an initial experimental probe of the “surface charging” concept developed in Chapter 3 by asking whether electrical bias alone can measurably alter CO₂ release at fixed macroscopic temperature. The interpretation prioritizes consistency verifications over claims of exceptional performance. Limitations impeding direct equivalence to idealized slab DFT models are explicitly recognized, encompassing the modest specific surface area of foams, native oxide overlayers, and surface roughness/defects, which may attenuate adsorption capacities or obscure fine electronic perturbations. Notwithstanding these constraints, the chapter furnishes empirical substantiation that the apparatus distinguishes subtle yet systematic divergences in dark versus illuminated desorption kinetics on metallic substrates, alongside qualitative congruence between experimental trends and computed adsorption energetics, plus pragmatic directives for future work, principally, augmenting interfacial area and refining surface chemistry and alloy formulations to exploit metallic platforms for photo-driven CO₂ desorption at viable capacities.

5.2 Methodology

5.2.1 Materials and samples

Open-cell metal foams served as model substrates to investigate CO₂ adsorption and photo-assisted desorption on pristine metallic frameworks possessing substantial gas-solid interfacial areas. Nickel and copper foams were sourced from MSE Supplies as 300 mm × 200 mm sheets with a nominal thickness of 1.6 mm. Manufacturer specifications indicate that the copper foam has a typical open-cell porosity of approximately 98% and a pore density of about 110 pores per inch (PPI). The nickel foam is reported to have a porosity of approximately 97% and a pore density of 110 PPI. Aluminium foam (100 mm × 100 mm) was sourced from Electrode Research/Customizable Solutions, with the product page listing a porosity of 95–98% and approximately 110 PPI. For each metal (Cu, Al, Ni), the as-received sheet was sectioned into five identical strips measuring 15.2 cm × 5.0 cm × 1.35 mm, affording a planar area of 76 cm² per strip and a total geometric exposed area of 0.076 m² across all five strips. The aggregate geometric volume of the loaded material amounted to 51.3 cm³. The strips were installed in the fixed-bed reactor with uniform orientation and inter-strip spacing to avert channeling effects; no binders or washcoats were applied, thereby ensuring that all observed adsorption/desorption phenomena capture the intrinsic behavior of the metallic foam skeletons under dark and illuminated conditions. The total masses of Cu, Al, and Ni foam loaded into the reactor were 21.8 g, 22.4 g, and 11.9 g, respectively. It is

Table 5.1 Geometric properties of Cu, Ni and Al foams used in the fixed-bed reactor. In all cases, five strips (15.2 cm × 5.0 cm × 1.35 mm) were loaded, corresponding to a total foam volume of 51.3 cm³.

Foam	Mass used (g)	Foam density (g cm ⁻³)	Solid fraction (vol. %)	Porosity (vol. %)	A_{total} (m ²)	S_m (m ² g ⁻¹)
Cu	21.813	0.425	4.75	95.25	≈0.215	0.00984
Ni	11.892	0.232	2.60	97.40	≈0.215	0.0180
Al	22.367	0.436	16.15	83.85	≈0.215	0.00959

important to distinguish between the macroscopic planar area of the cut strips (for example - Cu ≈ 0.076 m² for five strips) and the much larger ligament surface area of the Cu foam (≈0.215 m²) obtained from micro-CT analysis of the internal pore network (Section 5.2.4), which is used for geometric normalization of breakthrough curves. More details about the foams are mentioned in Table 5.1.

5.2.2 Breakthrough apparatus and instrumentation

The experiments employed the calibrated fixed-bed breakthrough apparatus detailed in Chapter 4. Mass-flow controllers regulated the CO₂/N₂ gas mixture and total flow rate F_{tot} . A downstream gas analyzer delivered a continuous CO₂ mole-fraction signal $y_{\text{out}}(t)$; periodic span/zero calibrations preceded each batch of runs. Bed pressure and temperature were monitored at fixed positions adjacent to the foam. For illuminated experiments, a collimated light source was directed through the optical window onto the bed; incident power at the sample plane was quantified via a calibrated meter, with the illuminated area recorded to determine irradiance “ I ” (W/m²). Identical configuration of foam and other experimental conditions were used across all runs to minimize hardware-related variability.

5.2.3 Gas composition and operating protocols

A standard adsorption/desorption cycle was used across all metals and conditions:

1. Purge/Conditioning - N₂ purge to a stable baseline and remove moisture.
2. Adsorption - Switch to a CO₂/N₂ mixture at total flow “ F_{tot} ” (= 110 SCCM); continue until the analyzer signal reached a steady outlet fraction (breakthrough).
3. Desorption (Dark) - For dark runs, switch to N₂ purge at “ F_{tot} ” (= 100 SCCM) without illumination.
4. Desorption (Illuminated) - For illuminated runs, switch to N₂ purge and apply light (irradiance I) at the bed. Temperature and optical power were logged continuously.

5. Desorption (Voltage, Cu only) - A separate experiment was performed on Cu foam in which both adsorption and desorption were done at 25 °C to isolate purely electrical effects. After an adsorption step identical to that described above (CO₂/N₂ at 110 SCCM), the system was switched to N₂ at 100 SCCM while the foam was held at 0V, +V (≈ 61 V), and/or -V (≈ 61 V). No external heating was applied, and any change in desorbed CO₂ relative to the adsorption (at 25 °C) and desorption (at 25 °C) blank run was attributed to electrostatic modification of the surface.
6. Replication - Each metal/condition was cycled in replicates to quantify repeatability and compute mean $\pm$ SD metrics.

5.2.4 Micro-CT based estimation of the geometric surface area

The complete procedure is described taking Cu foam as an example and same has been utilized for the other two foams as well.

Samples and bulk porosity

Five strips of copper foam, each with dimensions $152 \times 50 \times 1.35$ mm were cut from the as-received sheet, giving a combined foam volume of 51300 mm^3 (51.3 cm^3). The total mass was 21.813 g, yielding an effective bulk density $\rho_{eff} = 0.425 \text{ g/cm}^3$. Using bulk copper density $\rho_{Cu} = 8.96 \text{ g/cm}^3$, the solid volume fraction and porosity consistent with a highly open cellular structure.

$$\phi_{solid} = \frac{\rho_{eff}}{\rho_{Cu}} = 0.0475; \quad (5.1)$$

$$\varepsilon = 1 - \phi_{solid} = 0.9525 \quad (5.2)$$

Acquisition and field of view selection

The internal microstructure of the foam was characterized using micro-computed tomography (micro-CT) (SkyScan 1272 desktop X-ray microtomography). Reconstructed tomographic slices were 2452×2452 pixels in resolution, with a voxel size of $10.889 \mu\text{m}$. To eliminate incomplete or noisy peripheral regions, only slices 660–780 were retained for analysis. A representative central slice underwent thresholding to delineate the bright rectangular foam structure from the dark circular scanner background, followed by morphological closing and hole-filling. The bounding box of this binary mask was then applied to crop the full slice stack to the foam-only volume.

Segmentation with bulk-constrained thresholding

In the cropped volume, the grayscale image stack was subjected to smoothing (using 3D Gaussian filter, $\sigma = 1$ voxel). To avoid biases in solid fraction estimation inherent to purely image-based thresholding, the intensity threshold was calibrated using the independently measured bulk solid fraction. Voxel intensities within the foam were equalized through histogram flattening, with the brightest 4.75% designated as copper ligaments and the remainder as pores. Small isolated copper artifacts were subsequently removed. The CT-derived solid and pore fractions ($\phi_{solid} = 0.0473$, $\varepsilon = 0.9527$) aligned closely with bulk measurements, validating the segmentation approach.

Surface reconstruction and A/V

Multiple internal volumes of interest were delineated by cropping approximately 10–20% from each boundary (x, y, z) to alleviate edge artifacts. For each VOI, the binarized copper phase was rendered as a triangulated isosurface. Vertex coordinates were rescaled to millimeters according to the voxel resolution; the total surface area A was determined by summing the areas of triangular facets, while the VOI volume V was obtained from the voxel count. Across three representative VOIs (“center”, “upper”, “lower”), the surface-to-volume ratio was

$$(A/V) = 4.15, 4.42, 3.98 \text{ mm}^{-1},$$

with an average

$$(A/V)_{avg} = 4.18 \pm 0.18 \text{ mm}^{-1}.$$

Scaling to the tested load and specific area

Using the total loaded foam volume $V_{foam} = 51,300 \text{ mm}^3$, the geometric copper surface area is:

$$A_{geom} = (A/V)_{avg} \times V_{foam} = 4.18 \text{ mm}^{-1} \times 51,300 \text{ mm}^3 \approx 0.215 \text{ m}^2.$$

The corresponding mass-specific geometric surface area is

$$S_m = \frac{A_{geom}}{m} \approx \frac{0.215 \text{ m}^2}{21.813 \text{ g}} = 9.8 \times 10^{-3} \text{ m}^2 \text{ g}^{-1}.$$

Usage and limitations

This CT-resolved geometric area was employed to normalize CO_2 uptake values and enable configuration-level performance comparisons for foams. Given that the voxel resolution

cannot resolve sub-voxel roughness or micro-texture, A_{geom} provides a lower bound on the true microscopic surface area; BET-scale features would elevate the actual area. In the absence of micro-CT data, results are reported per unit mass, confining area-normalized analyses to foam.

5.3 Results

5.3.1 Temperature - CO₂ time-series overview

Figure 5.1 summarizes representative time series of bed temperature at four axial thermocouples (T1–T4) and the outlet CO₂ signal for Cu, Al, and Ni foams. Panels (a,c,e) show conventional thermal operation in which desorption is driven by 25→110 °C dark heating, while panels (b,d,f) show the corresponding light-assisted runs with illumination through the glass lid; panels (g,h,i) present the Cu runs operated at 25 °C/25 °C for the voltage-cycling experiments. Shaded bands mark the cleaning phase (high-temperature N₂ purge), the adsorption phase (CO₂/N₂ feed at ≈25 °C), and the desorption phase under thermal, light-assisted, or voltage-assisted conditions. In all cases the CO₂ trace remains near baseline during cleaning, drops toward zero during adsorption, and exhibits sharp peaks when the bed is heated or when the stimulus (light or voltage) is applied during desorption. In the light-assisted 25→110 °C runs, the thermocouples directly beneath the illuminated region reached peak temperatures on the order of 200 °C, whereas the inlet and outlet positions stayed closer to ≈110 °C; the quoted “110 °C” desorption temperature should therefore be interpreted as an average over a non-uniform axial temperature profile. These profiles verify the operating protocol and define the time windows used for computing uptake, working capacity, desorption yield, and voltage-induced release in the subsections that follow.

5.3.2 CO₂ adsorption/desorption capacities

Figure 5.2 displays the mean values $\pm 1\sigma$ from replicate measurements of CO₂ adsorption and desorption for Cu, Al, and Ni foams under three operating modes. For the glass-lid and thermal 25 °C/110 °C cycles, the net foam signal is obtained by subtracting the blank-bed response from the integrated breakthrough volumes and converting the resulting volumes to moles via the ideal-gas law at the appropriate adsorption (25 °C) or desorption (110 °C) temperature. For the 25 °C/25 °C voltage runs, an analogous correction is applied using a dedicated 25 °C/25 °C blank run. The plotted quantities therefore represent the net contributions attributable to the foam in each configuration; unless otherwise indicated,

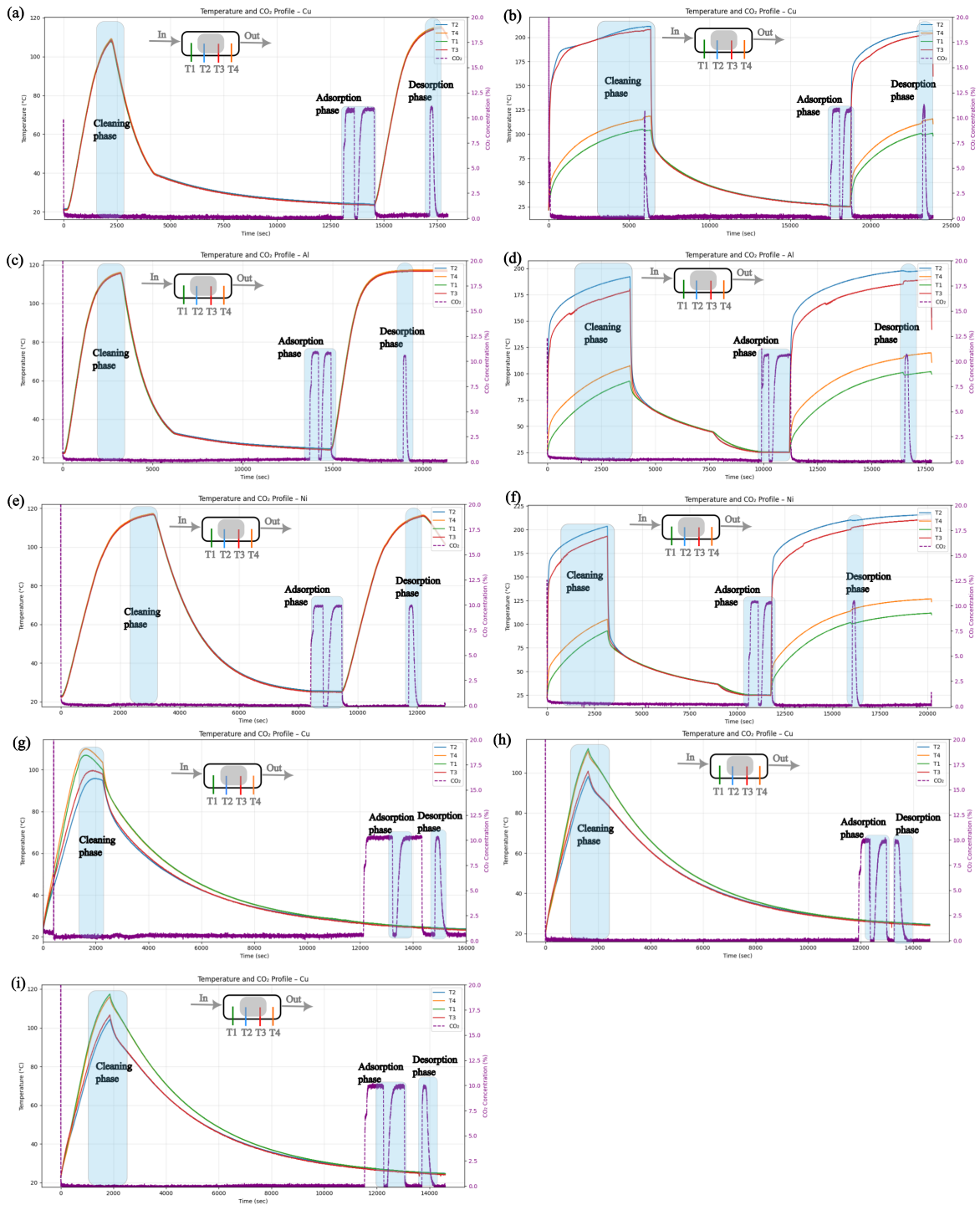


Fig. 5.1 Temperature (T1–T4) and outlet CO₂ concentration versus time for metal foams. Panels (a,c,e) show conventional thermal runs for Cu, Al, and Ni foams, respectively, with adsorption at $\approx 25^\circ\text{C}$ and desorption driven by $25 \rightarrow 110^\circ\text{C}$ dark heating. Panels (b,d,f) show the corresponding light-assisted runs with illumination through the glass lid. Panels (g,h,i) present Cu runs operated at $25^\circ\text{C}/25^\circ\text{C}$ for the voltage experiments (0 V and $\pm V$). Shaded regions indicate the cleaning phase (high-T N₂ purge), adsorption phase (CO₂/N₂ feed at $\approx 25^\circ\text{C}$), and desorption phase (N₂ purge under thermal, light-assisted, or voltage-assisted conditions)

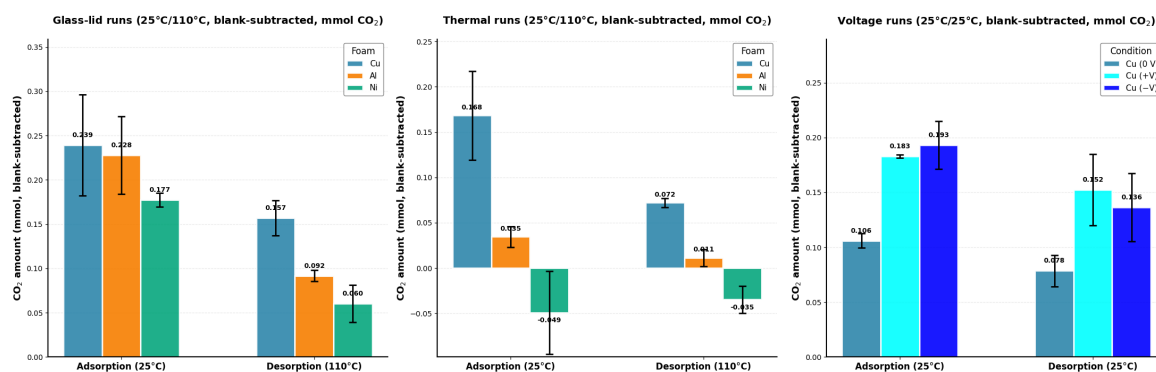


Fig. 5.2 Blank-subtracted CO₂ amounts (means $\pm 1\sigma$) obtained from breakthrough-curve integrals. Left: glass-lid (photo-assisted) 25 °C/110 °C cycles for Cu, Al, and Ni foams. Middle: corresponding dark thermal 25 °C/110 °C cycles. Right: isothermal 25 °C/25 °C voltage runs on Cu foam at 0 V, positive bias (“+V”), and negative bias (“-V”). Adsorption and desorption amounts are shown separately for each condition.

values correspond to the plotted means and the error bars denote the inter-run standard deviation.

Under photo-assisted 25 °C/110 °C operation, the blank-subtracted adsorption capacities are 0.239 ± 0.057 mmol for Cu, 0.228 ± 0.044 mmol for Al, and 0.177 ± 0.008 mmol for Ni foams. The corresponding desorption amounts are 0.157 ± 0.020 mmol, 0.092 ± 0.007 mmol, and 0.060 ± 0.021 mmol, respectively. Illumination therefore yields net cyclic uptakes on the order of 0.1-0.25 mmol per cycle, with Cu exhibiting the largest absolute capacity and Al and Ni delivering smaller but reproducible responses.

In thermal-only 25 °C/110 °C cycles, the net foam contribution is markedly reduced, and Ni becomes indistinguishable from zero within experimental uncertainty. The blank-subtracted adsorption capacities are 0.168 ± 0.049 mmol (Cu), 0.035 ± 0.011 mmol (Al), and -0.049 ± 0.046 mmol (Ni), while the corresponding desorption capacities are 0.072 ± 0.005 mmol (Cu), 0.011 ± 0.009 mmol (Al), and -0.035 ± 0.015 mmol (Ni). The small negative values for Ni simply reflect post-subtraction noise around zero rather than genuine CO₂ release or uptake by the foam.

The right-hand panel of Figure 5.2 adds isothermal 25 °C/25 °C runs on Cu foam with an applied DC potential. After subtraction of the dedicated 25 °C/25 °C blank, the adsorption capacity at 0 V is ≈ 0.11 mmol, increasing to ≈ 0.18 -0.19 mmol under positive and negative bias. The corresponding desorbed amounts grow from ≈ 0.08 mmol at 0 V to ≈ 0.15 -0.16 mmol under biased conditions. Thus, at constant temperature, electrical bias alone roughly doubles the net CO₂ released per cycle relative to the unbiased 25 °C/25 °C case and brings the isothermal desorption yield close to that achieved in 25 °C/110 °C thermal operation.

Taken together, these blank-subtracted measurements show that (i) illumination is essential for

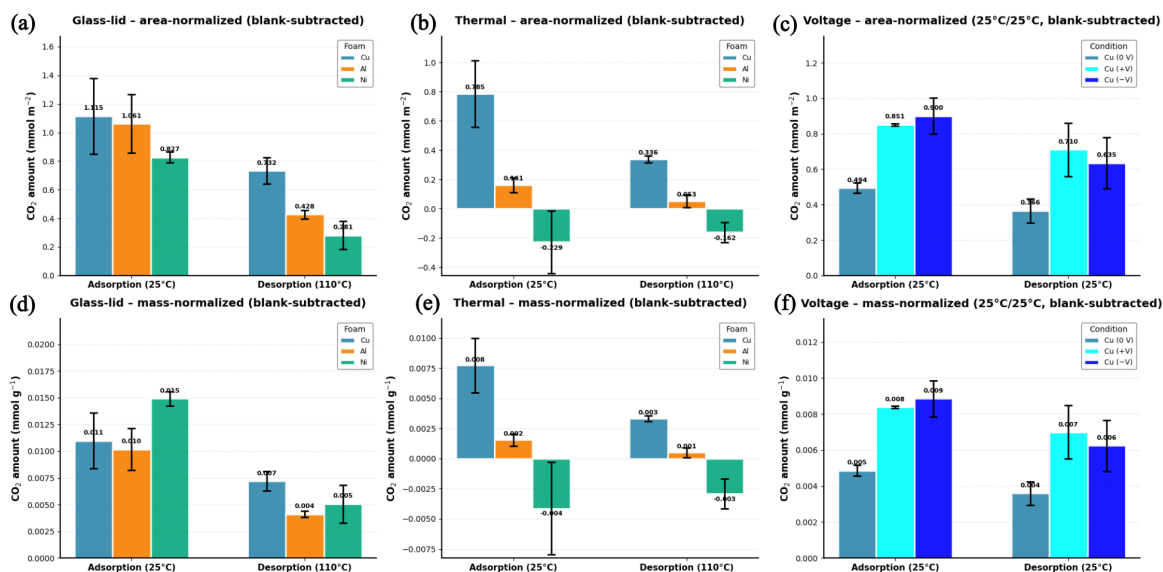


Fig. 5.3 CO₂ uptake on Cu, Al, and Ni foams, normalized and blank-subtracted (means $\pm 1\sigma$). Panels (a-c) show area-normalized adsorption and desorption capacities (mmol m⁻²) for glass-lid (photo-assisted) 25 °C/110 °C runs, dark thermal 25 °C/110 °C runs, and isothermal 25 °C/25 °C voltage runs on Cu foam (0 V, +V, -V), respectively. Panels (d-f) present the corresponding mass-normalized capacities (mmol g⁻¹) using the measured foam masses.

eliciting robust positive net adsorption and desorption across all three foams in 25 °C/110 °C cycles, (ii) in the absence of light only Cu retains a modest but quantifiable thermal capacity, and (iii) on Cu foam, an applied potential at 25 °C/25 °C provides a second, independent control parameter that significantly enhances desorption without the need for a macroscopic temperature swing. The absence of any beneficial illumination effect on the blank bed further confirms that these improvements arise from the intrinsic photo and electro-responsive properties of the metallic frameworks rather than nonspecific chamber heating or instrumental artefacts.

5.3.3 Area and mass normalized CO₂ uptakes

Figure 5.3 summarizes the CO₂ uptake capacities normalized by geometric surface area and by foam mass. Panels 5.3(a)-(c) report, respectively, the area-normalized adsorption/desorption amounts for glass-lid (photo-assisted) 25 °C/110 °C runs, dark thermal 25 °C/110 °C runs, and isothermal 25 °C/25 °C voltage runs on Cu foam. Panels 5.3(d)-(f) present the corresponding mass-normalized quantities. Only the metallic foams are shown, after blank-bed correction, expressed in mmol m⁻² and mmol g⁻¹.

Under photo-assisted conditions, the area-normalized adsorption capacities amount to approximately 1.11, 1.06, and 0.82 mmol m⁻² for Cu, Al, and Ni foams, respectively, with

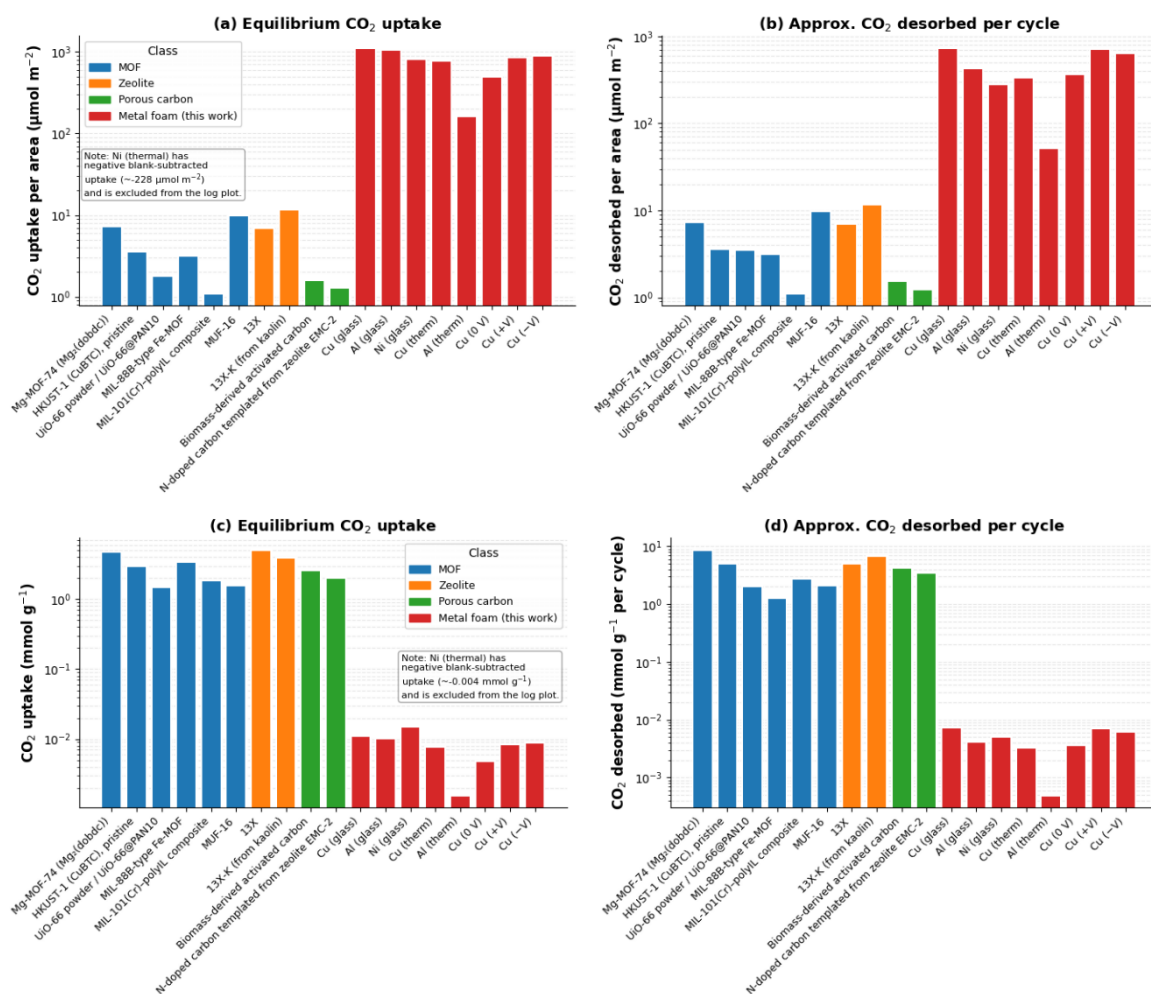


Fig. 5.4 Comparison of CO₂ capacities for literature sorbents and metal foams (this work) on surface-area- and mass-normalized bases. Panels (a,b) show equilibrium uptake at $\approx 25^\circ\text{C}$ and approximate CO₂ desorbed per cycle, normalized by BET area for porous materials and by micro-CT geometric area for foams ($\mu\text{mol m}^{-2}$). Panels (c,d) present the same quantities per unit mass (mmol g^{-1}). Bars labelled “Cu (glass)”, “Cu (therm)”, and “Cu (0 V) / Cu (+V) / Cu (-V)” correspond to glass-lid photo-assisted, dark thermal, and $25^\circ\text{C}/125^\circ\text{C}$ voltage runs on Cu foam, respectively. Ni foam under thermal operation has a slightly negative blank-subtracted capacity and is therefore omitted from the logarithmic plots. Data for literature sorbents are tabulated and cited in detail in Appendix C.

corresponding desorption capacities of 0.73, 0.43, and 0.28 mmol m⁻². In thermal-only 25 °C/110 °C operation (Figure 5.3), these decrease to ≈ 0.78 mmol m⁻² (Cu), ≈ 0.16 mmol m⁻² (Al), and a value statistically indistinguishable from zero for Ni (-0.23 mmol m⁻² within uncertainty), accompanied by desorption capacities of ≈ 0.33 mmol m⁻² (Cu), ≈ 0.05 mmol m⁻² (Al), and ≈ 0 mmol m⁻² (Ni). For a fixed reactor volume packed with 110-PPI foam, illumination therefore elevates the net CO₂ throughput per square metre of metallic surface into the ≈ 0.3 –1.1 mmol m⁻² range, substantially exceeding the area-normalized capacities under thermal-only operation.

The 25 °C/25 °C voltage runs on Cu foam [Fig. 5.3(c)] lie in between these two regimes. At 0 V, the area-normalized adsorption and desorption capacities are ≈ 0.49 and ≈ 0.36 mmol m⁻², respectively. Applying either a positive or negative bias increases these to ≈ 0.85 –0.90 mmol m⁻² for adsorption and ≈ 0.63 –0.71 mmol m⁻² for desorption. Thus, electrical bias recovers much of the areal working capacity of a 25 °C/110 °C thermal cycle while keeping the bed at 25 °C, suggesting that a combined photo and electro-stimulated mode could further amplify desorption at modest temperature swings.

Mass-normalized capacities [Figures 5.3(d)–(f)] underscore the influence of foam density. Under photo-assisted 25 °C/110 °C operation, adsorption capacities reach approximately 1.10×10^{-2} mmol g⁻¹ (Cu), 1.02×10^{-2} mmol g⁻¹ (Al), and 1.49×10^{-2} mmol g⁻¹ (Ni), accompanied by desorption capacities of $\approx 7.2 \times 10^{-3}$, 4.1×10^{-3} , and 5.0×10^{-3} mmol g⁻¹, respectively. Thermal operation diminishes these to $\approx 7.7 \times 10^{-3}$ mmol g⁻¹ (Cu) and 1.6×10^{-3} mmol g⁻¹ (Al) for adsorption, and $\approx 3.3 \times 10^{-3}$ (Cu) and $\approx 5 \times 10^{-4}$ mmol g⁻¹ (Al) for desorption, with Ni values fluctuating near zero.

For the 25 °C/25 °C voltage runs on Cu [Figure 5.3(f)], the blank-subtracted adsorption capacity at 0 V is $\approx 4.9 \times 10^{-3}$ mmol g⁻¹, increasing to ≈ 8 –9 $\times 10^{-3}$ mmol g⁻¹ under biased conditions. The corresponding desorption capacities rise from $\approx 3.6 \times 10^{-3}$ mmol g⁻¹ at 0 V to ≈ 6 –7 $\times 10^{-3}$ mmol g⁻¹ at finite bias. Although these gravimetric values remain modest compared to high-surface-area sorbents, they mirror the areal trends: illumination and/or electrical bias consistently enhance working capacity, and Ni retains the highest mass-specific response among the three metals because of its lower density and higher porosity.

5.3.4 Comparison with porous sorbents

To place these capacities in context, Figure 5.4 compares the metallic foams with representative metal–organic frameworks, zeolites, and porous carbons drawn from the literature. For each sorbent, the equilibrium CO₂ uptake at ≈ 25 °C and standard pressure, together with the approximate CO₂ released across a temperature swing, is reported on both a surface-area basis ($\mu\text{mol m}^{-2}$, using BET area for porous materials and micro-CT-derived geometric

area for foams) and a mass basis (mmol g^{-1}). In addition to the $25\text{ }^{\circ}\text{C}/110\text{ }^{\circ}\text{C}$ thermal and glass-lid runs, the plots include the isothermal $25\text{ }^{\circ}\text{C}/25\text{ }^{\circ}\text{C}$ voltage runs on Cu foam at 0 V, +V, and -V.

On a surface-area-normalized basis, conventional porous adsorbents display equilibrium CO_2 uptakes spanning approximately $\approx 1\text{--}12\text{ }\mu\text{mol m}^{-2}$, with desorbed quantities per thermal cycle of comparable magnitude. By contrast, the Cu, Al, and Ni foams examined here exhibit area-normalized capacities that are two to three orders of magnitude larger: under photo-assisted $25\text{ }^{\circ}\text{C}/110\text{ }^{\circ}\text{C}$ conditions, equilibrium uptakes reach $\approx 8 \times 10^2\text{--}1.1 \times 10^3\text{ }\mu\text{mol m}^{-2}$ with desorbed amounts of $\approx 2.8 \times 10^2\text{--}7.3 \times 10^2\text{ }\mu\text{mol m}^{-2}$. Even in dark $25\text{ }^{\circ}\text{C}/110\text{ }^{\circ}\text{C}$ operation, Cu and Al foams achieve $\approx 1.6 \times 10^2\text{--}8 \times 10^2\text{ }\mu\text{mol m}^{-2}$, whereas Ni's net response remains effectively zero after blank subtraction. The $25\text{ }^{\circ}\text{C}/25\text{ }^{\circ}\text{C}$ voltage runs on Cu foam fall within the same overall band, with equilibrium capacities of $\approx 5 \times 10^2\text{--}9 \times 10^2\text{ }\mu\text{mol m}^{-2}$ and desorbed amounts of $\approx 3.6 \times 10^2\text{--}7.1 \times 10^2\text{ }\mu\text{mol m}^{-2}$, achieved without any macroscopic temperature swing. These disparities largely reflect the different surface-area definitions: BET surface area captures the extensive internal pore networks of MOFs and carbons, while micro-CT quantifies only the macroscopic metal ligaments of the foams.

This trend reverses on a mass-normalized basis. Established MOFs, zeolites, and porous carbons typically exhibit equilibrium CO_2 capacities of $2\text{--}9\text{ mmol g}^{-1}$ with per-cycle desorption of similar magnitude, whereas the present metallic foams attain only $\sim 10^{-2}\text{ mmol g}^{-1}$ even under photo-assisted $25\text{ }^{\circ}\text{C}/110\text{ }^{\circ}\text{C}$ conditions. The $25\text{ }^{\circ}\text{C}/25\text{ }^{\circ}\text{C}$ voltage-biased Cu runs likewise remain in the $10^{-3}\text{--}10^{-2}\text{ mmol g}^{-1}$ range. Accordingly, while metallic foams exploit their restricted geometric surface area very efficiently, and can do so under either photothermal or isothermal voltage-driven operation, they remain intrinsically low-capacity sorbents on a gravimetric basis. This perspective reinforces their role as mechanistic platforms and conductive substrates for high-capacity coatings rather than as stand-alone bulk sorbents.

5.4 Summary

Employing geometric surface areas derived from micro-CT analysis and blank-subtracted breakthrough-curve integrals, this chapter quantifies the CO_2 uptake capacities of Cu, Al, and Ni foams under dark thermal, photo-assisted, and preliminary voltage-biased conditions, expressed on both area- and mass-normalized bases. For $25\text{ }^{\circ}\text{C}/110\text{ }^{\circ}\text{C}$ cycles, photoillumination enhances the net foam contribution from levels often indistinguishable from experimental noise to consistent uptakes of $\approx 0.2\text{ mmol}$ per cycle. When normalized by the $\approx 0.215\text{ m}^2$ foam surface area and the measured foam masses, these correspond to area-specific capacities

of $\approx 0.3\text{--}1.1\text{ mmol m}^{-2}$ and mass-specific capacities on the order of $10^{-2}\text{ mmol g}^{-1}$.

Preliminary $25\text{ }^{\circ}\text{C}/25\text{ }^{\circ}\text{C}$ runs on Cu foam demonstrate that electrical bias provides an additional lever for manipulating working capacity. After subtraction of a dedicated isothermal blank, the unbiased Cu foam exhibits $\approx 0.11\text{ mmol}$ of net CO_2 adsorption and $\approx 0.08\text{ mmol}$ of desorption per cycle, which increase to $\approx 0.18\text{--}0.19\text{ mmol}$ and $\approx 0.15\text{--}0.16\text{ mmol}$, respectively, under positive or negative bias. In areal terms, this corresponds to $\approx 0.5\text{ mmol m}^{-2}$ at 0 V and $\approx 0.85\text{--}0.9\text{ mmol m}^{-2}$ under bias, approaching the area-normalized desorption obtained in $25\text{ }^{\circ}\text{C}/110\text{ }^{\circ}\text{C}$ thermal operation despite the absence of a macroscopic temperature swing. Area-normalized capacities reveal that, for an adsorbed bed volume packed with 110-PPI foam, the illuminated $25\text{ }^{\circ}\text{C}/110\text{ }^{\circ}\text{C}$ cycles and biased $25\text{ }^{\circ}\text{C}/25\text{ }^{\circ}\text{C}$ cycles deliver broadly comparable CO_2 throughput per square metre of metallic surface across Cu, Al, and Ni foams, with minor differences arising from density and porosity. Mass-normalized capacities, by contrast, emphasize Ni's superiority as the lightest and most porous variant, providing roughly 1.5-fold higher photo-assisted adsorption per gram relative to Cu and Al despite their similar area-specific performance.

When benchmarked against metal–organic frameworks, zeolites, and porous carbons, the metallic foams display exceptionally high capacities per unit geometric surface area but markedly low gravimetric capacities. This places them in a distinctive operational niche: they are best viewed as electronically and photothermally (and potentially electrostatically) responsive supports that maximise utilisation of their exposed metallic surfaces, rather than as conventional bulk sorbents optimised for gravimetric performance. Viewed alongside the charged-slab DFT results of Chapter 3, the voltage runs (adsorption and desorption at $25\text{ }^{\circ}\text{C}$) are qualitatively consistent with the idea that changes in illumination and applied potential can modestly shift the balance between adsorption and desorption in the same direction as predicted when near-surface charge is varied in the calculations. Given the oxide formation, rough foams, and the absence of direct measurement of surface potential or band structure, these experiments should be interpreted as suggestive rather than as a quantitative validation of the electronic-structure model, but they nonetheless motivate future work that more tightly couples alloy design, surface chemistry, and electronic control in low-temperature DAC architectures.

5.5 Limitations

5.5.1 Native Oxide Overlayers and Surface Chemistry

All foams were tested in their as-received state without oxide removal or controlled surface passivation. Cu, Al, and Ni surfaces inevitably bear native oxide overlayers ($\text{Cu}_2\text{O}/\text{CuO}$, Al_2O_3 , NiO) that alter the surface electronic structure and work function relative to the idealized bare-metal slabs modeled in Chapter 3 [113]. CO_2 adsorption on these oxides proceeds via Lewis acid-base and hydroxyl assisted bicarbonate mechanisms distinct from the charge mediated metallic pathways investigated computationally [81, 143], meaning the measured capacities reflect a convolution of metallic and oxide contributions that cannot be disentangled with the current setup. Future work should incorporate in-situ H_2 reduction or pre-experiment XPS characterization to establish an oxide-free, well defined surface baseline.

5.5.2 Surface Area Resolution and the DFT to Experiment Gap

The micro-CT derived geometric areas ($\approx 0.215 \text{ m}^2$) are lower bounds, as the $10.889 \mu\text{m}$ voxel resolution cannot capture sub-voxel roughness or low-coordination defect sites that are active for CO_2 binding [108]. More fundamentally, the polycrystalline foam ligaments expose a distribution of facet orientations and defect densities absent from the single-crystal DFT slabs of Chapter 3. This structural heterogeneity broadens the binding energy distribution and may dampen the sharp charge state switching predicted computationally, an effect well documented for chemisorption on structurally heterogeneous surfaces [114], and may explain why the voltage-induced response is modest and symmetric in polarity rather than asymmetric as the DFT model would suggest.

5.5.3 Dry Conditions and Limited Metal Selection

All experiments were performed under dry, high-purity CO_2/N_2 feeds, whereas practical capture environments include moisture and trace contaminants (SO_2 , NO_2 , O_2) that modify oxide speciation and CO_2 binding thermodynamics on metallic surfaces [81, 143]. Fabrication of alloy foams via electrodeposition or dealloying and their testing under humidified conditions represents the most impactful near term extension of this work.

5.5.4 Scale-Up Considerations

The gram scale foam strips tested here present additional engineering challenges at larger scales that were not assessed in this study. Open cell metal foams are susceptible to fatigue and creep under repeated thermal cycling [8], particularly for Al foam whose creep resistance is limited near 110 °C. Differential thermal expansion between the foam and the reactor walls can induce channeling or contact loss over extended operation, degrading gas solid contact efficiency and thermal uniformity. Furthermore, at larger bed volumes, the high thermal conductivity of metallic foams, advantageous for heat distribution at the gram scale, may increase parasitic heat losses to the reactor structure during photothermal cycling [8]. These mechanical and thermophysical constraints must be addressed in scaled system design, motivating future work on foam geometry optimization, protective surface coatings, and reactor level thermal management strategies.

5.6 Conclusion

This chapter experimentally examined whether the qualitative trends forecasted by the DFT screening in Chapter 3 are observable on bare metallic foams via the calibrated breakthrough apparatus established in Chapter 4. Open-cell Cu, Al, and Ni foams were sectioned into identical strip geometries, cleaned, weighed, and mounted within the fixed-bed holder. Employing a standardized adsorption/desorption protocol under uniform illumination conditions, the reactor generated reproducible CO₂ breakthrough curves, facilitating direct comparisons of thermal (dark) versus photo-assisted performance across the metals and relative to a blank bed.

Given the modest geometric surface area of the foams, which cannot be accurately determined a priori from manufacturer specifications alone, this chapter first developed a micro-CT workflow to quantify the accessible metallic surface area. For example, Cu foam, bulk density, and porosity measurements were integrated with bulk-constrained segmentation of the CT image stack and marching-cubes surface reconstruction, yielding a surface-to-volume ratio (A/V) of Cu $\approx 4.18 \pm 0.18 \text{ mm}^{-1}$ and a total geometric area of $\approx 0.215 \text{ m}^2$ for the five strips loaded into the reactor.

On this basis, the three foams exhibited nearly identical area-normalized adsorption and desorption capacities under illumination, with blank-subtracted uptakes confined to $\approx 0.8\text{-}1.1 \text{ mmol m}^{-2}$ for adsorption and $\approx 0.3\text{-}0.7 \text{ mmol m}^{-2}$ for desorption. Thus, for a fixed bed volume packed with 110-PPI foam, Cu, Al and Ni provide comparable CO₂ processing per unit interfacial area once the geometric area is properly accounted for. In contrast, mass-

normalized metrics revealed a clear hierarchy: Ni, being the most porous and least dense, delivered roughly twice the illuminated CO₂ throughput per gram compared to Cu and Al, which showed nearly identical mass-specific capacities once density differences were taken into account.

Photoillumination induced modest yet reproducible enhancements in both adsorption and desorption capacities across the three metallic foams, whereas the blank bed exhibited marginally attenuated performance under illumination. Post-blank subtraction, the net foam contribution under thermal-only conditions remains negligible, while illuminated operation elicits consistent positive uptakes and releases from all foams. These results corroborate that the photoresponse derives from the electronic and/or photothermal attributes of the metallic architectures, avoiding non-specific chamber-wide artifacts, and they demonstrate that the apparatus can resolve subtle, material-dependent differences in light-assisted desorption on low-area metallic substrates.

In comparison to high-surface-area porous sorbents, metallic foams occupy a complementary niche: their CO₂ capacities per unit geometric surface area rival or surpass those of MOFs and zeolites, while their gravimetric capacities lag by orders of magnitude. This underscores a design paradigm wherein metallic foams function not as primary sorbents, but as electronically conductive, photothermally responsive scaffolds for high-capacity chemisorptive overlayers. In this capacity, they furnish a practical experimental platform for examining the interplay of surface electronic structure, external stimuli, and CO₂ binding, thereby forging a vital link between the idealized adsorption energetics and device-scale implementations.

6. Learning Adsorption Energetics on Transition-Metal Alloys

6.1 Introduction

Chapters 3 and 4 laid the foundational groundwork for this investigation, establishing two fundamental pillars: firstly, from DFT, the binding affinity of CO₂ on pure transition-metal surfaces demonstrates sensitivity to both surface charge and illumination, thereby proposing a pathway for light-assisted, energy-efficient regeneration; and secondly, a light-assisted breakthrough apparatus facilitates the quantitative assessment of these effects under precisely controlled experimental conditions. While pure metals offer essential mechanistic baselines, effective carbon capture materials necessitate a delicate balance among capacity, selectivity, kinetics, and regenerability, properties that can be significantly modulated through alloying, offering greater flexibility than elemental surfaces by enabling the modification of local electronic structure, optical absorptance, and thermal transport characteristics. However, the associated design space expands combinatorially, as numerous binary compositions, crystallographic facets, and distinct adsorption sites generate thousands of plausible configurations, making exhaustive DFT mapping computationally impractical.

To address the expansion of design space, a machine learning (ML) surrogate model is developed to predict CO₂ adsorption energy (E_{ads}) on alloy surfaces. The primary objective is methodological: to evaluate whether a small, rigorously curated DFT dataset contains sufficient signal to enable reliable E_{ads} prediction in a data-limited regime. In this context, the model is not intended to replace first-principles (DFT) calculations, but to provide a rapid estimator that can support preliminary screening and hypothesis generation.

Accordingly, the chapter first describes the dataset and target definition, and the representations used to encode alloy identity and local surface structure, combining physics-informed descriptors with local structural fingerprints. Next, it benchmarks a set of models appropriate for tabular learning under small-data conditions, using group-aware validation to assess

generalization beyond closely related alloy/site instances. Finally, model interpretability is reported alongside accuracy to identify which descriptors and local-structure signals most strongly correlate with adsorption strength. Stimulus-dependent effects (e.g., charge or illumination-induced changes in binding) and closed-loop active learning are treated as natural extensions enabled by this baseline model, but are not claimed as direct outputs of the neutral-data model developed here.

6.2 Terminology and evaluation metrics

This chapter uses standard machine-learning terminology and performance metrics. For clarity, I briefly define the key terms used throughout the modeling workflow.

6.2.1 Dimensionality reduction and feature compression

Principal component analysis (PCA)- PCA is a linear dimensionality-reduction method that transforms a set of correlated features into a new set of orthogonal variables called *principal components*. The components are ordered such that the first component captures the largest possible variance in the data, the second captures the next largest variance subject to orthogonality, and so on. In practice, PCA is used to compress high-dimensional descriptors (e.g., structural fingerprints) into a smaller number of variables while retaining most of the information content relevant for downstream learning [1]. Given a centered feature matrix $\mathbf{X} \in \mathbb{R}^{n \times d}$, PCA finds an orthonormal loading matrix $\mathbf{W} \in \mathbb{R}^{d \times k}$ (columns are principal directions) such that the projected variables $\mathbf{Z} = \mathbf{XW}$ capture maximal variance, with $\mathbf{W}$ given by the top- k eigenvectors of the covariance $\mathbf{C} = \frac{1}{n-1} \mathbf{X}^\top \mathbf{X}$.

6.2.2 Model families used in this chapter

Linear regression and regularization (Ridge/Lasso)- A linear model assumes the target property is a weighted sum of input features. When many correlated features are present, regularization helps stabilize the fit. *Ridge regression* (L2 regularization) penalizes large weights and tends to shrink coefficients smoothly, while *Lasso* (L1 regularization) promotes sparse solutions by driving some coefficients exactly to zero, which can aid interpretability [55, 134].

Kernel methods (RBF kernel)- Kernel methods learn nonlinear relationships by implicitly mapping inputs into a higher-dimensional feature space. A common choice is the *radial basis function (RBF)* kernel, which measures similarity that decays with distance in feature

space. Kernel models are effective when the target varies smoothly with descriptors but can become computationally expensive for large datasets [119].

Tree ensembles (Random Forest, AdaBoost, Gradient Boosting)- Decision trees partition the feature space into regions and fit simple predictors within each region. Tree *ensembles* combine many trees to improve accuracy and reduce variance. *Random Forest* is a *bagging* [16]-style ensemble where trees are trained on bootstrap-resampled datasets with random feature subsets, and predictions are averaged [17]. *AdaBoost* and *Gradient Boosting* are *boosting*-style ensembles that build trees sequentially; each new tree focuses on correcting errors made by the previous ensemble (AdaBoost via reweighting samples; gradient boosting via fitting residuals). These methods can capture nonlinear interactions between composition and structural descriptors [35, 36].

Gaussian process regression (GPR)- GPR is a probabilistic regression method that assumes the target function is drawn from a Gaussian process specified by a mean function and a kernel (covariance) function. A key benefit is that GPR naturally provides a predictive mean and a model-based uncertainty estimate, which is useful for guiding down-selection and active learning. Its main limitation is computational scaling with dataset size [109].

TabPFN- TabPFN (Tabular Prior-Data Fitted Network) is a transformer-based model trained on many synthetic tabular tasks to learn a general-purpose prior over functions. At inference time, it uses the training set as context and produces strong performance on small-to-medium tabular datasets with minimal hyperparameter tuning. In this thesis, TabPFN is used as a competitive baseline and as a practical surrogate model for ranking candidate alloy-site systems [58].

6.2.3 Ensembles, bagging, and uncertainty

Model ensemble- A model ensemble combines predictions from multiple models to improve robustness. The simplest approach averages the predictions from diverse models (or from the same model trained with different random seeds or bootstrapped datasets). Ensembles often reduce variance and can yield better generalization than any single constituent model [49].

Bagging (bootstrap aggregating)- Bagging is an ensemble strategy where multiple models are trained on bootstrap samples (random samples drawn with replacement) of the training data, and their predictions are averaged. Bagging is particularly effective for high-variance learners such as decision trees [49, 16].

6.2.4 Model evaluation: cross-validation and R^2

Cross-validation- Cross-validation (CV) is a resampling procedure used to estimate model performance on unseen data. In k -fold CV, the dataset is split into k disjoint folds; the model is trained on $k - 1$ folds and evaluated on the remaining fold, repeated k times so each fold serves once as the test set. The reported score is the mean (and often the standard deviation) across folds. CV provides a more reliable estimate than a single train/test split, especially for modest dataset sizes. For k -fold CV, the reported score is typically the mean across folds [49, 68]:

$$score_{cv} = \frac{1}{k} \sum_{j=1}^k score^{(j)} \quad (6.1)$$

Coefficient of determination (R^2)- R^2 quantifies how much of the variance in the target is explained by the model relative to predicting the mean of the training targets. For predictions $\hat{y}_i$ of true values y_i ,

$$R^2 = 1 - \frac{\sum_i (y_i - \hat{y}_i)^2}{\sum_i (y_i - \bar{y})^2}, \quad (6.2)$$

where $\bar{y}$ is the mean of y_i . An R^2 of 1 indicates perfect prediction; $R^2 = 0$ corresponds to performance equal to predicting the mean; and negative values indicate performance worse than that baseline [49].

6.2.5 Data preprocessing

Standard capping - Standard capping, also known as winsorization, reduces the leverage of extreme values by replacing them with boundary values defined from the empirical distribution. In percentile-based winsorization, values below the p th percentile are set to Q_p , and values above the $(100 - p)$ th percentile are set to Q_{100-p} . In this thesis, standard capping is used only during exploratory data analysis (EDA) to stabilize summary plots and sensitivity checks; all model training and reported performance metrics are computed using the original (uncapped) targets.

6.3 Methodology

6.3.1 Data and target

Data generation

The initial pure-metal dataset, established in Objective 1 (Al, Pt, Zn, V, Ni, Co, Cu, Fe), was extended to incorporate binary alloys selected through a thermodynamic stability screening process. Utilizing experimentally reported or database-curated prototypes as a foundation, candidate systems underwent filtration based on their energy above hull¹, ensuring the retention of composition/structure pairs situated close to the convex hull. Consequently, 75 distinct binary alloys were identified, each of which subsequently underwent bulk relaxation using consistent exchange-correlation and dispersion settings as mentioned in the subsequent sections of the current chapter. For each identified alloy, low-index facets were subsequently determined, prioritizing those energetically favored based on surface-energy considerations. Symmetric slab models, incorporating adequate vacuum spacing (~ 10 Å), were then constructed and subjected to surface relaxation to yield pristine reference surfaces.

Adsorption-site enumeration and down-selection

On each relaxed surface, distinct adsorption configurations for CO₂ were systematically generated based on symmetry principles (on-top, bridge, hollow variants) utilizing the python library known as pymatgen [95]. Each of these configurations was then initialized with physically informed poses (horizontal-linear CO₂) and subsequently optimized to its closest local energy minimum. To manage the computational scale of the investigation, the study focused on systems exhibiting no more than 12 unique adsorption sites per alloy-facet pair; combinations exceeding this limit were set aside for future research.

Target definition

The supervised target is the CO₂ adsorption energy, which is defined as:

$$E_{ads} = E_{slab+CO_2} - E_{slab} - E_{CO_2} \quad (6.3)$$

¹Energy above hull E_{hull} is the per-atom formation energy of a structure from the convex hull of all competing phases in the same chemical system (constructed from DFT total energies). By definition $E_{hull} = 0$ for thermodynamically stable phases on the hull; $E_{hull} > 0$ measures the decomposition driving force into adjacent tie-line phases. Small positive values indicate metastability that may still be experimentally accessible due to finite-temperature entropy, defects, or kinetic trapping. In this work, candidates with E_{hull} below 0.1 were retained.

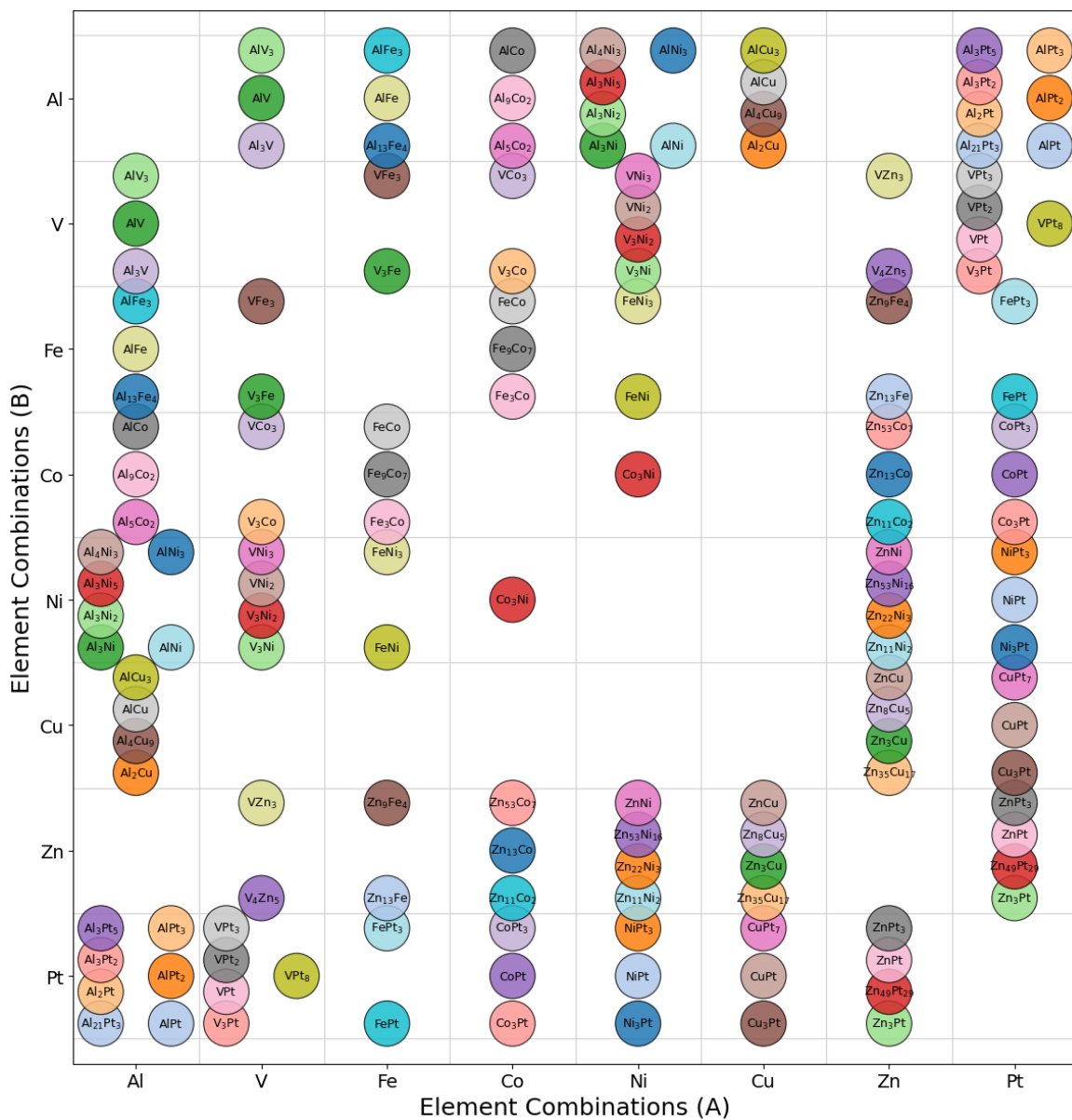


Fig. 6.1 Map of candidate binary alloys. Axes list parent elements; labeled circles indicate intermetallic phases that passed the energy-above-hull screen. Multiple labels per A-B cell reflect distinct stoichiometries. These alloys were used to generate slabs, enumerate adsorption sites, and compute CO_2 adsorption energies.

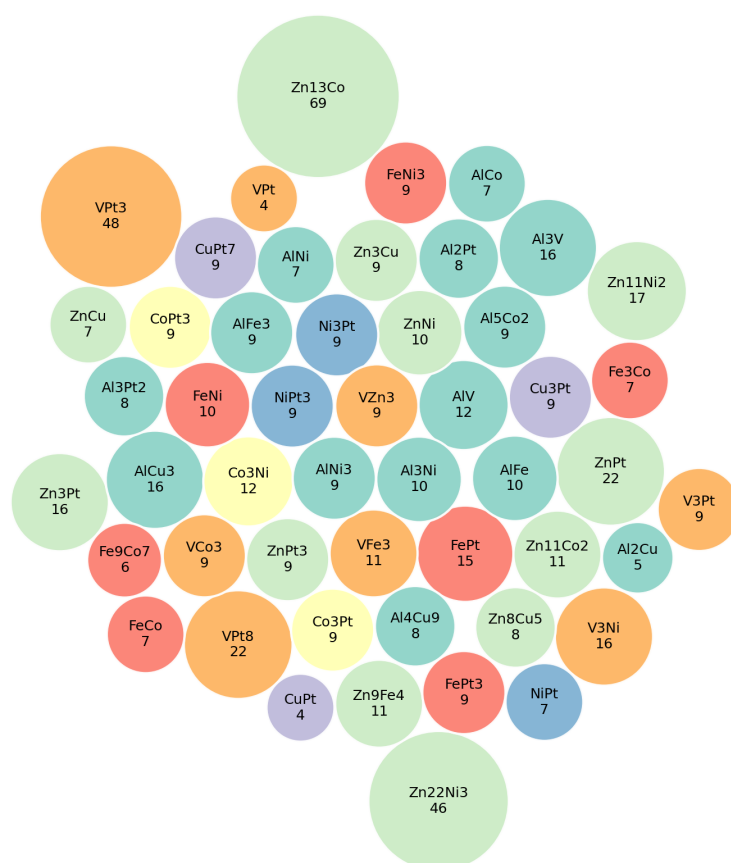


Fig. 6.2 Site multiplicity across alloys. Bubble area is proportional to the number of symmetry-distinct CO₂ adsorption sites (label: alloy composition, count), aggregated over the low-energy facets considered in this work and used to down-select (≤ 12 sites) representative sites for DFT calculations.

computed with identical consistent numerical parameters for all three components. Consistent with established conventions, a negative E_{ads} value signifies an exothermic adsorption process. Unless explicitly noted otherwise, the reported values correspond to the lowest-energy relaxed geometry for each site prototype, derived under conditions of neutral slabs. In addition to E_{ads} , supplementary labels (like O–C–O angle, C=O bond lengths, site coordination, elemental statistics of the local environment) are stored to facilitate subsequent feature construction and post-hoc interpretability.

Quality control and splits

Tighter force and energy convergence thresholds were mandated for all bulk, surface, and adsorbate relaxations; non-converged or metastable outcomes were identified and subsequently excluded from the training dataset. Each data row was uniquely indexed (using alloy and their corresponding site) to enable the application of group-aware validation, i.e., train/test splits that keep all entries from the same alloy (or alloy-facet) together in a single fold. This prevents information leakage where the model is trained on one adsorption site of a given alloy and then evaluated on another, which would overestimate performance because the test point is chemically and geometrically very similar to the training data. As a result, the reported metrics more faithfully reflect generalization to unseen alloys or unseen alloy-facet systems, rather than near-duplicate predictions within the same parent material.

6.3.2 Representation (features)

1. Physics-informed/low-cost descriptors

- Atomic number
- Electronegativity
- First ionization energy
- Density
- Period
- Atomic radius
- Metallic radius
- van der Waals radius
- Specific heat capacity
- Group number

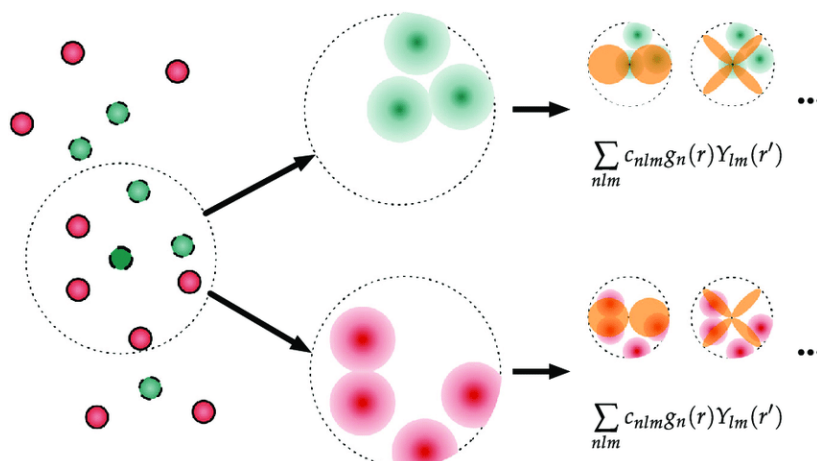


Fig. 6.3 The local density around the central atom is modeled by atom-centered normal distributions and expanded into radial and spherical harmonics basis functions [10].

- First electron affinity
- Electrophilicity
- Heat of formation
- Dipole polarizability

2. Structure-derived descriptors

- Smooth Overlay of Atomic Positions (SOAP) - SOAP encodes how atoms are arranged around a center atom by using a smoothed atomic density, built from Gaussian distributions. This density is then expanded using radial basis functions and spherical harmonics, which gives us a rotationally and translationally invariant representation. Mathematically, the similarity between two atomic environments, say from two different alloy surfaces, is given by the dot product between their expansion coefficients. As shown in the Figure 6.3, each environment is decomposed into these orthogonal components. The final fingerprint vector captures both the type of atoms and their spatial arrangement [10].
- Many-body Tensor Representation/Local Many-body Tensor Representation (MBTR/LMBTR) - MBTR encodes the structure by analyzing statistical distributions of atomic environments. It does this by considering different body-order interactions:
 - $k=1$: just the element types (how many H, O, etc.)
 - $k=2$: inverse distances between pairs of atoms
 - $k=3$: angles formed between triplets of atoms

Each of these is converted into a Gaussian-smeared histogram, capturing the full geometric fingerprint of the system. In the illustration (Figure 6.4), I use a water molecule as an example, one can see how the $k=1-3$ levels progressively add more structural information. This ultimately results in a multi-dimensional matrix, a compact and meaningful numerical representation of the structure.

For surfaces, MBTR compactly encodes pairwise distance and angular statistics over the set of species present $\{\text{Al, Pt, Zn, V, Ni, Co, Cu, Fe}\}$, providing sensitivity to both geometry and chemistry while remaining invariant to rotation, translation, and indexing. The final configuration was selected by small grid searches on the training folds and is reported below for reproducibility:

- Species set: $Z = \{\text{Al, Pt, Zn, V, Ni, Co, Cu, Fe}\}$ (same across all alloys/facets).
- Terms: $k = 2, 3$ (I omit $k = 1$ as it added little information beyond composition features).
- Grids and broadening:
 - $k=2$ grid: $r_{min} = 1.0 \text{ \AA}$, $r_{max} = 8.0 \text{ \AA}$, $n_r = 200$; Gaussian broadening $\sigma_2 = 0.05$
 - $k=3$ grid: $\cos \theta \in [-1, 1]$, $n_\theta = 200$; Gaussian broadening $\sigma_3 = 0.05$
- Normalization: L^2 normalization per term; terms concatenated and flattened.
- Sparsity and dimensionality: Post-concatenation dimensionality reduced by PCA (with variance of $\approx 80\%$).

6.3.3 Model Ensembles

- Linear/Ridge/Lasso
- Kernel methods (kernel ridge) (RBF)
- Tree ensembles (GradientBoost, RandomForest, AdaBoost)
- Gaussian process regression (GPR)
- TabPFN

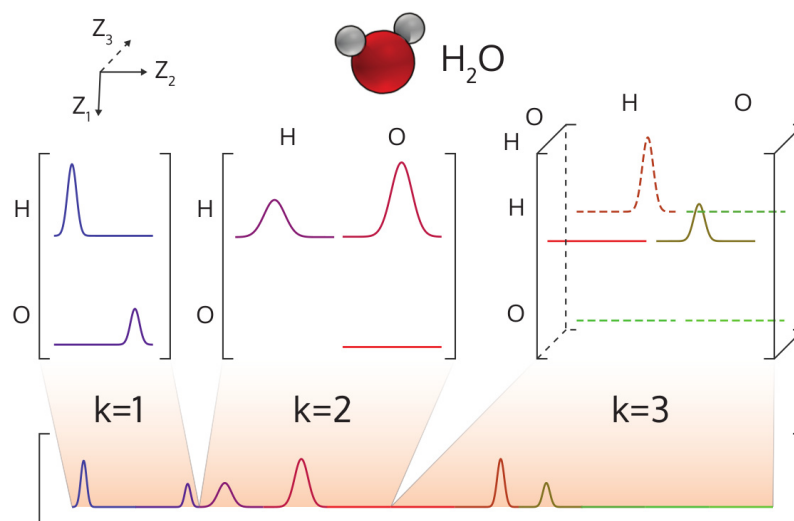


Fig. 6.4 Illustration of MBTR output for water molecule

Rationale for model selection

The models evaluated in this chapter were chosen to provide (i) strong and diverse baselines, (ii) coverage of the main inductive biases used for tabular regression, and (iii) a practical path to uncertainty-aware ranking under limited data. Specifically, linear and regularized linear models (linear/ridge/lasso) serve as transparent baselines and test whether adsorption energy trends can be captured by approximately additive descriptors. Kernel methods with an RBF kernel provide a smooth nonlinear benchmark that performs well when the target varies continuously with feature distance. Tree ensembles (Random Forest, AdaBoost, Gradient Boosting) capture nonlinear feature interactions and typically perform strongly on heterogeneous tabular data without heavy feature scaling. Gaussian process regression was included because it yields a probabilistic prediction with a natural uncertainty estimate, which is useful for screening and down-selection, albeit with less favorable scaling. Finally, TabPFN was evaluated as a modern foundation-model baseline for tabular data that often achieves competitive accuracy with minimal hyperparameter tuning, making it attractive for rapid iteration and candidate ranking in small-to-medium datasets.

6.3.4 Training validation and optimization

Models were trained on the site-resolved alloy dataset using group-aware splits that prevent leakage across chemically related entries. Specifically, all samples from a given alloy-facet pair were assigned to the same fold to ensure that reported performance reflects generalization to unseen compositions and surfaces rather than interpolation among near-duplicates. Hy-

perparameters for each algorithm (linear/ridge/lasso, kernel ridge, random forest, Gaussian process regression, and TabPFN) were tuned via nested group-k-fold ($k \sim 5$), balanced to keep a similar number of alloy–facet groups per fold. Model selection prioritized mean absolute error (MAE) as the principal metric, with root-mean-square error (RMSE) and R^2 reported for completeness. To stabilize small-data training, I used repeated cross-validation with different random seeds and averaged scores across repeats. For TabPFN, I adopted an ensemble-of-seeds strategy (bagging) by training N independent instances with distinct data permutations and aggregating predictions by simple or variance-weighted averaging; this materially reduced variance and improved worst-case errors. Where uncertainty estimates were required (for active-learning down-selection), I used quantile regression forests/GPR or empirical residual bootstrapping; conformal prediction was applied post-hoc to yield coverage-calibrated intervals at a desired confidence level. All preprocessing (feature scaling where required, descriptor generation, and curation) was pipeline-bound and fit only on the training folds to prevent information leakage.

6.4 Results

6.4.1 Dataset overview and statistics

This chapter builds a supervised learning dataset for predicting site-resolved CO_2 adsorption energies on binary alloy surfaces. Each data point represents a distinct adsorption site (e.g., bridge, hollow, atop) on a given low-index alloy facet, uniquely identified via a canonical site label (e.g., `Al2Cu5_ad_site`). $N \approx 560$ sites (combining all alloys), number of alloys ≈ 75 , facets per alloy ≈ 1 , and sites per facet ≈ 10 , so sampling imbalance across alloys/facets/sites is explicit. The final modeling table combines physics-informed compositional and periodic descriptors with MBTR fingerprints computed from local atomic environments.

Scope and size. Following data cleaning and normalization of identifiers, the dataset for model selection comprises 560 site-resolved samples. Adsorption energies E_{ads} are given in eV per CO_2 , with negative values signifying exothermic adsorption against the selected gas-phase reference. These values range from approximately -0.10 to +0.02 eV, spanning weakly physisorbed to mildly destabilized states representative of the surfaces examined.

Target variable. The distribution of the target E_{ads} exhibits a mild left skew, meaning that a small number of samples exhibit strong binding (more negative E_{ads}) compared with the bulk of the dataset (as seen in Figure 6.5a). To mitigate spurious leverage from heavy-tailed predictor components during EDA, I apply standard percentile-based capping (Section 6.2.5) to the MBTR-PCA features at the 1st and 99th percentiles; the resulting feature

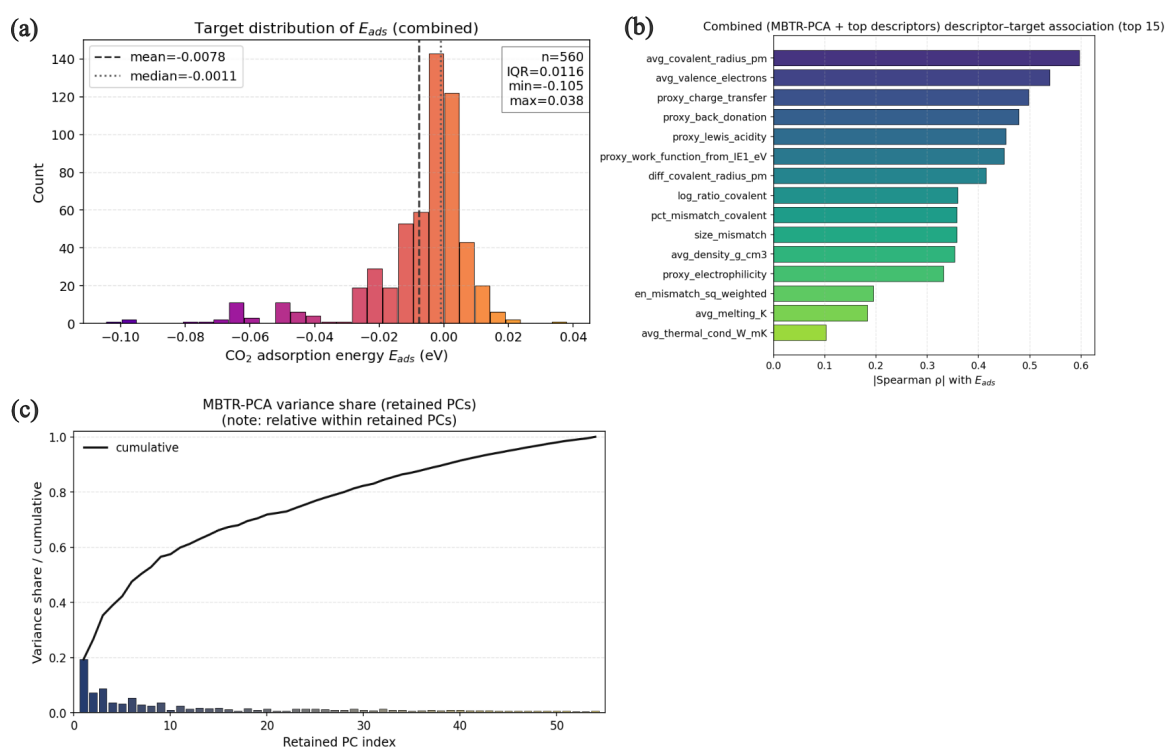


Fig. 6.5 Data landscape and descriptor relevance. (a) Histogram of DFT CO_2 adsorption energies E_{ads} for $n = 560$ alloy surface sites. (b) Top-15 descriptors ranked by $|\rho_{spearman}|$ with E_{ads} combining MBTR-PCA components and physicochemical features; average covalent radius, valence-electron count, and charge-transfer/back-donation proxies show the strongest associations. (c) Screen and cumulative variance for retained MBTR-PCA components, indicating rapid eigenvalue decay and that a compact set of PCs captures most of the retained variance.

distributions are shown in Figure 6.7. All reported metrics are computed using the original (uncapped) targets. Figure 6.5(b) ranks the top 15 descriptors by their absolute Spearman correlation with E_{ads} , combining MBTR-PCA components and physicochemical features. The strongest associations are carried by *avg_covalent_radius* and *avg_valence_electrons*, reflecting the well-established dependence of CO₂ binding strength on the spatial extent of the d-orbitals and the electron count available for back-donation into the CO₂ π^* states. Charge transfer and *backdonation* proxies rank prominently alongside the *proxy_lewis_acidity* and *proxy_work_function* descriptors, collectively suggesting that the electrostatic and electron-donation character of the alloy surface, rather than geometric packing alone, is the primary driver of adsorption strength across the binary alloy space examined here. Size-mismatch and covalent radius difference features (*pct_mismatch_covalent*, *diff_covalent_radius*) appear in the mid-tier, indicating that lattice strain arising from dissimilar atomic radii in the alloy modulates the local binding environment, consistent with strain-induced shifts in the d-band center reported for surface alloys. Notably, the thermal conductivity proxy (*avg_thermal_cond*) appears at the lower end of the ranking with a weak but non-negligible correlation, which is likely a secondary reflection of the metallic character and electron density of the constituent elements rather than a direct physical driver of CO₂ adsorption. Taken together, the descriptor importance profile is physically consistent: the dominant signals are electronic in character, validating the inclusion of charge-transfer and work-function proxies in the feature set alongside the MBTR structural fingerprint.

6.4.2 Baseline regressors: performance and ablations

Unless noted, models use MBTR + phys/chem with identical CV splits and the same preprocessing pipeline. I benchmarked a set of non-neural regressors—linear models (OLS/ridge/lasso), kernel ridge regression (RBF kernel), random forest (RF), gradientboost, adaboost, and Gaussian process regression (GPR), under the group-aware protocols described in §6.2.4. To isolate representation effects, I first trained each model on single-family descriptors and then on hybrid feature sets. Among stand-alone structural fingerprints, MBTR consistently delivered the lowest errors across alloys and facets, while SOAP and LMBTR underperformed and exhibited larger tail errors on sparsely represented site types. I therefore adopted MBTR as the primary local-structure descriptor. Physics/chemistry descriptors (elemental/periodic statistics, simple electronic heuristics, composition and facet metadata) alone were competitive with linear models but could not match non-linear baselines. The best overall performance was obtained by hybridizing MBTR with the phys/chem feature block, which reduced MAE relative to either block alone and narrowed the interquartile spread across folds.

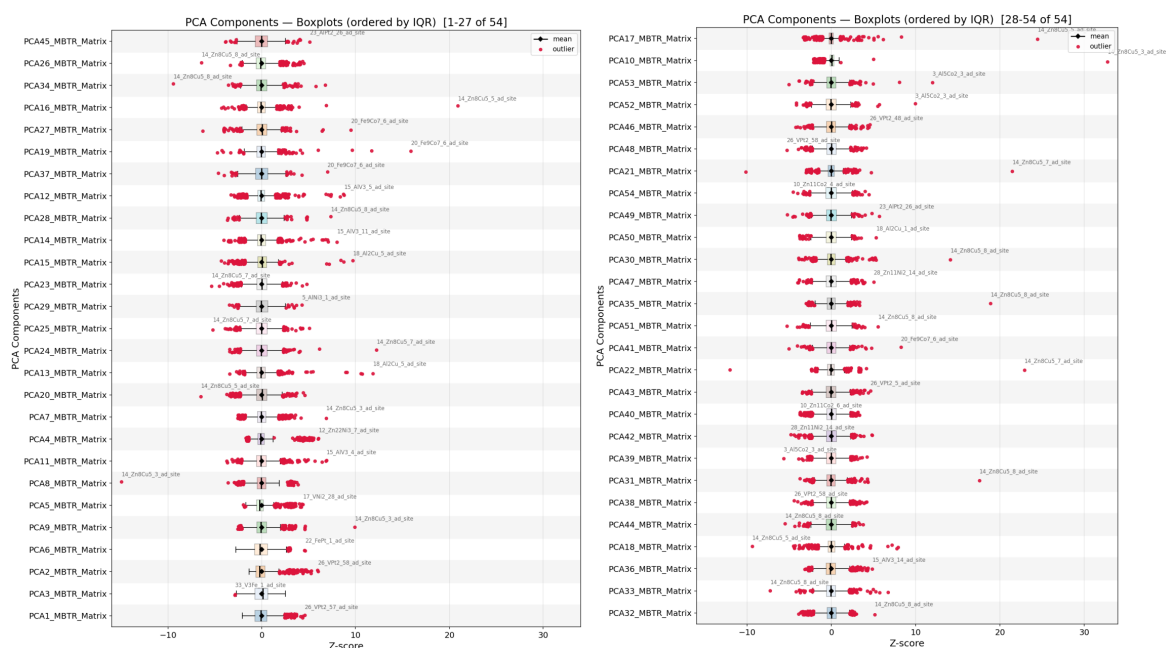


Fig. 6.6 Distributions of MBTR-PCA features across alloy sites. Boxplots of the 54 retained principal components derived from MBTR (z-scored), ordered by interquartile range => left: PCs 1-27; right: PCs 28-54. Squares mark component means; red points are outliers; annotated labels indicate the most extreme alloy-site cases. Several components exhibit heavy-tailed behavior, highlighting rare geometries/chemistries that dominate variance and may act as leverage points for regression.

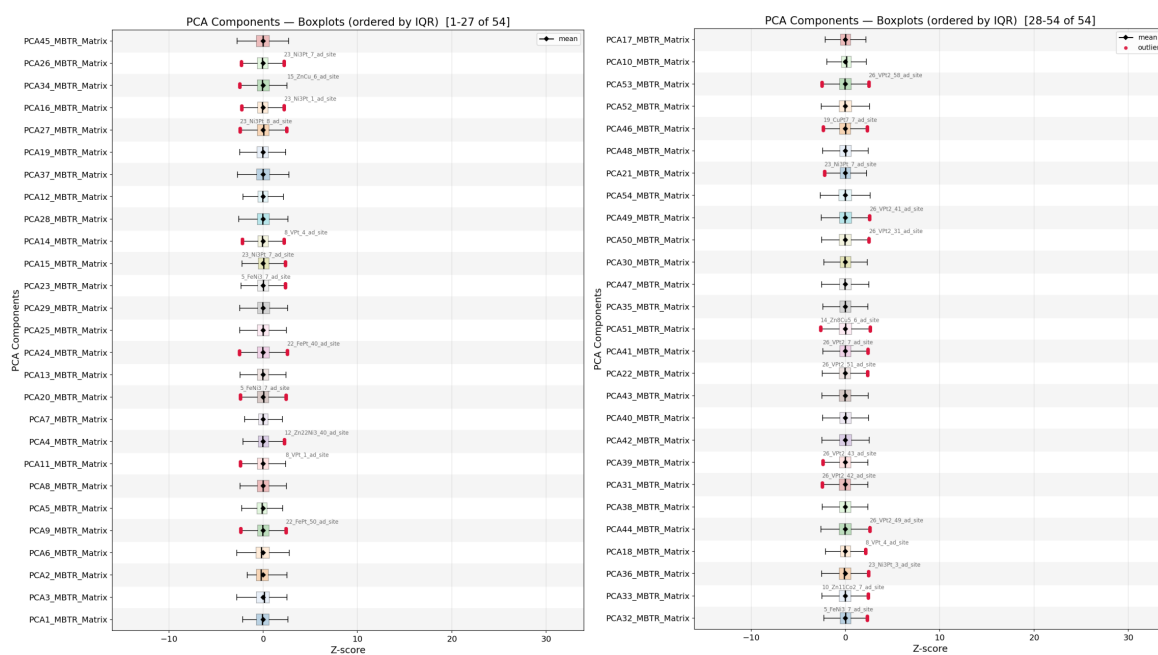


Fig. 6.7 MBTR-PCA feature distributions after outlier capping. Box-and-whisker plots of the 54 retained principal components (z-scored), ordered by interquartile range => left: PCs 1–27; right: PCs 28–54. Squares mark component means; red points are remaining extremes. Relative to the uncapped case, dispersion and outlier frequency are reduced, and most components are near-zero centered, yielding features better conditioned for regression.

Algorithmically, RF and kNN were the most reliable classical baselines; GPR produced calibrated uncertainties but degraded when descriptor dimensionality became large relative to fold size. I did not evaluate XGBoost in this study; based on problem structure and prior experience on similar tabular sets, I expect performance broadly comparable to RF. Importantly, ablations reaffirm that single-parameter electronic summaries (e.g., the pristine-surface d-band center) are insufficient to explain alloy/site variability in E_{ads} ; adding MBTR-based local geometry and neighbor identity/contrast is essential to recover observed trends.

6.4.3 TabPFN benchmarking

Under the same group-aware protocol (§6.2.4), TabPFN achieved one of the lowest average MAE and the tightest fold-to-fold spread among all evaluated models. Relative to kernel ridge and RF, TabPFN reduced both the mean error and the 95th-percentile absolute error, indicating improved robustness on sparsely represented alloy–facet–site combinations. Performance further improved when ensembling multiple TabPFN instances trained with different seeds/permutations (bagging), which reduced variance and stabilized difficult cases. Uncertainty calibration based on residual conformalization delivered near-nominal empirical coverage, supporting the model’s use for active-learning down-selection. Overall, TabPFN (single) is comparable to the best classical baseline in error and most robust across folds, especially when bagged; I therefore adopt it for candidate ranking and uncertainty-aware screening in subsequent sections.

Table 6.1 Model performance for adsorption-energy prediction under group-aware cross-validation (stratified by alloy; 5 folds, repeated). Feature set: MBTR (k=2,3) concatenated with physical/chemical descriptors; target: DFT adsorption energy (eV). Values are fold-averaged. “TabPFN (single)” is the pretrained transformer fine-tuned on the training folds; “TabPFN (bagged, N=8)” aggregates 8 base learners trained on bootstrapped subsamples ($\approx 80\%$) with mean prediction. (SOAP and LMBTR alone underperformed MBTR; therefore only MBTR+phys/chem is reported).

Model	MAE (eV)	RMSE (eV)	R^2
Ridge (phys/chem + MBTR)	0.0065	0.0100	0.71
Kernel Ridge (RBF)	0.0063	0.0126	0.53
Random Forest	0.0042	0.0091	0.82
GPR	0.0062	0.0113	0.63
Adaboost	0.0059	0.0095	0.74
Gradient-boost	0.0043	0.0076	0.81
KNN	0.0050	0.0097	0.72
TabPFN (single)	0.0043	0.0077	0.82
TabPFN (bagged, $N = 8$)	0.0043	0.0077	0.83

Across classical baselines, Random Forest attains the lowest MAE (0.0042 eV), while Gradient Boosting yields the lowest RMSE (0.0076 eV), reflecting the usual bias-variance trade-off of tree ensembles. TabPFN achieves the highest R^2 (0.84) with MAE/RMSE comparable to the best classical models; bagging primarily stabilizes out-of-fold predictions and produces a modest R^2 gain without materially changing absolute error. Given that differences in MAE/RMSE among RF, GB, and TabPFN are within typical fold-to-fold variability, I consider these models statistically comparable in error and carry TabPFN forward as the primary predictor due to its calibration behavior, strong R^2 , and robustness under group-aware splits. For completeness and sanity checks, RF/GB remain as secondary baselines in sensitivity analyses. Finally, preliminary trials showed MBTR alone outperformed SOAP and LMBTR alone; hence the final feature set combines MBTR + phys/chem descriptors, which delivered the most reliable cross-validated performance.

6.5 Summary

This chapter developed and validated a machine-learning surrogate to predict site-resolved CO₂ adsorption energies on binary alloy surfaces using a curated dataset and hybrid descriptors that combine MBTR (as the primary local-structure representation) with physics/chemistry features. Under group-aware evaluation, non-linear regressors (kernel methods and random forests) outperformed linear baselines, while TabPFN delivered the most robust accuracy in the small-data regime. Ensembling (bagging) multiple TabPFN instances further reduced variance and tail error, yielding stable, decision-grade ranking with uncertainty estimates amenable to active-learning loops. Importantly, the present model is intended as a neutral-energetics screening tool; extension to stimulus-dependent targets (e.g., charged slabs or photo-proxy descriptors) is left to future work.

6.6 Limitations

6.6.1 Dataset Size and Compositional Coverage

The training dataset comprises ≈ 560 site-resolved samples across ≈ 75 binary alloys, which is small by conventional ML standards. While group-aware cross-validation mitigates overfitting to specific alloy facet combinations, the effective number of independent groups per fold is limited, making fold level variance a poor proxy for true out-of-distribution generalization. The alloy space is further restricted to binary intermetallics drawn from eight parent elements (Al, Pt, Zn, V, Ni, Co, Cu, Fe); ternary and higher-order alloys, which may

offer superior tunability of the CO₂ binding site, are entirely absent. Additionally, the energy-above-hull threshold of 0.1 eV per atom used for stability screening, while practical, may exclude metastable phases that are experimentally accessible under synthesis or operational conditions. Expanding the dataset through high-throughput DFT or active learning, and extending the compositional space to ternary systems, are the most impactful near-term routes to improving model reliability.

6.6.2 Neutral-Slab Targets and Absence of Stimulus-Dependent Labels

All training targets are neutral-slab CO₂ adsorption energies computed under standard DFT conditions. The central motivation of this thesis is charge and light-assisted CO₂ desorption, yet the present surrogate contains no stimulus-dependent signal: charged-slab energies, work-function shifts under illumination, or photo-proxy descriptors are absent from both the features and the labels. As a result, the model cannot rank alloys by their responsiveness to surface charging or photothermal excitation, the properties most relevant to the regeneration strategy developed in Chapters 3-5. The surrogate should therefore be interpreted strictly as a neutral energetics screening tool, useful for eliminating non-binding alloy surfaces early in the design pipeline, but insufficient to identify light-responsive candidates without further extension. Incorporating charged-slab calculations as additional training targets, and including electronic descriptors sensitive to charge state (e.g., work function, Bader charge transfer, d-band center shift under bias) as features, is identified as the essential next step.

6.6.3 Model Scope: Thermodynamics Only

The surrogate predicts adsorption energy as a static thermodynamic quantity and contains no information about adsorption/desorption kinetics, activation barriers for CO₂ dissociation, or surface diffusion rates. For CO₂ capture applications, these kinetic properties, particularly the desorption activation energy, which governs regeneration temperature and rate, are at least as important as binding thermodynamics. A material with a moderate but kinetically favorable adsorption energy may outperform one with a stronger binding site that requires higher desorption temperatures. Predicting transition-state energies and activation barriers from ML surrogates is significantly more demanding in terms of data and descriptor design, typically requiring nudged elastic band (NEB) calculations as training labels, and is identified as a future extension of this framework.

6.6.4 Generalization and Experimental Validation

The group-aware cross-validation protocol ensures that reported metrics reflect generalization to held-out alloy facet groups rather than near-duplicate interpolation, which represents a more honest estimate of out-of-distribution performance than standard k-fold. Nevertheless, all evaluation remains in-distribution relative to the eight parent elements and the binary intermetallic crystal prototypes used for training; the model has not been validated against experimental adsorption data or against DFT calculations from independent databases such as the Open Catalyst Project or the Catalysis-Hub. Discrepancies between the PBE-GGA adsorption energies used as training labels and higher-level references (hybrid functionals, coupled-cluster benchmarks) represent an additional source of systematic error that propagates into model predictions. Experimental validation of the top-ranked alloy candidates, ideally via temperature-programmed desorption (TPD) or microcalorimetry on well-defined alloy surfaces, is a necessary step before the surrogate’s rankings can be used to direct synthesis efforts.

6.7 Conclusion

A central bottleneck in screening materials for CO₂ capture and regeneration, whether under neutral conditions or under externally assisted pathways (e.g., photothermal or photoelectronic stimuli), is the cost of reliably estimating the CO₂ adsorption energy E_{ads} across many candidate surfaces and adsorption sites. The primary objective of this chapter is therefore methodological: to determine whether adsorption-energy prediction is feasible from a modestly sized DFT dataset, i.e., whether a surrogate trained on rigorously curated neutral-slab calculations can achieve reliable E_{ads} predictions suitable for rapid screening.

Using MBTR-based local structural fingerprints together with physicochemical descriptors, and enforcing alloy-grouped validation to avoid information leakage, the best-performing models achieve strong predictive performance (Table 6.1). These results demonstrate that meaningful site-resolved adsorption-energy trends can be learned from the present dataset, enabling faster exploration of adsorption energetics than direct DFT alone.

Importantly, this chapter does not claim to identify light-responsive materials directly: the training targets here are neutral adsorption energies, and stimulus-dependent effects (e.g., surface charging, work-function shifts, or photo-proxy descriptors) are not included in the learning targets. Consequently, the surrogate should be interpreted as a baseline model for E_{ads} that can (i) accelerate preliminary screening, (ii) support sensitivity studies and hypothesis generation, and (iii) provide a foundation for future extensions.

Future work will extend this framework toward stimulus-aware screening by incorporating charged-slab calculations and/or photo-proxy targets, calibrating uncertainty for decision-making, and integrating model recommendations into an active-learning loop coupled to DFT and experimental validation. In that sense, the closed-loop discovery workflow is a natural next step enabled by the present surrogate, rather than a deliverable concluded within this chapter.

7. Conclusion and Future Direction

7.1 Thesis summary and research objectives

The central aim of this thesis was to advance a materials-to-device framework for light-assisted CO₂ capture and regeneration, motivated by the need to reduce the energy and carbon intensity of sorbent regeneration and to enable integration with renewable energy inputs. The work was designed to progress from mechanistic understanding to experimental validation and, finally, to accelerated materials discovery. Specifically, the thesis pursued four coupled objectives: (i) establish first-principles trends for CO₂ binding and charge-mediated tunability on pure metals; (ii) design and calibrate a breakthrough platform capable of isolating illumination effects from purely thermal baselines; (iii) experimentally test whether qualitative computational trends are observable on metallic substrates under controlled dark versus illuminated operation; and (iv) develop and validate a machine-learning surrogate model trained on curated DFT adsorption-energy data, establishing a scalable basis for future alloy screening and prioritization.

Across these objectives, the thesis contributes a coherent, experimentally grounded perspective: illumination can influence CO₂ desorption in measurable ways, but extracting and amplifying that signal in practical systems depends critically on (a) managing thermal fields and photon delivery, (b) scaling interfacial area while controlling surface chemistry, and (c) using computation and machine learning to target material classes where light sensitivity is intrinsically plausible.

7.2 Key scientific findings

7.2.1 Charge-mediated tunability and “photoswitch-like” behaviour from first-principles screening

The DFT investigation established that CO₂ adsorption energetics and adsorption states on metal surfaces can be sensitive to imposed surface charge, providing a mechanistic proxy for photo-induced charge modulation. This supports a design concept in which a surface exhibits strong adsorption under one charge state and facile desorption under another—a “photoswitch-like” criterion that, if realized in engineered materials, could reduce the reliance on large thermal swings for regeneration. For example as mentioned in Chapter 3 metals that give us decent adsorption, as well as desorption efficiency, include Cu (100% adsorption in electron-rich conditions and 50% desorption in electron-deficient conditions), Zn (75% adsorption and desorption in neutral and electron-deficient conditions, respectively), Co_{alpha} and Al_{beta} (50% adsorption and desorption efficiency in neutral and electron-rich conditions, respectively). Beyond simplified descriptors, the results reinforced that adsorption/desorption trends cannot be reliably inferred from a single electronic scalar (e.g., a pristine-surface band-centre) alone when geometric rearrangements and charge redistribution at the interface are significant. Collectively, the computational analysis provided both candidate metals for experimental probing and a conceptual basis for extending to alloying as a means to independently tune adsorption strength, optical/thermal response, and charge-handling properties.

7.2.2 A calibrated photothermal breakthrough platform to separate light effects from thermal baselines

A major experimental contribution of this thesis is the development and commissioning of a light-assisted breakthrough apparatus that integrates controlled CO₂/N₂ delivery, in-line NDIR concentration measurement, distributed thermometry, and an illumination module, together with calibration and uncertainty practices suitable for small effect sizes. The calibration study emphasized that illumination effects cannot be interpreted purely as “light on” versus “light off”: at comparable peak temperatures, the spatial and temporal distribution of heat within the bed strongly governs observed desorption kinetics. Indirect illumination through a solar-selective lid promoted more homogeneous heating and improved desorption yield relative to direct illumination, which produced undesirable axial/radial gradients and observable sample degradation. At comparable operating temperatures, indirect photothermal

regeneration shortened the characteristic desorption time from ≈ 3890 s for purely thermal heating to ≈ 3060 s ($\approx 22\%$ reduction) while increasing the desorbed amount from ≈ 0.23 to ≈ 0.28 mmol g $^{-1}$; direct illumination desorbed a similar amount (≈ 0.28 mmol g $^{-1}$) but required ≈ 6025 s and produced visible discoloration and local degradation of the sorbent. These laboratory-scale results demonstrate that PEI-silica beds can, in principle, be regenerated efficiently using an indirect photothermal configuration. Importantly, the operating temperature window around 110°C and the irradiance levels employed are compatible with renewable heat delivery concepts such as flat-plate solar thermal collectors, supporting a feasible pathway toward low-carbon regeneration in modular systems.

7.2.3 Experimental validation on metallic foams and the role of micro-CT normalization

To connect theoretical slab models with realistic porous substrates, this thesis assessed open-cell Cu, Al, and Ni foams using identical adsorption/desorption protocols under both dark and illuminated conditions, including a blank-bed reference. As foam performance comparisons depend critically on the accessible interfacial area, a micro-CT workflow was developed to quantify the geometric surface area and support area-normalized uptake metrics. For the Cu foam loading, the reconstructed surface-to-volume ratio provided a total geometric area of ≈ 0.215 m 2 , permitting configuration-specific comparisons unattainable from manufacturer specifications.

By integrating the geometric calibration with the measured foam masses, the breakthrough integrals were transformed from CO $_2$ volumes to adsorbed amounts and blank-subtracted to quantify the net contribution of each foam. Upon normalization to geometric surface area, the three metallic foams demonstrated comparable adsorption and desorption capacities per unit area under illuminated conditions, with net uptake and release in the range of ≈ 0.3 - 1.1 mmol m $^{-2}$ for a fixed 110-PPI foam volume. By contrast, purely thermal operation produced a moderate yet reduced area-normalized capacity for Cu, a weaker response for Al, and essentially zero net capacity for Ni after blank subtraction, emphasizing that illumination is essential for reproducible, positive contributions from all three metals.

Analysis on a mass-normalized basis provided a contrasting perspective shaped by differences in density and porosity. While the absolute capacities of the bare foams were merely on the order of 10^{-2} mmol g $^{-1}$, considerably lower than those of advanced porous sorbents, Ni exhibited the highest illuminated uptake per unit mass, followed by Cu and Al, owing to its lower density and greater porosity. Under both normalization schemes, illumination consistently afforded a modest enhancement of adsorption and desorption on the metal

foams, with a concomitant slight decline in blank performance, thereby substantiating that the photoresponse arises from the metallic frameworks rather than a nonspecific chamber artifact. Notwithstanding the small effect sizes on bare foams, their reproducibility and the capacity to distinguish metal- and condition-specific variations affirm the apparatus's sensitivity, enabling pursuit of more advanced hybrid materials in future investigations.

In addition to these photothermal and purely thermal campaigns, preliminary isothermal 25 °C/25 °C runs on Cu foam with an applied DC bias showed that charging the metallic ligaments can nearly double the net CO₂ desorbed per cycle at constant temperature, relative to the unbiased 25 °C/25 °C case. This result reinforces the central premise of this thesis: that the working capacity of metallic frameworks can be modulated not only by macroscopic heat supply, but also by direct control of their surface electronic structure. Viewed alongside the charged-slab DFT results of Chapter 3, the illumination and $\pm$ bias experiments on metallic foams are qualitatively consistent with a charge-sensitive picture of CO₂ binding. Given the rough, (potentially/probably) oxidized surfaces and lack of direct surface-potential measurements, this agreement should be interpreted as suggestive rather than as a quantitative validation of the electronic-structure model, but it does provide an experimental bridge between the Chapter 3 predictions and device-scale behavior.

7.2.4 Machine-learning surrogates for scalable alloy screening and closed-loop discovery

To extend beyond pure metals and enable scalable exploration, the thesis developed a machine-learning surrogate model trained on a curated DFT dataset of site-resolved CO₂ adsorption energies on binary alloy surfaces. Using hybrid descriptors that combine local-structure representations (MBTR with dimensionality reduction) and physics/chemistry features, the study showed that non-linear regressors outperform linear baselines under group-aware validation, and that transformer-based tabular modelling (TabPFN) provides robust accuracy in the small-data regime. Fold-averaged performance reached decision-grade error levels (MAE on the order of a few meV and R^2 exceeding 0.8 for top-performing models), and ensembling further reduced variance and tail error. Conceptually, this establishes a pathway to an active-learning workflow in which ML prioritizes alloy–facet–site combinations for additional DFT or experimental follow-up, thereby accelerating materials triage under the light-assisted regeneration framework built in the earlier chapters.

7.3 Integrated contributions and implications

Taken together, the thesis advances three integrated contributions:

First, it demonstrates a mechanistically informed pathway for light-assisted regeneration rooted in charge-mediated control of CO₂ binding, establishing why certain metals (and by extension alloys) may be more amenable to light/field perturbations than others.

Second, it delivers an experimental platform and data-reduction methodology capable of resolving small, systematic differences between dark and illuminated operation, while explicitly showing that thermal-field management (uniformity, gradients, hotspot avoidance) is a first-order requirement for interpreting illumination effects and for preventing material degradation.

Third, it establishes an acceleration strategy: curated DFT data coupled with group-aware ML can generalize across alloy families and provide practical ranking guidance, enabling a closed-loop vision where computation, experiment, and ML inform one another rather than proceeding as isolated activities.

At an application level, these outcomes reinforce a realistic role for metallic materials in light-assisted capture systems: bare metal foams are not competitive with high-capacity amine sorbents as standalone adsorbents, but they are valuable as electronically conductive and photothermally responsive substrates and as mechanistic testbeds. Area and mass-normalized benchmarking against representative MOFs, zeolites, and porous carbons confirms this interpretation, placing the foams roughly two to three orders of magnitude below state-of-the-art sorbents in equilibrium uptake and per-cycle desorption. Building on the encouraging 25 °C voltage-assisted runs, a natural next step is to systematically map the combined effects of illumination, temperature, and applied bias on CO₂ uptake and release in foams and coated foams, with the goal of designing DAC modules that rely on electronically and photothermally driven desorption rather than large, energy-intensive temperature swings. The most compelling device concept emerging from this thesis is therefore a hybrid architecture in which metallic foams (or structured metals) serve as supports for higher-capacity chemisorptive layers, leveraging the metal's optical/thermal/electronic functionality while the overlayer provides the working capacity.

7.4 Limitations

Several limitations shape the interpretation and motivate the next research steps.

(i) *Environmental realism and chemistry*: many experiments were performed under dry purge conditions and relied primarily on ex-situ diagnostics; humidity effects, amine

chemistry evolution (where relevant), and operando chemical state measurements remain incompletely resolved.

(ii) *Thermal-field and photon-field coupling*: while temperature gradients were quantified and compared across illumination configurations, full through-thickness mapping and direct coupling of photon flux to local reaction kinetics were beyond the scope of the current platform and should be refined for mechanistic attribution.

(iii) *Surface state mismatch between theory and experiment*: DFT models focus on idealized, low-index, atomically clean metal slabs and facets at effectively 0 K, with different adsorption sites, coverage, and controlled charge states, whereas foams present native oxides, roughness, defects, and multi-scale transport phenomena. Moreover, they are probed under finite and nearly uniform temperatures. The real surfaces expose a broad distribution of sites (different facets, grain boundaries, edges, defect sites) rather than a single crystallographic environment, and they inevitably carry impurities such as native oxides, adventitious carbon, trace moisture, and fabrication residues. These differences in temperature, surface cleanliness/impurity content, and site distribution are expected to broaden the underlying spectrum of CO₂ binding energies and to smear out any sharp charge-induced switching behaviour predicted for ideal surfaces; as a result, agreement between Chapter 3 and the foam experiments should be interpreted at the level of qualitative trends rather than quantitative one-to-one correspondence. These differences can obscure fine electronic effects and reduce direct quantitative comparability.

(iv) *ML target scope*: the surrogate models primarily predict adsorption energies under baseline conditions; direct selection for light sensitivity requires extending targets toward charged-slab proxies, work-function shifts, or multi-task descriptors that encode coupled electronic and geometric responses relevant to photo-assisted desorption.

These limitations are not weaknesses of the overall approach; rather, they delineate the boundary between proof-of-principle measurability and the engineering required for scalable, mechanistically attributed, and deployment-relevant light-assisted capture.

7.5 Future directions

Future work should focus on converting the thesis outcomes into a genuinely predictive, closed-loop discovery and validation pipeline and on moving from “detectable illumination effects” to “engineering-relevant performance gains.”

7.5.1 Materials development: from bare foams to functional hybrid architectures

A priority direction is to move beyond bare metallic foams toward hybrid systems that combine (a) the conductivity, photon absorption, and thermal transport of metals with (b) the high capacity of chemisorptive capture layers. Candidate approaches include conformal coatings of amine-rich polymers, inorganic sorbents, or MOF/porous composites on structured metallic supports. Key tasks are to (i) preserve high effective area and mass transfer while adding capacity, (ii) maintain adhesion and stability under cycling, and (iii) select substrate/coating pairs that maximize light-to-regeneration coupling while minimizing hotspot formation and oxidative degradation.

7.5.2 Mechanistic resolution under realistic operating environments

Mechanistic attribution requires combining improved sensing with chemically informative diagnostics. Near-term steps include humidified cycling tests; operando or quasi-operando characterization (e.g., FTIR/XPS where feasible) to track binding states and degradation pathways; and enhanced thermal metrology to resolve through-thickness gradients and local hotspots. Parallel kinetic analysis should parameterize illumination effects in a way that enables cross-platform comparisons, for example by reporting apparent rate constants under fixed optical conditions and/or photon-flux-normalized yields when photon delivery is quantified.

7.5.3 System integration and renewable heat/light delivery

A device-relevant next step is to explicitly link the reactor-scale findings to a solar-thermal or solar-electric regeneration concept. Experiments could emulate realistic solar-collector outlet temperatures and diurnal cycling, quantify energy input on a per-mmol-CO₂ basis, and test control strategies for stable operation under intermittent irradiation. This would connect the apparatus-level conclusions (thermal-field uniformity and irradiation distribution) to a deployable module concept, including modular direct-air-capture units where autonomy and low-carbon regeneration are decisive advantages.

7.5.4 Extending computation and ML toward light sensitivity

On the computational side, future work should extend beyond neutral adsorption energies to descriptors and targets that better encode light/field response: charged-slab calculations,

work-function and surface dipole shifts, and proxies for carrier-mediated interfacial charging. On the ML side, the most impactful steps are: (i) active-learning DFT to fill composition/facet gaps, (ii) multi-task learning to jointly predict energetics and geometric/electronic response indicators (e.g., charge transfer, O–C–O angle change, bond elongations), and (iii) incorporation of experimental priors so that the model learns not only adsorption strength but also which candidates are experimentally realizable and robust. Ultimately, the goal is a closed-loop workflow that iterates between ML ranking, targeted DFT, and benchtop validation, rapidly converging on alloy/coating/substrate systems that show both strong capacity and meaningful light-assisted regeneration gains.

7.5.5 Techno-economic and life-cycle implications

Finally, deployment relevance requires quantifying how illumination-assisted regeneration affects system-level energy intensity, cost, and carbon balance. Future work should therefore integrate experimentally measured regeneration metrics with simplified process models and life-cycle considerations to identify regimes where light-assisted operation provides decisive advantages (e.g., remote modular units, low-grade heat availability, intermittent renewable integration).

7.6 Closing perspective

This thesis demonstrates that light-assisted CO₂ desorption effects can be measured reproducibly in a calibrated breakthrough framework and that their magnitude and interpretation depend strongly on thermal management and material selection. By coupling mechanistic DFT insights, experimental validation on structured metals, micro-CT normalization for fair comparisons, and ML-accelerated alloy screening, the work lays a foundation for a closed-loop discovery paradigm. The most promising pathway forward is not the direct use of bare metals as sorbents, but the deliberate engineering of hybrid materials where metallic substrates provide optical/thermal/electronic functionality while high-capacity capture layers supply the working uptake. With improved mechanistic attribution under realistic environments and ML-guided exploration of alloy/coating architectures, light-assisted regeneration can evolve from a measurable laboratory phenomenon into an engineering strategy for low-carbon, scalable CO₂ capture devices.

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A. Kinetic parameterizations of photodesorption (rate constant vs yield per photon)

Photodesorption can be described kinetically either (i) by an apparent desorption rate constant under a specified illumination condition, or (ii) by an intensity-normalized photodesorption yield per photon. These two descriptions are equivalent once the photon flux at the surface is specified.

A.1 Rate-constant form (time domain)

Let $\Theta(t)$ denote the fractional surface coverage of an adsorbed species. Under steady illumination, a commonly used phenomenological form is first-order in coverage:

$$-\frac{d\Theta}{dt} = k_{photo}\Theta \quad (\text{A.1})$$

where $k_{photo}(s^{-1})$ is an apparent photodesorption rate constant. This parameter is convenient for fitting time-dependent desorption/coverage-decay data acquired under fixed optical conditions.

A.2 Yield-per-photon form (photon-flux normalized)

To express the kinetics in terms of photon delivery, define the photon flux Φ at the sample (photons $\text{cm}^2 \text{s}^{-1}$). The rate constant can be written as:

$$k_{photo} = Y_{\gamma}\Phi, \quad (\text{A.2})$$

so that

$$-\frac{d\Theta}{dt} = Y_\gamma \Phi \Theta \quad (\text{A.3})$$

Here Y_γ is the photodesorption yield per photon. In this formulation, $Y_\gamma \Phi$ is the desorption probability per unit time per adsorbed molecule. Conceptually, Y_γ is an intensity-normalized efficiency parameter that lumps together the probability that an incident photon generates the relevant excitation (e.g., hot carriers or excited adsorbate states) and the probability that this excitation leads to successful escape (desorption) before relaxation.

A.3 Relationship and practical use

The equivalence between the two parameterizations is

$$Y_\gamma = \frac{k_{photo}}{\Phi} \quad (\text{A.4})$$

Thus, k_{photo} is useful for describing a specific experiment (fixed lamp power, spot size, and spectrum), whereas Y_γ is better suited for comparing photodesorption efficiencies across different illumination intensities or optical setups because it explicitly normalizes by photon flux.

B. Python routine for integrating CO₂ breakthrough curves (adsorption/desorption volumes)

B.1 Overview

The CO₂ uptake or release during an adsorption/desorption step can be estimated by integrating the difference between the measured CO₂ concentration signal and an appropriate baseline over a specified time window. If the CO₂ signal is recorded as percent concentration, the integral yields units of (% · s), which can be converted to a volumetric CO₂ quantity (cm³) by multiplying by the total volumetric flow rate.

```

1      import numpy as np
2      import pandas as pd
3      import matplotlib.pyplot as plt
4
5
6      def read_dat_whitespace(file_path: str, ncols: int | None = None)
          ↪ -> pd.DataFrame:
7          """
8          Read a whitespace-delimited .dat file with no header.
9
10         Parameters
11         -----
12         file_path : str
13         Path to the .dat file.
14         ncols : int or None
15         Optional: expected number of columns (for sanity checking).
16

```

```

17     Returns
18     -----
19     df : pandas.DataFrame
20     DataFrame with integer column labels (0, 1, 2, ...).
21     """
22     df = pd.read_csv(file_path, sep=r"\s+", header=None,
23                       ↪ engine="python")
24     if ncols is not None and df.shape[1] != ncols:
25         raise ValueError(f"Expected {ncols} columns, found {df.shape[1]}.")
26     return df
27
28     def add_time_seconds(df: pd.DataFrame, time_col: int, new_col: str
29                       ↪ = "time_s", zero_at_start: bool = True) -> pd.DataFrame:
30         """
31         Create a time (s) column from a chosen time column.
32
33     Parameters
34     -----
35     df : pandas.DataFrame
36     time_col : int
37     Column index containing time values.
38     new_col : str
39     Name of the new time column.
40     zero_at_start : bool
41     If True, subtract the first time value so time starts at 0.
42
43     Returns
44     -----
45     df : pandas.DataFrame
46     Copy of df with an added time column.
47     """
48     out = df.copy()
49     t = out[time_col].astype(float).values
50     if zero_at_start:
51         t = t - t[0]
52     out[new_col] = t
53     return out

```



```

54
55 def integrate_between_curve_and_baseline(
56     t: np.ndarray,
57     y: np.ndarray,
58     t_start: float,
59     t_end: float,
60     baseline: float,
61     mode: str = "absolute",
62 ) -> dict:
63     """
64     Integrate the area between y(t) and a constant baseline over a time
65     ↪ window.
66
67     Parameters
68     -----
69     t, y : np.ndarray
70     Time (s) and signal arrays (e.g., %CO2).
71     t_start, t_end : float
72     Integration window [t_start, t_end].
73     baseline : float
74     Constant baseline line (same units as y).
75     mode : str
76     "absolute" : integrate |y - baseline| (recommended when you want
77     ↪ magnitude)
78     "signed" : integrate (y - baseline) (keeps sign; useful if
79     ↪ baseline is inlet)
80     "above" : integrate only where y > baseline
81     "below" : integrate only where y < baseline
82
83     Returns
84     -----
85     results : dict
86     Contains filtered arrays and computed area in (y-units)*s.
87     """
88     mask = (t >= t_start) & (t <= t_end)
89     t_f = t[mask]
90     y_f = y[mask]
91
92     if len(t_f) < 2:

```

```

90     raise ValueError("Not enough points in the selected time window to
    ↪ integrate.")
91
92     if mode == "absolute":
93         integrand = np.abs(y_f - baseline)
94     elif mode == "signed":
95         integrand = (y_f - baseline)
96     elif mode == "above":
97         integrand = np.where(y_f > baseline, y_f - baseline, 0.0)
98     elif mode == "below":
99         integrand = np.where(y_f < baseline, baseline - y_f, 0.0)
100    else:
101        raise ValueError("mode must be one of: absolute, signed, above,
    ↪ below")
102
103    area = np.trapz(integrand, t_f) # units: (y-units)*s
104
105    return {
106        "t_window": t_f,
107        "y_window": y_f,
108        "integrand": integrand,
109        "area_y_s": area,
110    }
111
112
113    def convert_area_percent_to_volume_cm3(area_percent_s: float,
    ↪ flow_sccm: float) -> float:
114        """
115        Convert integrated area in (%CO2)*s to CO2 volume (cm^3), assuming:
116        - y is in percent (0-100)
117        - flow_sccm is total flow in sccm (cm^3/min)
118
119        Calculation:
120        area_fraction_s = area_percent_s / 100
121        volume_cm3 = area_fraction_s * (flow_sccm / 60)
122
123        Returns
124        -----
125        volume_cm3 : float

```

```

126     Integrated CO2 volume in cm^3.
127     """
128     area_fraction_s = area_percent_s / 100.0
129     return area_fraction_s * (flow_sccm / 60.0)
130
131
132     def plot_window_with_baseline(t_f, y_f, baseline,
133     ↪ title="Integration window"):
134         """Simple visualization of the selected window and baseline."""
135         plt.figure(figsize=(9, 4.5))
136         plt.plot(t_f, y_f, linewidth=1.5, label="CO$_2$ signal")
137         plt.axhline(baseline, linestyle="--", linewidth=1.5,
138         ↪ label=f"Baseline = {baseline:g}")
139         plt.xlabel("Time (s)")
140         plt.ylabel("CO$_2$ (%)")
141         plt.title(title)
142         plt.grid(True, alpha=0.35)
143         plt.legend(frameon=False)
144         plt.tight_layout()
145         plt.show()
146
147     # -----
148     # Example usage (edit inputs)
149     # -----
150     file_path = "combine_data.dat"
151
152     TIME_COL = 0          # column index for time
153     CO2_COL = 5           # column index for %CO2 (your example uses
154     ↪ col 5)
155
156     df = read_dat_whitespace(file_path)
157     df = add_time_seconds(df, time_col=TIME_COL, new_col="time_s",
158     ↪ zero_at_start=True)
159
160     t = df["time_s"].to_numpy()
161     y = df[CO2_COL].to_numpy() # %CO2
162
163     # ---- Example: desorption window ----

```

```

161     t_start, t_end = 12099, 19000
162     baseline = 10.5          # %CO2 baseline (e.g., inlet concentration)
163     flow_sccm = 111         # total flow rate in sccm
164
165     res = integrate_between_curve_and_baseline(
166     t, y, t_start=t_start, t_end=t_end, baseline=baseline,
167         ↪ mode="absolute"
168     )
169
170     area_percent_s = res["area_y_s"]
171     volume_cm3 = convert_area_percent_to_volume_cm3(area_percent_s,
172         ↪ flow_sccm)
173
174     print("=== Integration results ===")
175     print(f"Window: {t_start:g} to {t_end:g} s")
176     print(f"Area: {area_percent_s:.3f} (%CO2)*s")
177     print(f"CO2 volume: {volume_cm3:.3f} cm^3 (using {flow_sccm:g}
178         ↪ sccm)")
179
180     plot_window_with_baseline(res["t_window"], res["y_window"],
181         ↪ baseline,
182     title="CO$_2$ signal with baseline (selected window)")

```

C. CO₂ adsorption-desorption metrics of MOFs, Zeolites, and Carbons

C.1 Overview

The table enumerating working capacities was compiled by assembling experimental CO₂ adsorption capacities and BET surface areas, measured at approximately 298 K and 1 bar, from primary literature and reviews on metal–organic frameworks, zeolites, and porous carbons. Data selection was confined to dry or nearly dry conditions to eliminate biases from competitive water adsorption. For materials where complete adsorption–desorption cycles were explicitly documented (e.g., MUF-16, MIL-101(Cr), and some 13X systems), the desorbed quantity was either directly extracted or inferred from cycling data demonstrating near-quantitative regeneration. Accordingly, the working capacity was computed as the difference $q_{\text{ads}} - q_{\text{des}}(T_{\text{regen}}, 1 \text{ bar})$. For the majority of entries, adsorption isotherms were available only at 298 K and one or more elevated temperatures below 383 K. Consequently, the equilibrium loading at 383 K and 1 bar was estimated by extrapolating the temperature dependence observed in the data, drawing on trends from analogous adsorbents and dual-site Langmuir models where available, yielding an approximate residual loading at the desorption temperature and a corresponding desorbed quantity for a 298 K $\rightarrow$ 383 K TSA cycle. This methodology assumes attainment of equilibrium at both adsorption and desorption temperatures; preservation of structural integrity and pore accessibility across the thermal cycle; ideal-gas behavior of CO₂ as an adsorbate, with monotonic decrease in uptake versus temperature within the studied pressure regime; and, for physisorptive materials featuring reversible isotherms and stable cyclability, effective equivalence between the desorbed quantity, under adequate purge or vacuum conditions, and the equilibrium adsorption capacity, in accord with conventional TSA working-capacity formulations in the literature.

Table C.1 Representative CO₂ sorbents and performance near 298 K and 1 bar.

Class	Material	BET (m ² g ⁻¹)	q_{CO_2} (mmol g ⁻¹) at $\approx 298\text{K}$, 1 bar	q/A ($\mu\text{mol m}^{-2}$)	Desorbed per cycle (mmol g ⁻¹)	Basis/Notes
MOF	Mg– MOF-74 (Mg ₂ (dobdc))	1174	8.61	7.3	8.6	Breakthrough tests show no deterioration in adsorption capacity over 10 cycles and “reversible adsorbent regeneration at $\sim 323\text{ K}$ (He purge)” implying essentially 100% desorption; stable over cycles [9, 152].
MOF	HKUST-1 (CuBTC), pristine	1380	5.00	3.6	5.0	HKUST-1 studies typically show overlapping adsorption-desorption isotherms and stable capacity over several cycles under moderate-T regeneration, so desorbed amount is effectively equal to the adsorbed capacity within a few percent [39].
MOF	UiO-66 powder / UiO-66@PAN10	1130	2.00	1.8	2.0	UiO-66 systems are usually fully regenerable at $\lesssim 150^\circ\text{C}$ with minimal cyclic loss. Desorption curves follow adsorption closely, so working capacity is $\approx$ adsorption capacity under their regeneration protocols [30].
MOF	MIL-88B-type Fe-MOF	400	1.27	3.2	1.27	Adsorption-desorption isotherms at 298 K show good reversibility and negligible capacity loss over multiple cycles; amount desorbed per cycle is essentially equal to the adsorbed loading [156].

(table continues)

(continued)

Class	Material	BET ($\text{m}^2 \text{g}^{-1}$)	q_{CO_2} (mmol g^{-1}) at $\approx 298\text{K}$, 1 bar	q/A ($\mu\text{mol m}^{-2}$)	Desorbed per cycle (mmol g^{-1})	Basis/Notes
MOF	MIL-101(Cr)–polyIL composite	2462	2.76	1.1	2.76	For MIL-101(Cr) itself, regeneration experiments show near-100% desorption at $\sim 328\text{ K}$ (TSA, N_2 purge); PolyIL composites are described as fully regenerable at mild temperatures, so desorbed amount $\approx$ adsorbed capacity [111, 83].
MOF	MUF-16	215	2.13	9.9	2.10	Dynamic capacity maintained over ~ 200 cycles; regeneration at up to 130°C yields essentially full recovery of the 2.13 mmol g^{-1} loading, so desorbed CO_2 per cycle $\approx 2.1 \text{ mmol g}^{-1}$ [105, 104].
Zeolite	13X (generic)	721	5.00	6.9	5.0	Cyclic breakthrough experiments on 13X show average adsorbed CO_2 of 2.87 mmol g^{-1} under specific test conditions with “no loss in capacity after 5 runs”, implying essentially all loaded CO_2 is desorbed each cycle under their activation conditions. For 1 bar, 100% CO_2 , 298 K, full-capacity runs, working capacity is effectively equal to the equilibrium uptake when sufficient high regeneration T or deep vacuum is used [63, 14].

(table continues)

(continued)

Class	Material	BET ($\text{m}^2 \text{g}^{-1}$)	q_{CO_2} (mmol g^{-1}) at $\approx 298\text{K}$, 1 bar	q/A ($\mu\text{mol m}^{-2}$)	Desorbed per cycle (mmol g^{-1})	Basis/Notes
Zeolite	13X-K (from kaolin)	591	6.90	11.7	6.9	Elevated-T purge nearly releases full loading; repeated runs remain stable. So desorbed $\approx$ adsorbed [63].
Porous carbon	Biomass-derived activated carbon	2695	4.24	1.6	4.24	Microporous carbons typically show reversible physisorption; capacity recovered after moderate-T regeneration, indicating that nearly all of the 4.24 mmol g^{-1} is desorbed each cycle under their conditions [40].
Porous carbon	N-doped carbon templated from EMC-2	2850	3.50	1.3	3.50	CO_2 sorption is largely physisorptive; adsorption-desorption branches at 298 K; small cyclic loss. So desorbed amount $\approx$ equilibrium uptake under the reported regeneration temperature [149].