Calcium Looping for Carbon Dioxide and Sulfur Dioxide Co-capture from Sulfurous Flue Gas

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Sally L. Homsy

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The dissertation of Sally L. Homsy is approved by the examination committee.

Committee Chairperson: Prof. Mani Sarathy
Committee Members: Prof. Robert W. Dibble, Prof. William L. Roberts, Prof. Deanna Lacoste, and Prof. Larry Baxter
Global decarbonization requires addressing local challenges and advancing appropriate technologies. In this dissertation, an investigation of appropriate carbon capture technologies for CO$_2$ capture from heavy fuel oil (HFO) fired power plants, common locally, is presented. Two emerging technologies are considered, chemical looping combustion (CLC) and calcium looping (CaL). In a preliminary study, CLC and CaL implementation at an HFO-fired power plant are modeled using Aspen software, and based on the results, CaL is selected for further experimental investigation. Briefly, CaL is a high temperature separation process that utilizes limestone-derived CaO to simultaneously concentrate CO$_2$ and capture SO$_2$ from flue gas. The solid CaO particles are cycled between carbonation and calcination, CaO + CO$_2$ ⇌ CaCO$_3$, in a dual fluidized bed system and experience capture capacity decay with cycling.

Structurally distinct limestones were procured from the two geologic regions where limestone is mined in Saudi Arabia. Using bubbling fluidized bed reactor systems, the capture performance of these two limestones, and a German limestone of known performance, were compared. The combined and individual influence of flue gas H$_2$O and SO$_2$ content, the influence of textural changes caused by sequential calcination/carbonation cycles, and the impact of CaSO$_4$ accumulation on the sorbents’
capture performance were examined. It was discovered that metamorphosed limestone-derived sorbents exhibit atypical capture behavior: flue gas H$_2$O negatively influences CO$_2$ capture performance, while limited sulfation can positively influence CO$_2$ capture. The morphological characteristics influencing sorbent capture behavior were examined using imaging and material characterization tools, and a detailed discussion is presented.

Saudi Arabian limestones’ deactivation rates were examined by thermogravimetric analysis. A quantitative correlation describing sulfation deactivation was developed. The validity of amending the conventional semi-empirical sorbent deactivation model with the novel correlation was supported by subsequent pilot scale (20 kW$_{th}$) experiments. Solving process mass and energy balances, reasonable limits on operating parameters for CaL implementation at HFO-fired power plants were calculated. The influence of power plant configuration, carbonator design, and limestone source on power plant energy efficiency are considered and a discussion is presented. Finally a commentary on the potential of this technology for local implementation and required future work is presented.
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<th>Description</th>
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<tr>
<td>ASU</td>
<td>Air separation unit</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller theory</td>
</tr>
<tr>
<td>BFB</td>
<td>Bubbling fluidized bed</td>
</tr>
<tr>
<td>CaL</td>
<td>Calcium looping</td>
</tr>
<tr>
<td>CC</td>
<td>Combined cycle</td>
</tr>
<tr>
<td>CCRC</td>
<td>KAUST Clean Combustion Research Center</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon capture and sequestration</td>
</tr>
<tr>
<td>CFB</td>
<td>Circulating fluidized bed</td>
</tr>
<tr>
<td>CLC</td>
<td>Chemical looping combustion</td>
</tr>
<tr>
<td>CSP</td>
<td>Concentrated solar power</td>
</tr>
<tr>
<td>DAC</td>
<td>Direct air capture</td>
</tr>
<tr>
<td>DEU</td>
<td>Decentralized Energy Conversion department in the IFK</td>
</tr>
<tr>
<td>DFB</td>
<td>Dual fluidized bed</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>EOR</td>
<td>Enhanced oil recovery</td>
</tr>
<tr>
<td>FGD</td>
<td>Flue gas desulfurization</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>HFO</td>
<td>Heavy fuel oil</td>
</tr>
<tr>
<td>HPST</td>
<td>High-pressure steam turbine</td>
</tr>
<tr>
<td>HRSG</td>
<td>Heat recovery steam generator</td>
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<tr>
<td>IFK</td>
<td>The University of Stuttgart’s Institute of Combustion &amp; Power Plant Technology</td>
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<tr>
<td>IGCC</td>
<td>Integrated gasification combined cycle</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental panel on climate change</td>
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<tr>
<td>IPST</td>
<td>Intermediate pressure steam turbine</td>
</tr>
<tr>
<td>KCC</td>
<td>KAUST Catalysis Center</td>
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<tr>
<td>LLS</td>
<td>Lower loop seal</td>
</tr>
<tr>
<td>LOI</td>
<td>Loss on ignition</td>
</tr>
<tr>
<td>LPST</td>
<td>Low-pressure steam turbine</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
</tr>
<tr>
<td>MeO(_n)</td>
<td>Reduced metal oxide</td>
</tr>
<tr>
<td>MeO(_{n+1})</td>
<td>Oxidized metal oxide</td>
</tr>
<tr>
<td>NGCC</td>
<td>Natural gas combined cycle</td>
</tr>
<tr>
<td>OC</td>
<td>Oxygen carrier</td>
</tr>
<tr>
<td>PC</td>
<td>Pulverized coal</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle size distribution</td>
</tr>
<tr>
<td>SEC</td>
<td>Specific energy consumption</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective catalytic reduction</td>
</tr>
<tr>
<td>STA</td>
<td>Simultaneous thermal analysis</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>---------</td>
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<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
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<tr>
<td>TCES</td>
<td>Thermochemical energy storage</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<tr>
<td>ULS</td>
<td>Upper loop seal</td>
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<tr>
<td>UMIC</td>
<td>United Mining Investments Co.</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<td>XRF</td>
<td>X-ray florescence</td>
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<tr>
<td>$a$</td>
<td>Semi-empirical exponent</td>
</tr>
<tr>
<td>$A$</td>
<td>Deactivation rate correction factor, accounting for sorbent reactivation</td>
</tr>
<tr>
<td>$A^*$</td>
<td>Deactivation rate correction factor, accounting for slow stage sulfation</td>
</tr>
<tr>
<td>$B$</td>
<td>Deactivation rate correction factor, accounting for sorbent sulfation</td>
</tr>
<tr>
<td>$B^*$</td>
<td>Deactivation rate correction factor, accounting for sulfation in the calciner</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Specific heat</td>
</tr>
<tr>
<td>$D$</td>
<td>Particle diameter</td>
</tr>
<tr>
<td>$E$</td>
<td>Capture efficiency</td>
</tr>
<tr>
<td>$\dot{F}$</td>
<td>Molar flow rate</td>
</tr>
<tr>
<td>$H$</td>
<td>Enthalpy</td>
</tr>
<tr>
<td>$H_{comb}$</td>
<td>Power plant’s base energy input</td>
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<tr>
<td>$\Delta H^r$</td>
<td>Standard enthalpy of reaction</td>
</tr>
<tr>
<td>$k$</td>
<td>Deactivation constant</td>
</tr>
<tr>
<td>$k_s$</td>
<td>Surface reaction rate constant</td>
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<tr>
<td>$k_x$</td>
<td>Kinetic constant</td>
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<tr>
<td>$LHV$</td>
<td>Lower heating value</td>
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<tr>
<td>$LR$</td>
<td>Looping ratio</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar mass</td>
</tr>
<tr>
<td>$\dot{m}_f$</td>
<td>HFO mass flow rate</td>
</tr>
<tr>
<td>$MR$</td>
<td>Make up ratio</td>
</tr>
<tr>
<td>$n$</td>
<td>Molar amount</td>
</tr>
<tr>
<td>$N$</td>
<td>Cycle number</td>
</tr>
<tr>
<td>$N_{age}$</td>
<td>Theoretical number of full calcination/carbonation cycles associated with $X_N$</td>
</tr>
<tr>
<td>$N_{eq}$</td>
<td>Equivalent number of full calcination/carbonation cycles</td>
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<tr>
<td>$P$</td>
<td>Pressure</td>
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<tr>
<td>$R$</td>
<td>Gas constant</td>
</tr>
<tr>
<td>$r_{SO_2/CO_2}$</td>
<td>Ratio of SO$_2$ to CO$_2$ [mmol/mol]</td>
</tr>
<tr>
<td>$S$</td>
<td>Surface area</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$V$</td>
<td>Pore volume</td>
</tr>
<tr>
<td>$W$</td>
<td>Work</td>
</tr>
<tr>
<td>$W_{in}$</td>
<td>Work required to power auxiliaries such as pumps</td>
</tr>
<tr>
<td>$W_{out}$</td>
<td>Work generated by gas and steam turbines</td>
</tr>
<tr>
<td>$x$</td>
<td>Mole fraction</td>
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<td>$X$</td>
<td>Conversion</td>
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$X_{\text{max}}$ Maximum achievable CaO conversion to CaCO$_3$ and CaSO$_4$ while maintaining a fast CO$_2$ capture rate

$X_N$ Maximum conversion to CaCO$_3$ at cycle number $N$

$X_r$ Residual sorbent activity

$z_N$ Fraction of particles that have been cycled $N$ times

Greek letters

$\alpha$ Statistical significance level

$\varepsilon$ Porosity

$\eta$ Efficiency

$\rho$ Density

$\tau$ Space time

Subscripts

$\text{act}$ Actual

$\text{ave}$ Average

$c$ Captured

$\text{calc}$ Calcination

$\text{calciner}$ Calciner

$\text{carb}$ Carbonator

$\text{eq}$ Equilibrium

$\text{exp}$ Experimental

$i$ Inert

$j$ Stream number

$m$ On a mass basis

$max$ Relating to the end of the fast CO$_2$ capture stage

$min$ Minimum

$o$ Initial

$r$ Residence

$rel$ Relative

$\text{theo}$ Theoretical
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Chapter 1

Introduction

This chapter: (1) briefly outlines the motivation guiding the doctoral research presented in this dissertation, (2) introduces carbon capture and sequestration (CCS), and (3) clarifies the specific interest in chemical looping combustion and calcium looping carbon capture technologies. Note that CLC and CaL are the focus of the experimental campaigns detailed in subsequent chapters. While subsequent chapters contain more comprehensive literature reviews and specific experimental objectives, Section 1.3 outlines the overarching experimental objects, approaches and recognizes the contributions of colleagues to this research.

1.1 Motivation

Atmospheric CO\(_2\) levels have increased by 46% since the industrial revolution and continue to rise by 2-3 ppm per year [1]. At this rate, the intergovernmental panel on climate change (IPCC) estimates that the remaining carbon budget, or allowable emissions before global warming likely (\(\alpha > 0.66\)) surpasses 1.5 °C, will be exceeded between 2030 and 2052 [2]. Immediate and drastic reductions in CO\(_2\) emissions are required to avoid the negative consequences of global warming, which potentially include: increased extreme weather events, sea level rise, and periods of extreme heat leading to disruptions in critical services and infrastructure, food and water shortages,
increased poverty and displacement of people, damage to ecosystems and loss of biodiversity [2].

IPCC reports suggest that global decarbonization requires investment in a portfolio of technologies, with CCS playing an important role [2,3]. CCS is a group of technologies aimed at capturing \(\text{CO}_2\) from large point sources, such as power plants, and transporting it to suitable long-term storage sites. Depending on the location of the point sources, captured \(\text{CO}_2\) may be: (1) stored in depleted oil and gas fields, saline aquifers, deep un-mineable coal fields and other suitable geological formations, or (2) injected in oil wells or coal beds for enhanced oil recovery (EOR) or enhanced coal bed methane recovery, respectively [4]. One major advantage of CCS is that this technology addresses the decarbonization of intrinsically polluting industrial processes, such as cement and steel production.

Without CCS implementation at industrial plants, counteracting the volume of \(\text{CO}_2\) emissions generated by the industrial sector would require atmospheric \(\text{CO}_2\) reduction by direct air capture (DAC). Other approaches to atmospheric \(\text{CO}_2\) reduction, such as reforestation and enhanced weathering are limited by the availability of arable land, biomass growth rates, and natural weathering rates [5]. DAC, however, is a controversial technology in part due to the high energy requirement and cost associated with concentrating \(\text{CO}_2\) from atmospheric levels (415 ppm) to concentrations relevant for sequestration (> 95.5%). A quick calculation of the minimum work required for concentrating \(\text{CO}_2\) reveals that at least 4x more energy is required to concentrate the same amount of \(\text{CO}_2\) from air vs. from cement plant flue gas (~25% \(\text{CO}_2\)) (see Figure
1.1). Note that minimum work, $W_{\text{min}}$, is calculated assuming a reversible, isothermal, isobaric change such that $W_{\text{min}}$ is a function of the entropy change due to the concentration change [6]:

$$W_{\text{min}} = -RT \sum x_j \ln x_j$$  \hspace{1cm} (1.1)

**Figure 1.1.** Minimum work required for concentrating CO$_2$ to 95.5%.

Consulting empirical data from real-world industrial separation processes, a relationship between second law efficiency ($W_{\text{min}}/W_{\text{act}}$) and the separation process feed-stream concentration is revealed (see Figure 1.2) [6]. This relationship results from process cost optimization; while operating costs typically decrease with increasing $W_{\text{min}}/W_{\text{act}}$, capital costs increase with both increasing $W_{\text{min}}/W_{\text{act}}$ and decreasing feed stream concentration. Accounting for the second law efficiencies, CCS from cement plant flue gas is about 20x more efficient than subsequent DAC. Furthermore, Sherwood
*et al.* demonstrated that separation costs scale with feed-stream concentration, and capturing CO$_2$ by DAC is estimated to cost 20x more than capturing CO$_2$ by CCS integration at a concentrated point source [6].

**Figure 1.2.** Relationship between second law efficiency and separation process feed-stream concentration. Adapted from [6,7].

The second major advantage of CCS implementation is that this technology can reduce the financial burden of global decarbonization. In addition to allowing relatively low cost industrial decarbonization, CCS can reduce the cost of power sector decarbonization. The power sector is the primary driver of anthropogenic greenhouse gas emissions, and transitioning to renewable energy sources requires a substantial change in infrastructure [3]. The installation of add-on CCS systems at power plants allows decarbonization with minimal disruption to current energy systems, and
therefore the avoidance of stranded assets. More than 50% of hypothetical pathways to decarbonization published in the IPCC’s 5th Assessment Report require CCS to maintain warming levels within 2°C, and the pathways that do not include CCS are estimated to cost ~ 40% more to achieve the same level of emissions reductions [3]. In summary, CCS technologies are required for cost and energy efficient industrial sector decarbonization, and they provide a means for cost effectively reducing CO₂ emissions from the electricity generation sector, bridging the gap while the world transitions to cleaner renewable energy.

This research’s overarching objective is to study carbon capture implementation at heavy fuel oil-fired power plants in Saudi Arabia. Heavy fuel oil (HFO) is a low cost sulfurous residual petroleum distillation byproduct representing 2-5% of the world’s refinery yield. While typically used in marine fuels, HFO is also regionally fired in boilers for electricity production. Currently, about 58% of Saudi Arabia’s power plants are powered by liquid fuels, including HFO, crude oil and diesel fuel, with financial incentives favoring increased reliance on HFO [8]. Saudi Arabia is a Paris Agreement signatory, with very ambitious emissions reduction goals. Developing CCS technologies for implementation at HFO-fired power plants contributes to the global decarbonization objective and facilitates meeting emissions reduction goals cost effectively. While numerous studies have been published on the implementation of CCS at gas- and coal-fired power plants, the literature on CCS implementation at HFO-fired power plants is scarce.
1.2 CCS Background

Power plant carbon capture technologies can be divided into three main classes: post-combustion, oxy-combustion and pre-combustion. Of these, the simplest form is post-combustion. In this scenario, CO₂ is captured from the flue stream of a conventional power plant, often by means of a physical or chemical solvent or solid sorbent. The current leading post-combustion CO₂ capture technology involves using amine-based chemical solvents such as monoethanolamine (MEA). Amine-based solvents have been used for acid gas (CO₂ and H₂S) removal from natural gas streams for over 60 years [4]. Although this established technology is available for implementation, amine-based CO₂ capture may not be ideal for CO₂ capture from HFO-fired power plants due to the high SO₂ content in HFO flue gas (~ 2000 ppm SO₂). Amine sorbents experience degradation upon exposure to SO₂, and are highly sensitive to even minute amounts of SO₂. A techno-economic assessment performed by Rao et al. recommends flue gas desulfurization (FGD) with 99% SO₂ removal efficiency prior to CO₂ capture by amine scrubbing [9]. Note that while SO₂ is an increasingly regulated pollutant, 99% SO₂ removal overshoots emission standards, with the EUs latest emissions standards requiring ≤ 97% SO₂ emissions reductions [10].

In general, post-combustion CO₂ capture requires treating a high volume of gas with typically low (< 15%) CO₂ concentration. HFO-flue gas is generally about 11-13% CO₂, 2000 ppm SO₂, 2-3% O₂, 10-15% H₂O and the balance N₂. As the minimum work requirement for CO₂ capture is tied to the CO₂ concentration, the concentration of CO₂
in the flue gas constrains the process energy efficiency. Furthermore, an average 550 MW HFO-fired power plant generates flue gas at a rate of about 670 m$^3$/s. The large volumes of gas requiring treatment typically translate to a relatively large post-combustion carbon capture plant land footprint. The second class of carbon capture technologies, oxy-combustion, sidesteps CO$_2$ dilution in nitrogen by separating oxygen from air prior to combustion.

During oxy-combustion, fuel is burned with purified oxygen diluted in recycled process flue gas. The resulting flue stream is therefore mainly composed of CO$_2$ and steam. The CO$_2$ is relatively easily isolated from the steam by cooling the flue stream. Oxygen separation from air is generally achieved by means of cryogenic air separation units (ASU), an established technology. However, the capital cost and energy consumption of ASUs capable of producing sufficient oxygen to sustain power plant operations is a concern.

Pre-combustion CO$_2$ capture is suitable for implementation at integrated gasification combined cycle (IGCC) power plants. Like oxy-combustion, pre-combustion CO$_2$ capture necessitates oxygen separation from air, however it requires relatively less pure oxygen and therefore reduces the burden on ASU. During pre-combustion, fuel is first gasified in the presence of steam and sub-stoichiometric oxygen. The resulting syngas is then processed in a water-gas shift reactor to convert the CO to CO$_2$ while producing additional H$_2$. Physical or chemical solvents or solid adsorbents can then separate the CO$_2$ from the H$_2$, and finally the H$_2$ is combusted in air.
Two emerging CCS technologies are the focus of this study: (1) chemical looping combustion (CLC), a CO₂ capture technology that is analogous to oxy-combustion and, (2) calcium looping (CaL), a post-combustion CO₂ capture technology. These technologies were selected because they offer unique advantages when implemented at HFO-fired power plants. Both CLC and CaL are high-temperature separation processes that employ solid sorbents. Typically, the solid sorbents are cycled between sorption and regeneration steps by cycling the sorbents between two interconnected fluidized beds, referred to as dual fluidized bed (DFB) systems (see Figure 1.3) [11,12]. The high temperature nature of CaL and CLC allows high-grade heat recovery downstream of the sorption and regeneration steps and the possibility of auxiliary power generation by a Brayton (would require pressurization) and/or Rankine cycle. The additional power
generation can lead to improved process energy efficiency when compared to first
generation capture technologies such as amine scrubbing [13].

Furthermore, both CaL and CLC systems have high energy density
thermochemical energy storage (TCES) potential. The high working temperatures, high
thermal conductivity, and easy storage associated with CaL and CLC sorbents have
fueled previous studies into using these sorbents as an alternative to molten salts for
concentrated solar power energy storage [14–16]. The TCES potential of CaL and CLC
systems integrated at power plants permit temporal uncoupling of the sorption and
regeneration steps and therefore uninterrupted CCS regardless of the flexible operation
of the power plant. TCES integration with CaL and CLC may also have economic benefits
when implemented at a flexibly operated power plant; a recent study by Criado et al.
demonstrated that implementing CaL sorbent based TCES at a flexibly operated power
plant with integrated CaL reduces the financial penalty associated with operating a CaL
system at reduced plant capacity [17].

1.2.1 Chemical Looping Combustion

Chemical looping combustion (CLC) is an advanced carbon capture technology
that is analogous to oxy-fuel combustion but eliminates the need for ASUs and instead
makes use of an oxygen carrier (OC) to avoid direct contact between fuel and air during
combustion. This process divides the fuel combustion process into two distinct oxidation
and reduction stages and intrinsically eliminates the dilution of the combustion product
gases in air (see Figure 1.4). Briefly, the OC, generally a metal or reduced metal oxide, MeO\textsubscript{n}, is first oxidized in air in the first fluidized bed reactor, the air-side reactor:

\[
\text{MeO}_n(s) + \text{air} \rightarrow \text{MeO}_{n+1}(s) + \text{hypoxic air} \quad (1.2)
\]

The oxidized carrier, MeO\textsubscript{n+1}, subsequently oxidizes the fuel, leading to OC reduction and the production of a concentrated CO\textsubscript{2} stream in the fuel-side reactor:

\[
\text{MeO}_{n+1}(s) + \text{Fuel} \rightarrow \text{MeO}_n(s) + \text{H}_2\text{O}(g) + \text{CO}_2(g) \quad (1.3)
\]

The reduced OC then re-oxidizes in air and the process repeats. SO\textsubscript{2} emitted during HFO combustion must be captured in a separate step. OC oxidation is highly exothermic, whereas OC reduction is mildly exothermic to endothermic [18]. Therefore, the majority of the energy is produced during OC oxidation and not fuel oxidation. For efficient operation, typically the oxidation and reduction steps are performed at the same temperature, with operating temperatures ranging from 800 -1200°C [19].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{CLC_process_diagram}
\caption{Simplified block diagram of the CLC process.}
\end{figure}
The main advantage of CLC is that this process allows the incorporation of an air turbine for energy recuperation downstream of the air-side reactor. Typically, HFO-fired power plants only employ a Rankine cycle for power generation, with HFO-fired in a boiler. Deployment of a more efficient combined cycle at HFO-fired power plants is not advisable due to the high level of impurities in HFO; gas turbine operational life span is reduced by a factor of 3-4 by exposure to HFO flue gas. CLC can therefore potentially increase HFO power plant efficiency, while capturing CO₂, through the introduction of an added Brayton cycle.

1.2.2 Calcium Looping

CaL is an advanced post-combustion CO₂ capture technology that utilizes calcium oxide as a CO₂ sorbent. CaL cycles between two main steps, calcium oxide carbonation and calcium carbonate calcination (see Figure 1.5):

$$\text{CaO}(s) + \text{CO}_2(g) \rightleftharpoons \text{CaCO}_3(s) \quad \Delta H_f^o = -178 \text{ kJ/mol}$$ (1.4)

![Figure 1.5. Simplified block diagram of the CaL process.](image-url)
Flue gas CO₂ is captured by exothermic carbonation (Eq. 1.4: forward reaction) in the first fluidized bed reactor, the carbonator. The resulting CaCO₃ is transferred to the second fluidized bed reactor, the calciner, where the CaO is regenerated and a highly enriched CO₂ gas stream is produced by endothermic calcination (Eq. 1.4: reverse reaction). Calcination energy often comes from in situ oxy-combustion, which leads to a high CO₂ partial pressure in the calciner and shifts the thermodynamic equilibrium, discouraging calcination [13,20]. Calcination temperatures > 900 °C are therefore required for efficient and fast sorbent regeneration [21]. Carbonation is performed at 650 °C to limit equilibrium constraints on efficient CO₂ capture while maintaining a fast carbonation rate [22]. The high-temperature nature of CaL allows heat recovery downstream of the calciner and carbonator and auxiliary power generation by a Rankine cycle. A Brayton cycle is not advisable since HFO impurities are present in both the calciner and carbonator gas effluent streams.

The CaO sorbent is typically derived from limestone, a widely available low cost natural CaCO₃ source. As the limestone is exposed to calcination/carbonation cycles, its CO₂ capture capacity, or “activity”, decays due to sintering, attrition and exposure to deactivating flue gas constituents [23,24]. Accordingly, a limestone make up feed and corresponding purge stream are introduced.

A major advantage of CaL is that this process can simultaneously concentrate CO₂ and capture SO₂. At typical carbonator and calciner operating temperatures, sorbent sulfation occurs [25]:
\[ \text{CaO}(s) + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CaSO}_4(s) \quad \Delta H_r^0 = -502 \text{ kJ/mol} \quad (1.5) \]

\[ \text{CaCO}_3(s) + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CaSO}_4(s) + \text{CO}_2(g) \quad \Delta H_r^0 = -324 \text{ kJ/mol} \quad (1.6) \]

Note that under conditions where the CO\textsubscript{2} concentration is greater than the equilibrium CO\textsubscript{2} concentration, direct sulfation (Eq. 1.6) is the favored pathway, and alternately indirect sulfation is favored (Eq. 1.5) [26]. Since temperatures exceeding 1,300°C are required to regenerate CaO from CaSO\textsubscript{4} (gypsum), typically the CaSO\textsubscript{4} is eliminated through the purge stream.

### 1.3 Objectives and Experimental Outline

The overarching objective of this work is the selection and the advancement of an appropriate CCS technology for implementation at HFO-fired power plants. More specifically, this objective is achieved by completing the following tasks:

1. The implementation of CaL and CLC at HFO-fired power plants is modeled using Aspen software. A preliminary parametric study is performed, and based on the results of this study CaL is selected for further investigation.

2. The capture performances of structurally distinct limestones, procured from the two geologic regions where limestone is mined in Saudi Arabia, are compared against the performance of a previously characterized German limestone. Using thermogravimetric analysis and bubbling fluidized bed reactor systems, the influence of the following factors on CO\textsubscript{2} capture behavior are investigated:
2.1 The combined and individual influence of HFO flue gas H\textsubscript{2}O and SO\textsubscript{2} content.

2.2 The influence of textural changes caused by sequential calcination/carbonation cycles.

2.3 The influence of CaSO\textsubscript{4} accumulation.

Through this process, it is discovered that metamorphosed limestone-derived sorbents exhibit atypical capture behavior: flue gas H\textsubscript{2}O negatively influences CO\textsubscript{2} capture performance, while limited sulfation can positively influence CO\textsubscript{2} capture. This unusual capture behavior has not been previously reported in literature. The morphological characteristics underlying this capture behavior are examined using multiple imaging and material characterization tools, including Hg porosimetry, N\textsubscript{2} adsorption, X-ray florescence, scanning electron microscopy, energy-dispersive X-ray spectroscopy. A detailed discussion, that has implications for future sorbent selection and design efforts, is presented.

3. Saudi Arabian limestone-derived sorbent deactivation rates are examined by thermogravimetric analysis. A semi-empirical deactivation model accounting for sorbent sulfation and reactivation is developed, with a novel quantitative correlation describing the influence of sulfation deactivation on the overall deactivation rate introduced. Moreover, a simple three-step thermogravimetric method for characterizing sulfation deactivation by different limestones is presented. The validity of the proposed semi-empirical deactivation model is supported by subsequent pilot scale (20 kW\textsubscript{th}) experiments.
4. Process mass and energy balances are solved, and reasonable limits on operating parameters for CaL implementation at heavy fuel oil-fired power plants are calculated. Implications for plant configuration, carbonator reactor design, and limestone source selection are discussed. A commentary on the potential of this technology for local implementation and required future work is presented.

The research reported in this dissertation was completed under the guidance of Prof. Robert Dibble and Prof. William Roberts. Experimental work was performed at the University of Stuttgart’s Institute of Combustion and Power Plant Technology (IFK) facilities, at KAUST Core Labs, and in the KAUST Catalysis Center (KCC) labs. IFK provided access to a custom thermogravimetric analyzer, a 7 kW$_{th}$ bubbling fluidized bed system, and a 20 kW$_{th}$ DFB system. IFK’s Dr. Reinhold Spörl, Joseba Moreno, and Max Schmid provided invaluable insight that helped guide planning and design of experiments performed using IFK’s equipment. Joseba Moreno and Tim Seitz provided training and technical assistance as needed with IFK’s equipment. Moreover, Joseba Moreno performed a number of the experimental sets that were completed using the 7 kW$_{th}$ bubbling fluidized bed system (reported in Chapter 3). KAUST Core Labs provided access to equipment for material imaging and characterization, and Core Labs personnel provided equipment training. KCC’s Dr. Alla Dikhtiarenko performed X-ray diffraction analysis on sorbents and limestone samples and interpreted the results. Her findings and expertise helped guide the reported insight into the influence of sorbent structure on sorbent capture behavior. KAUST Catalysis Center’s Dr. Selvedin Telalovic provided training on and access to a thermogravimetric analyzer equipped with effluent gas
analysis by Fourier-transform infrared spectroscopy (FTIR). The experimental work reported in Chapter 3 has been reviewed by Joseba Moreno, Dr. Alla Dikhtiarenko and Prof. Jorge Gascon and is published in ACS Omega, DOI: /10.1021/acsomega.0c04157.
Chapter 2

Preliminary ASPEN Study: CaL vs. CLC

2.1 Introduction

Previous techno-economic studies performed on CaL and CLC systems have focused on implementation at coal- and gas-fired power plants. Nevertheless, both CLC and CaL appear promising for implementation at HFO-fired power plants. In this chapter, the technological progression of CLC and CaL are outlined, and current technological bottlenecks are highlighted. Aspen software is used to perform a preliminary analysis comparing CLC and CaL implementation at HFO-fired power plants. A discussion of the results is presented, concluding with the selection of CaL for further examination.

2.1.1 Chemical Looping Combustion

Techno-economic studies on CO₂ capture by CLC predict that CLC can be: (1) economically competitive with established and emerging CCS technologies, and (2) operated with a limited energy penalty [27]. The economic advantage of using CLC is expected for both coal and natural gas fired power plants, with predictions calculated through numerous approaches. Studies using contingency factors, probabilistic variables, and expert elicitations consistently predict that the cost of CO₂ avoided through CLC will be lower than the cost of CO₂ avoided using other emerging and
established CCS technologies, with reference plant electricity generation costs impacted less by CLC relative to other technologies [28–33]. CLC’s cost benefit can be attributed to the process’ relatively low parasitic load and low exergy destruction. For this same reason, the energy penalty due to CO₂ capture by CLC, is lower than that expected by other carbon capture technologies, emerging and established [29,30,34,35]. However risk assessment studies indicate that there is still uncertainty regarding the feasibility of CLC, as this is a relatively new technology [31,32].

The concept of CLC was introduced by Lewis and Gilliland in 1950 as a method for pure CO₂ production, and in 1994, Ishida and Jin proposed using CLC as a carbon capture technology [36,37]. In 2005, CLC was first demonstrated in a 10 kWth system; the CLC plant was operated continuously for 100 hours, with a fuel conversion efficiency of 99.5% and no signs of damage to the OCs or any decline in OC reactivity [38]. Since then, this technology has been demonstrated at numerous small pilot plants (< 150 kWth). The promising cost and process efficiency estimates are contingent on successfully scaling up CLC technology, and on successful technological advancements. Specifically, a proof of concept that CLC can be operated at scale and at pressure is required.

CLC operation at pressure is of interest because the promising cost and process efficiency estimates are based on models that assume CLC integration with a combined cycle (CC-CLC) for power generation. In this scenario, a combination of gas turbines, heat recovery steam generators (HRSGs), and steam turbines are used to optimize energy production by exploiting both the Brayton and Rankine cycles. Basic diagrams of
a Brayton, Rankine and combined cycle (CC) are shown in Figure 2.1. Power plants using state-of-the-art combined cycle technology are capable of electrical efficiencies of around 55-65%, while power plants relying solely on boilers and the Rankine cycle typically achieve electrical efficiencies of around 35-45% [39]. Due to the greater electrical efficiency tied to CC power plants, CC-CLC is preferred, but would require CLC operation at pressure.

![Simplified diagram of basic power cycles](image)

**Figure 2.1.** Simplified diagram of basic power cycles.
Due to the high level of impurities in HFO, which can reduce a gas turbine’s operational life span by a factor of 3-4, conventional HFO-fired power plants generate power using a Rankine cycle. However, since CLC separates the heat generating step from the fuel combustion step, an air turbine can be introduced downstream of the air-side reactor, allowing the use of a Brayton cycle and therefore CLC can potentially increase HFO power plant efficiency.

2.1.2 Calcium Looping

A major advantage of calcium looping is its propensity for synergy with numerous industrial processes, specifically when limestone-derived CaO is used as the sorbent. Limestone is a widely available natural CaCO3 source used in cement production, steel manufacturing, and flue gas desulfurization. Using the spent limestone-derived sorbent (largely CaO), post-CaL, as feedstock in industries such as cement production reduces the calcination energy burden on these industrial processes, and increases the overall energy efficiency of CaL [40]. The opportunity for synergy with industrial processes, coupled with the low cost of limestone, contribute to the economic viability of CaL, with competitive capture costs estimated by multiple techno-economic studies [4,40,41]. Additionally, unlike CLC, CaL is a post-combustion, or add-on CCS technology. CaL implementation at operational power plants reduces the overall economic penalty of decarbonization by avoiding stranded asset.

CaL, like CLC, allows high-grade heat recuperation downstream of the DFB system, and possible auxiliary power generation. This additional power generation can
lead to improved process energy efficiency when compared to first generation capture
technologies such as amine scrubbing [42–44]. However, it is recommended that
auxiliary power is generated by means of a Rankine cycle; implementing a Brayton cycle
is not advisable since HFO impurities are present in both the calciner and carbonator gas
effluent streams. Therefore, CC-CaL is not feasible. It should be noted that sulfur is the
primary impurity present in HFO, producing SO$_2$ upon combustion. The SO$_2$ and CO$_2$
capture potential of CaL can eliminate the need for a standalone FGD, and can
potentially reduce the overall cost and efficiency penalty of CaL.

Note that CaL technological development has progressed beyond that of CLC and
has been demonstrated at three pilot plants ($\geq 1$ MW$_{th}$), achieving a technology
readiness level of 6 [13,45–47]. CaL proof of concept has been demonstrated under
relevant conditions at pilot scale, with the current primary technological concern
relating to CaO sorbent performance and deactivation with cycling [4].

In this preliminary study, commercial process simulation software is used to
simulate HFO-fired power plants incorporating CaL and CLC. Various configurations are
considered, and a parametric study is performed on the optimal plant configuration.
How plant efficiency is impacted by CaL and CLC implementation at HFO-fired power
plants is examined, and a discussion is presented.

2.2 Power Plant Simulation

Aspen Plus® and Aspen Hysys® were used to simulate an HFO-fired power plant
incorporating CaL and CLC. Aspen Plus® and Aspen Hysys® are process simulation
software packages that predict the performance of a user specified process by iteratively solving mathematical models. The process flow diagram is constructed by the user, and appropriate thermodynamic models selected. In this study, the Peng Robinson cubic equation of state with the Boston-Mathias alpha function was used to calculate most thermodynamic properties, and the 1995 IAPWS steam table correlations were used to calculate the thermodynamic properties of water. A surrogate molecule developed by Abdul Jameel et al. was used to represent HFO in the Aspen simulations [48]. Physical properties of interest estimated from the surrogate molecule’s structure were found to align reasonably well with available experimental data on bulk HFO properties. This surrogate molecule was added to the Aspen simulation via the User Defined Component Wizard. The surrogate’s lower heating value (LHV) was specified and its remaining physical properties were estimated from the molecule’s structure through the Aspen Property Estimation System.

A conventional HFO-fired power plant incorporating a double reheat steam cycle was modelled as the reference plant. An excess air ratio of 1.15 was selected. The reference plant did not incorporate any mode of CCS or SO₂ capture. Simulation specifics, valid for the reference plant and the HFO-fired power plants incorporating CLC and CaL, are presented in Table 2.1. For the HFO-fired power plants incorporating CLC and CaL, multistage CO₂ compression to 200 bars (compression ratio ~ 2) was simulated. Note that a quick estimate reveals that injection into Saudi Arabia’s Ghawar Field (1.8-2.2 km below sea level) requires CO₂ pressurization to ~ 200 bar [49]. Process efficiency was calculated using the following formula:
where $W_{out}$ is the thermodynamic work of gas and steam turbines, $0.97$ is the turbine to grid efficiency, $W_{in}$ is the work required to power all plant auxiliaries such as pumps, and the denominator is the product of the HFO mass flow rate and lower heating value.

Relative plant efficiency is defined as the ratio of the CaL or CLC plant efficiency to the reference plant efficiency.

### Table 2.1. Aspen simulation specifics

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2.2.1 CLC Simulation Specifics

The HFO-fired power plant incorporating CLC comprises five main building blocks: (1) CLC reactor system, (2) air turbine, (3) desulfurization system, (4) Rankine cycle, and (5) CO₂ dewatering and compression. Different power plant configurations were considered, and the configuration with the highest energy efficiency is presented in Figure 2.2. An air turbine is used to generate power from the air-side reactor effluent gas stream, with excess heat recouped for inlet line heating. The fuel-side exhaust stream is fed into a third fluidized bed where it is desulfurized by direct sulfation of limestone (see Eq. 1.6). A double reheat Rankine cycle is used to generate power from
the fuel-side exhaust stream post-desulfurization. Complete conversion of HFO in the fuel-side reactor, and complete OC conversion in the air-side reactor are assumed. Two OC systems were considered, Fe$_2$O$_3$/Fe$_3$O$_4$ and Mn$_3$O$_4$/MnO, temperature was varied from 800-1200 °C, and pressure was varied between 1 and 30 bars. Note that operating temperature was controlled by varying OC and air flow rates.

2.2.2 CaL Simulation Specifics

![Simplified schematic diagram of the HFO-fired power plant incorporating CaL.](image)

**Figure 2.3.** Simplified schematic diagram of the HFO-fired power plant incorporating CaL.

The HFO-fired power plant incorporating CaL comprises the following five main building blocks: (1) boiler, (2) CaL reactor system, (3) Rankine cycle, (3) ASU, and (5) CO$_2$
dewatering and compression. Different power plant configurations were considered, and a simplified schematic of the configuration with the highest energy efficiency is presented in Figure 2.3. Double reheat steam cycles were employed to recover heat as energy from three locations in the process: (1) the HFO-boiler, (2) the CO$_2$-depleted flue stream and (3) the CO$_2$-rich flue stream. Note that the air separation unit (ASU) was not modelled in this study; industry reported values for ASU specific energy consumption (SEC) were used to calculate the ASU energy penalty instead. Two ASU SEC values representing high and low process efficiencies were selected and these values are reported in Table 2.1 [50,51]. The carbonator temperature was held at 650 °C, and the calciner temperature at 950 °C. Equilibrium sorbent conversions in the calciner and carbonator were assumed, and a 4:1 mol:mol ratio of sorbent to CO$_2$ was maintained. The sorbent make up ratio, $MR$, and carbonator pressure were varied from 0.05-1.00 and 1-8 bars, respectively, and to maintain the process heat balance, the boiler-fired HFO to calciner-fired HFO was varied between a ratio of 2:1 to 1:1.

2.3 Results and Discussion

2.3.1 CLC Simulation Results

Figure 2.4 shows the influence of operating pressure on the energy efficiency of an HFO-fired power plant incorporating CLC. At pressures > 1 bar, incorporating an air turbine for power generation is possible, and an increase in relative plant efficiency is observed. The optimal operating pressure is found to be in the range of 10-20 bars.
Note that the CLC system's relative efficiency is poor when the system is operated at 1 bar.

Figure 2.4. The influence of operating pressure on the energy efficiency of an HFO-fired power plant incorporating CLC. Representative curve conditions: Fe$_2$O$_3$/Fe$_3$O$_4$ oxygen carrier at 1000 °C.

The influence of operating temperature on the energy efficiency of an HFO-fired power plant incorporating CLC is shown in Figure 2.5. Process relative efficiency increases with increasing temperatures, as increasing the operating temperature enhances power generation by both the Brayton and Rankine cycles. Ultimately the operating temperature is constrained by the maximum material/equipment temperature ratings and OC properties. Figure 2.5 also shows the influence of different OCs. Note that the selected OC systems are somewhat resistant to sulfation.
deactivation [11]. Optimistically assuming complete conversion of HFO during the reduction stage and complete oxidation of the OC by air, the use of a Mn₃O₄/MnO OC system can theoretically allow the energy efficiency of an HFO-fired power plant incorporating CLC to surpass reference plant efficiency, even after CO₂ pressurization to 200 bars. Note that the efficiencies that were deduced using the Aspen simulation for an HFO-fired power plant incorporating CLC are in line with those previously reported for a coal-fired power plant incorporating CLC [39]. The additional Brayton cycle, which is not included in the traditional HFO-fired power plant, is responsible for the bump in energy efficiency demonstrated by incorporating CLC at the HFO-fired power plant. It should be noted that the model used makes many simplifying and optimistic assumptions.

Figure 2.5. The influence of operating temperature on the energy efficiency of an HFO-fired power plant incorporating CLC. System pressure = 20 bars.
The simulated HFO-fired power plant incorporating CLC is theoretically capable of achieving ~ 100% CO₂ capture efficiency, ~ 99% SO₂ capture efficiency, and CO₂ compression to 200 bar while surpassing conventional HFO-fired power plant efficiency. Promising CLC performance is predicated on operation at 10-20 bar, 1200°C, and selection of an appropriate OC that is resistant to sintering, attrition, and deactivation by HFO impurities. Dual fluidized bed operation at raised pressure has yet to be demonstrated and therefore advancements in reactor design are required. The feasibility of high efficiency CLC also requires OC screening studies as reactivity and kinetic data on HFO oxidation by OCs is very limited.

2.3.2 CaL Simulation Results

Figure 2.6 shows the energy penalty associated with varying the sorbent make up ratio in an HFO-fired power plant incorporating CaL. Sorbent make up ratio, $M_R$, is defined as the ratio of the fresh limestone feed rate to the carbonator CO₂ feed rate. Note that the fresh limestone feed rate is equivalent to the sorbent purge rate. As expected, plant efficiency decreases with increasing sorbent purge fraction due to the additional energy requirement associated with heating the make up limestone from ambient temperature to process temperatures and calcining the make up limestone.

The energy penalty associated with changes in $M_R$ likely lies between the two curves plotted in Figure 2.6. An ASU SEC of 460 kWh/tO₂ is the energy penalty reported for 1st generation ASUs and an ASU SEC of 160 kWh/tO₂ is reported as the energy penalty associated with state-of-the-art systems [50,52]. Using a state-of-the-art ASU,
CaL remains competitive with amine-based carbon capture systems when an $MR$ of up to 0.6 is used. While it seems optimistic, previous studies modeling coal-fired power plants have reported that an $MR < 0.05$ is feasible even after accounting for sulfation deactivation [53]. Since limestone deactivation with calcination/carbonation cycles and exposure to HFO impurities is a primary technological concern for CaL, the limited energy penalty with increasing $MR$ is encouraging.

**Figure 2.6.** The influence of sorbent purge fraction on the energy efficiency of an HFO-fired power plant incorporating CaL. System pressure = 1 bar.

The influence of pressure on CO$_2$ capture efficiency and CaL system energy penalty is presented in Figure 2.7. Note that the CO$_2$ capture efficiency in the carbonator is thermodynamically limited. The equilibrium partial pressure of CO$_2$ in a system containing CaO can be calculated from [54]:

$$
\text{Equilibrium partial pressure of CO}_2\text{ in CaO system} = \ldots
$$
\[ \log P = 7.079 - \frac{38000}{4.574 T} \]  

(2.2)

where \( P \) is in atm and \( T \) is in K. For simulations run at ambient pressure only \( \sim 91\% \) of the \( \text{CO}_2 \) entering the carbonator can be captured. Since total \( \text{CO}_2 \) from oxy-combustion is captured, \( \sim 95\% \) combined \( \text{CO}_2 \) capture efficiency is achievable through CaL at ambient pressure. Increasing carbonator operating pressure improves \( \text{CO}_2 \) capture efficiency. However, increasing the carbonator pressure increases the energy efficiency penalty. Note that increasing calciner pressure negatively impacts CaO regeneration and should be avoided.

**Figure 2.7.** The influence of pressure on CaL system \( \text{CO}_2 \) capture efficiency (left) and relative plant efficiency (right). \( MR = 0.05 \text{ mol/mol} \).

The simulated HFO-fired power plant with integrated CaL is theoretically capable of achieving \( \sim 95\% \) \( \text{CO}_2 \) capture efficiency, \( > 99\% \) \( \text{SO}_2 \) capture efficiency, and \( \text{CO}_2 \)
compression to 200 bar while maintaining > 85% of the reference plant’s efficiency.

Since CaL sidesteps the 2-4% efficiency point penalty imparted by traditional limestone slurry FGD (for > 95% SO₂ emissions reductions), CaL has an overall lower efficiency penalty than expected for other established CCS technologies (see Figure 2.8) [29,42,55]. Note that spray dry SO₂ scrubbers can have an energy penalty as low as 0.5%, however they have higher operating costs, are unsuitable for high SO₂ content flue gases, and have lower SO₂ capture efficiencies (due to low SO₂ removal rates) [56].

The CaL system low efficiency penalty is predicated on CaL operation at 1 bar and the incorporation of a state of the art ASU with a low specific energy of consumption. The energy requirement for O₂ separation constitutes a significant parasitic load. Depending on the SEC estimate used, O₂ separation was found to account for 27-55% of the total plant energy requirement. Reduction of the ASU SEC, or reduction of the calciner load can greatly reduce the energy penalty associated with CaL.

Figure 2.8. Efficiency penalty of CCS technologies.
2.4 Conclusions and Recommendations

With respect to energy efficiency penalty, this preliminary study indicates that CLC is a competitive technology for implementation at an HFO-fired plant when operated at pressures \( \geq 10 \) bar. At atmospheric pressure however, the CLC energy penalty is relatively high. The feasibility of DFB operation at high pressure and at scale is uncertain. Alternately, the CaL energy penalty is acceptable under demonstrable conditions. It was therefore decided that this project will mainly focus on CaL implementation at HFO-fired power plants. The \( \text{CO}_2 \) capture performance of Saudi Arabian limestone derived CaO, and its resistance to deactivation by HFO impurities requires further investigation. Chapter 3 addresses the capture behavior of Saudi Arabian limestone, Chapter 4 focuses on modeling the deactivation of Saudi Arabian limestone due to co-capture, and in Chapter 5 the potential for CaL implementation and HFO-fired power plants is reassessed.
3.1 Introduction

While limestone is a promising CaO precursor, its CO₂ capture capacity, or “activity”, decays due to sintering, attrition and exposure to deactivating flue gas constituents such as SO₂ with increasing calcination/carbonation cycles [23,57,58]. This loss in sorbent activity, or deactivation, is offset by continuously adding fresh limestone to the system and purging spent sorbent. Fresh limestone addition, however, should be limited as it leads to an increase in calcination load, which translates to reduced process efficiency and increased costs [59,60]. Consequently, much research has focused on investigating different CaO sources, sorbent pretreatments, and approaches to spent sorbent reactivation; details can be found in recent reviews by Erans et al. and Hu et al. [61,62].

Limestone is mined from two geological regions in Saudi Arabia: the Red Sea coastal plane and the Arabian platform (see Figure 3.1). Limestone samples obtained from each of these geological regions was studied. While the “Riyadh” limestone, obtained from the Arabian platform is an unmetamorphosed limestone, the “Saabar” limestone obtained from the Red Sea coastal plane is a metamorphosed limestone. Most previous studies on limestone-derived sorbent CO₂ capture performance have
focused on unmetamorphosed limestones and dolomites, with the influence of different limestone impurities, specifically in the form of inert supports, examined. Little research examining the capture behavior of metamorphosed limestone-derived sorbent has been published. Note that metamorphosed limestone, commonly referred to as marble, is widely available and priced comparably to unmetamorphosed limestone.

Metamorphosed limestone is limestone that has been subjected to elevated temperatures and pressures during natural geological processes. Under these conditions, the limestone experiences deformation and recrystallization, which lead to distinct metamorphic morphologies. While the specific metamorphic morphologies that evolve depend on the geological conditions of metamorphism, limestone metamorphism primarily results in increased grain sizes [63]. The CO₂ capture performance of metamorphosed limestone-derived sorbent is expected to differ from

**Figure 3.1.** Limestone rich geological regions in Saudi Arabia.
that of unmetamorphosed limestone-derived sorbent because limestone-derived sorbent activities and reactivities are determined by sorbent morphology, specifically crystalline structure, porosity, and surface area [64–66].

The primary sintering mechanisms responsible for reducing unmetamorphosed limestone-derived sorbent activity with progressing calcination/carbonation cycles, entail grain coarsening, or growth, by crystallite migration and coalescence, and particle shrinkage, or densification [66]. These morphological changes result in an increase in the sorbent’s average pore diameter and a reduction in surface area and porosity [66,67]. A recent study by Pinheiro et al. demonstrated that metamorphosed limestone-derived sorbents experience a reduction in mean pore diameters and therefore an increase in CaO surface area with calcination/carbonation cycles [68]. Moreover, Pinheiro et al., correlated these observations with lower deactivation rates and improved CO₂ capture capacity relative to unmetamorphosed limestone-derived sorbents [68].

The underlying cause of the anomalous behavior reported by Pinheiro et al. merits further exploration [68]. Deeper insight into this unexpected behavior can inform natural sorbent selection and synthetic sorbent design efforts. Moreover, flue gas H₂O and SO₂ content impact CO₂ capture by sorbents, but this impact has not been previously studied for metamorphosed limestone-derived sorbents. Examining capture in realistic chemical environments, by a sorbent that exhibits atypical structure and capture behavior, can shed more light on the physio-chemical characteristics and interactions that dominate CO₂ and SO₂ capture behavior.
In this chapter, the CO₂ capture behavior of sorbents derived from unmetamorphosed Riyadh, metamorphosed Saabar and a third unmetamorphosed limestone that has been previously studied are compared [69]. The underlying causes of the structural changes experienced by metamorphosed limestone due to cycling are examined, and the influence of the CaO matrix and realistic chemical environments on capture are studied. Fluidized bed reactor systems are used to investigate the individual and combined influence of flue gas H₂O and SO₂ content the limestone-derived sorbent’s CO₂ capture behavior. While H₂O typically positively influences CO₂ capture, and SO₂ negatively influences CO₂ capture in unmetamorphosed limestone-derived sorbents, experimental results indicate that metamorphosed limestone-derived sorbent unexpectedly demonstrates the opposite behavior [23,70]. The influence of particle structure is further explored by considering two distinct particle size distributions for each limestone. Furthermore, the influence of multiple calcination/carbonation cycles and of CaSO₄ accumulation on limestone-derived sorbent textural evolution and capture behavior are examined. Imaging and material characterization tools are used to examine the limestones and their calcines at different instances in the process and a discussion is devoted to the underlying factors that control the morphological changes observed in metamorphosed limestone-derived sorbents.

3.2 Experimental Section

Metamorphosed Saabar limestone, from the Red Sea costal plane and unmetamorphosed Riyadh limestone, from the Arabian platform were provided by
United Mining Investments Co. (UMIC), Saudi Arabia. These limestones were milled by BHS-Sonthofen GmbH and sieved by Allgaier Process Technology GmbH to “fine” and “coarse” size fractions: 100-400 µm and 400-1000 µm respectively. Unmetamorphosed German limestone, from the Central Uplands was also obtained in the fine and coarse size fractions. Particle size distributions (PSDs) were measured using a Malvern Mastersizer 3000, equipped with an Aero S dry particle dispersion unit. The elemental composition of each limestone fraction was determined by X-ray fluorescence (XRF), performed using an XGT-7000 (Horiba). Elemental distribution within the limestone samples, and limestone surface morphology were mapped and imaged using a Zeiss MERLIN field emission scanning electron microscope (SEM) equipped with a Gemini II electron optical column, and Oxford Instruments X-Max80 silicon drift detector for energy dispersive spectroscopy (EDS).

Two bubbling fluidized bed (BFB) reactor systems were used to study the individual and combined influence of flue gas H₂O and SO₂ content on CO₂ capture by each of the limestone fractions. A 150-mm diameter, 3.5-m tall electrically heated 20-kW th BFB (BFB 1) was used to pre-calcine 5-kg samples of each limestone fraction. This BFB is equipped with a double cyclone system and candle filter for separating entrained fines from the reactor effluent before sampling by a gas analyzer (ABB Advance Optima 2020) for continuous CO₂, SO₂, and O₂ monitoring. The limestones were calcined under N₂ for 20 minutes at 850 °C.

The capture performance of the pre-calcined samples was examined using the second 70-mm diameter 7-kW th BFB (BFB 2), described in detail elsewhere, and also
equipped with effluent line sampling for continuous CO\textsubscript{2}, SO\textsubscript{2}, and O\textsubscript{2} gas analysis (X-STREAM Emerson Process Management GmbH & Co. OHG) [71]. A schematic diagram of BFB 2 is presented in Figure 3.2.

![Diagram of BFB 2 test facility](image)

**Figure 3.2.** Schematic diagram of BFB 2 test facility.

BFB 2 was pre-heated to 650 °C with an initial inert bed inventory composed of silica sand. Gas flow rates were set to achieve a fluidization velocity of 0.5 m/s and, depending on the experimental run, an influent gas composition of either (i) 12-14% CO\textsubscript{2}, 3% O\textsubscript{2} (ii) 12-14% CO\textsubscript{2}, 10-14% H\textsubscript{2}O, 3% O\textsubscript{2}, (iii) 12-14% CO\textsubscript{2}, 2000 ppm SO\textsubscript{2}, 3% O\textsubscript{2}, or (iv) 12-14% CO\textsubscript{2}, 10-14% H\textsubscript{2}O, 2000 ppm SO\textsubscript{2}, 3% O\textsubscript{2}, with the balance N\textsubscript{2}. Baseline gas concentrations were recorded. A sample of pre-calcined limestone was then dropped into BFB 2 and the semi-batch carbonation/sulfation reaction was allowed to proceed
for 30 minutes while gas concentration readings were recorded. Four runs with variable initial space times, $\tau_0$, were performed per gas atmosphere composition, and per pre-calcined limestone fraction. The total BFB 2 bed inventory was held constant at 1 kg for all runs while the mass of pre-calcined limestone added into the reactor was varied to achieve different initial space times corresponding to 9.3, 4.7, 2.3, and 0.9 mins. A number of random experimental repeats were performed with results used to calculate experimental error.

The influence of limestone cycling and CaSO$_4$ content on CO$_2$ and SO$_2$ co-capture was studied using the same two BFB systems. Fine Riyadh and Saabar limestones were cycled between carbonation and calcination conditions in BFB 1. BFB 1 was electrically preheated to 400 °C and a 10 kg limestone sample was added in an inert atmosphere of N$_2$ with fluidization maintained at $\sim$ 0.4 m/s. The temperature was then raised to calcination temperatures between 850-900°C and held for 15 minutes. In addition to electrical heating, in situ methane combustion was employed to raise the reactor temperature from 750 °C to 900 °C. The resulting calcination atmosphere was $\sim$ 30% CO$_2$, 13% H$_2$O with the balance nitrogen. The calcined limestone was then collected by means of a valve at the bottom of BFB 1, the reactor was cooled to 650 °C, and carbonation conditions were set. The calcined limestone was then added back into BFB 1 and allowed to carbonate for 20 minutes. Afterwards, the recarbonated sorbent was reheated to 750 °C in an inert atmosphere and the calcination and carbonation process repeated with multiple cycles performed per experimental run. Two runs were performed per limestone source with different carbonation gas atmospheres: (i) 12%
CO₂, 10% H₂O, and (ii) 12% CO₂, 10% H₂O, 2000 ppm SO₂ and 0.5% O₂ with the balance N₂. Calcined and recarbonated/sulfated samples were collected after each calcination and carbonation. Fines generated by particle attrition and fragmentation were collected from the cyclones and weighed after each calcination. The limestones were cycled until sorbent activity, \( X_N \), was reduced to about 0.1 mol/mol. The co-capture performance of samples of the calcined limestones with \( X_N \approx 0.6, 0.3 \) and 0.1 mol/mol were evaluated using BFB 2 and the experimental method previously described. A synthetic flue gas composed of 12% CO₂, 10% H₂O, 2000 ppm SO₂, 3% O₂, with the balance N₂ was used.

A custom simultaneous thermal analysis (STA) unit (Linseis GmbH) equipped with a gas mixing manifold was used to assess calcined limestone activity at different cycle numbers. Note that activity is defined as the maximum achievable conversion of CaO to CaCO₃ at the end of the fast carbonation stage when the sample is recarbonated at 650 °C in a 12% CO₂ atmosphere with the balance N₂ (see Figure 3.3a). The subscript \( N \) refers to the cycle number. Fresh limestone samples that have undergone one calcination (\( N = 1 \)) correspond to \( X_1 \approx 0.6 \) mol/mol (see Figure 3.3b). Briefly, thermogravimetric analysis (TGA) was performed on 10-mg samples of calcined limestone by heating (200 ° C/min) the sample to 650 °C in N₂ and then isothermally carbonating the sample in a 12% CO₂ atmosphere with the balance N₂ for 30 minutes. The recorded changes in sample mass were used to calculate \( X_N \). TGA was also used to support the capture trends observed in BFB 2 runs; capture behavior of calcined limestone samples was examined with TGA carbonation atmospheres set to either: (i) 12-14% CO₂, (ii) 12-14% CO₂, 10-14% H₂O, (iii)
12-14% CO₂, 2000 ppm SO₂, or (iv) 12-14% CO₂, 10-14% H₂O, 2000 ppm SO₂, with 3% O₂ and the balance N₂.

Figure 3.3. (a) Definition of $X_N$. (b) Overlay of sampled sorbent, used in BFB 2 experimental runs, on a typical sorbent deactivation curve.

Imaging and characterization were performed on calcined and recarbonated limestone samples taken at different experimental stages. The effect of cycling on PSDs was monitored using the Mastersizer. Morphological changes were followed using SEM-EDS. BFB 1 calcination and carbonation efficiencies and sorbent sulfur accumulation were monitored using the XRF and a Flash 2000 CHNOS Organic Elemental Analyzer (Thermo Scientific) equipped with a thermal conductivity detector (TCD). Brunauer-Emmett-Teller (BET) theory was used to evaluate ASAP 2420 N₂ adsorption data and determine the surface area of calcined limestone. Combined results from N₂ adsorption and Hg intrusion porosimetry, performed using an Autopore IV 9510 (Micromeritics), were used to determine calcined limestone porosity and map pore size distribution.

Note that the TGA and BFB experiments were performed at The University of Stuttgart’s
Institute of Combustion & Power Plant Technology (IFK) facilities, and imaging and characterization was performed in KAUST Core Labs.

3.3 Results and Discussion

3.3.1 Experimental Approach Theory & Validation

The capture performance of the calcined metamorphosed and unmetamorphosed limestones is compared using two key CaL system metrics that influence energy efficiency and thus financial viability: capture efficiency and capture capacity. Capture efficiency, \( E \), is defined as the rate of CO\(_2\) or SO\(_2\) uptake by the sorbent, \( \dot{F}_c \), normalized to the rate of CO\(_2\) or SO\(_2\) entering the carbonator:

\[
E_{CO_2} = \frac{\dot{F}_{CO_2,c}}{x_{CO_2,o} \dot{F}_o} \quad (3.1)
\]

\[
E_{SO_2} = \frac{\dot{F}_{SO_2,c}}{x_{SO_2,o} \dot{F}_o} \quad (3.2)
\]

Sorbent capture capacity, \( X_{max} \), is pragmatically defined as the maximum achievable CaO conversion to CaCO\(_3\), \( X_N \), and CaSO\(_4\), \( X_{CaSO_4,max} \), while maintaining a fast CO\(_2\) capture rate [59]:

\[
X_{max} = X_N + X_{CaSO_4,max} = \frac{1}{n_{CaO,o}} \int_{0}^{t_{max}} \dot{F}_{CO_2,c} + \dot{F}_{SO_2,c} \, dt \quad (3.3)
\]

Note that carbonation is a two stage process, with an initial fast reaction stage followed by a slow reaction stage (see Figure 3.3a). The initial fast reaction stage is controlled by CO\(_2\) diffusion into sorbent pores, CO\(_2\) surface diffusion, and carbonation kinetics [54,72]. As newly formed CaCO\(_3\) blocks access to available CaO, carbonation enters its slow
reaction stage, which is controlled by solid-state diffusion through the product layer. In Eq. 3.3, $t_{max}$ is the time at which the fast reaction stage ends. Sorbent capture efficiency and capture capacity are calculated using BFB 2 gas analyzer data and a mass balance across the gas phase:

\[
\hat{F}_{\text{CO}_2,c} = x_{l,0} \hat{F}_o \left( \frac{x_{\text{CO}_2,o}}{x_{l,o}} - \frac{x_{\text{CO}_2}}{x_l} - \frac{d \left( \frac{x_{\text{CO}_2}}{x_l} \right)}{dt} \right)
\]  

(3.4)

\[
\hat{F}_{\text{SO}_2,c} = x_{l,0} \hat{F}_o \left( \frac{x_{\text{SO}_2,o}}{x_{l,o}} - \frac{x_{\text{SO}_2}}{x_l} - \frac{d \left( \frac{x_{\text{SO}_2}}{x_l} \right)}{dt} \right)
\]  

(3.5)

Sorbent capture behavior is visualized by plotting capture efficiency vs. CaO conversion, $X$. CaO conversion is calculated by solving Eq. 3.3 at discrete time intervals, $t$. Note that CaO conversion refers to the combined conversion of CaO to CaCO$_3$, $X_{\text{CaCO}_3}$, and CaSO$_4$, $X_{\text{CaSO}_4}$. The extent of CaO conversion in the carbonator, or carbonator conversion ($X_{\text{carb}}$), is a key CaL system design parameter. Carbonator conversion is selected to minimize cost and energy requirements, while maintaining sufficient capture efficiency [73]. Therefore monitoring changes to capture efficiency with respect to CaO conversion provides a valuable perspective.

The solid lines in Figure 3.4a show the CO$_2$ capture behavior of once-calcined 100-400 µm metamorphosed Saabar and unmetamorphosed Riyadh and German limestones when exposed to a 14% CO$_2$ in N$_2$ influent in BFB 2. Two unmetamorphosed
limestones were studied to resolve the roles of chemical composition and structure:
while both metamorphosed Saabar and unmetamorphosed Riyadh limestones have
nearly the same impurity content, with a relatively high quartz (SiO₂) content,
unmetamorphosed German limestone reveals higher purity in terms of carbonate phase

Figure 3.4. CO₂ capture performance of once-calcined 100-400 µm limestones at τ₀ =
4.7 mins. BFB 2 influent gas composition dashed lines: 14% CO₂ in N₂, solid lines: 14%
CO₂, 14% H₂O, 2000 ppm SO₂ and 3% O₂ in N₂. The grey dashed line indicates X_{max}. 
composition (see Table 3.1). Note that the loss on ignition (LOI) reported in Table 3.1 is dominantly CO\textsubscript{2} evolution from carbonate decomposition. This was confirmed by TGA-FTIR analysis, which indicated that both magnesium and calcium are originally present in carbonate form in the limestone samples.

**Table 3.1.** Chemical composition of fine (100-400 µm) limestones (wt.%)

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO\textsubscript{2}</th>
<th>MgO</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>Fe\textsubscript{2}O\textsubscript{3}</th>
<th>SO\textsubscript{3}</th>
<th>Na\textsubscript{2}O</th>
<th>K\textsubscript{2}O</th>
<th>LOI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saabar</td>
<td>51.2</td>
<td>3.91</td>
<td>0.64</td>
<td>0.25</td>
<td>0.18</td>
<td>0.20</td>
<td>0.05</td>
<td>0.02</td>
<td>41.6</td>
</tr>
<tr>
<td>Riyadh</td>
<td>51.8</td>
<td>3.17</td>
<td>0.36</td>
<td>0.33</td>
<td>0.21</td>
<td>0.51</td>
<td>0.05</td>
<td>0.07</td>
<td>42.6</td>
</tr>
<tr>
<td>German</td>
<td>54.2</td>
<td>0.61</td>
<td>0.61</td>
<td>0.09</td>
<td>0.07</td>
<td>0.14</td>
<td>0.01</td>
<td>0.04</td>
<td>43.2</td>
</tr>
</tbody>
</table>

Sorbent capture capacity, visualized in Figure 3.4b as the inflection point CaO conversion between fast and slow capture rates, coincides with capture efficiency reduction to ~ 0.2 mol/mol (see Figure 3.4a). The capture capacity varies per limestone source, with Riyadh sorbent exhibiting the greatest CO\textsubscript{2} capture capacity followed by Saabar and German. This discrepancy in capture capacity does not significantly impact the CO\textsubscript{2} capture efficiency during the initial fast capture stage where \(X < X_{max}\). The capture efficiency peak seen in Figure 3.4a coincides with the semi-batch addition of CaO into the reactor. Relatively low initial molar ratios of CaO to CO\textsubscript{2}, or space times (\(\tau\)), are used to ensure that the recorded capture efficiency is not reflective of the thermodynamic equilibrium of carbonation, but provides insight into reaction kinetics and diffusion rates. At low space times, recorded CO\textsubscript{2} and SO\textsubscript{2} capture efficiencies are dependent on the sorbent’s initial morphology and subsequent morphological changes.
caused by sulfation and carbonation. In this study, gas analyzer data from the BFB experiments are used to compare sorbent capture performance and correlate these observations with morphological differences. The validity of this approach and methodology are supported by solving for the apparent carbonation kinetic constant.

The CaO fast carbonation rate can be calculated using the following semi-empirical model adapted by Hawthorne et al. from Nitsch’s kinetic rate model [72,74]:

\[
\frac{dX_{CaCO_3}}{dt} = k_x (X_N - X_{CaCO_3})^a (C_{CO_2} - C_{CO_2,eq})
\] (3.6)

where \(a\) is a semi-empirical exponent that varies from 2/3 under kinetically-controlled conditions to 4/3 under diffusion-controlled conditions [59]. Note that Eq. 3.6 is a one of many carbonation kinetics models that have been developed; the different carbonation kinetics models are reviewed in detail by Fedunik-Hofman et al. and Martinez et al. [75,76]. Fast stage carbonation involves CO\(_2\) reacting with CaO at the solid-gas interface, and this reaction is geometrically constrained. Pore size, particle size, and sorbent area all play a role. The particle structure influences CO\(_2\) access to active CaO sites, which determines the reaction rate and the end of the fast reaction stage. The fast reaction stage shifts to the slow reaction stage when a CaCO\(_3\) layer of critical thickness is formed impeding further CO\(_2\) diffusion to active CaO sites, and requiring solid-state diffusion for further carbonation. Typically a shrinking core model, pore filling model, grain model, or CaCO\(_3\) nucleation and growth model is used to track carbonation kinetics [76–80]. Eq. 3.6 is a semi-empirical model based on a spherical grain model, which assumes that a CaCO\(_3\) layer forms on the surface of each CaO grain present in the particle. Bhatia and
Perlmutter noted that in accordance with a spherical grain model, the kinetic constant in Eq. 3.6, $k_x$, is a function of the surface reaction rate constant, $k_s$, the sorbent’s initial surface area, $S_o$, and porosity, $\varepsilon_o$ such that [22]:

$$k_x = \frac{k_s S_o}{1 - \varepsilon_o}$$

(3.7)

The assumption that capture behavior recorded in BFB 2 is correlated with sorbent morphology is supported by solving for the apparent kinetic constant using gas analyzer data and Eq. 3.6 ($k_{x,exp}$), and evaluating the results against the kinetic constant calculated from BET surface area and porosimetry data using Eq. 3.7 ($k_{x,tho}$). Relevant sorbent morphological data is presented in Table 3.2.

The apparent kinetic constant, $k_{x,exp}$, is calculated for each of the 100-400 μm once-calcined limestones (see Figure 3.5a). Combined CO$_2$ capture data is used from all four BFB runs performed at different initial space times when a 14% CO$_2$ with N$_2$ balance reactor influent is used. Eq. 3.6 is fit to data corresponding to $X > 0.3$ and $X < X_{max}$, where $a \approx 1.17$. The CO$_2$ concentration in the BFB, $C_{CO_2}$, is assumed uniform, and is estimated using the logarithmic average of the inlet and outlet CO$_2$ concentrations, as proposed by Shimizu et al. [12]. This simplifying assumption disregards the complex fluid dynamics of the BFB system. Regardless, the apparent kinetic constants calculated from the BFB experimental data, and the kinetic constants predicted by sorbent material analysis are remarkably similar when a simple correction factor is introduced (see Figure 3.5b). The good fit obtained, with $R^2 = 0.94$, suggests that this study’s approach and methodology are reasonable for the comparative evaluation of these sorbents.
### Table 3.2. Relevant sorbent textural and morphological data

<table>
<thead>
<tr>
<th>Sorbent D</th>
<th>N</th>
<th>( S_o ) [m²/cm³]</th>
<th>( \varepsilon_o )</th>
<th>( k_x \cdot 10^3 ) [m³/mol·s]</th>
<th>( S_m ) [m²/cm³·g CaO]</th>
<th>( \varepsilon_m ) [g⁻¹ CaO]</th>
<th>( \rho ) [g/cm³]</th>
<th>CaSO₄ [wt. %]</th>
<th>CaO [wt. %]</th>
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Figure 3.5. (a) Derivation of the apparent kinetic constant, $k_{x,exp}$ by fitting Eq. 3.6 to experimental BFB data. (b) Comparison of the experimental and theoretical kinetic constants ($R^2 = 0.94$).

Kinetic constant calculations also indicate that assuming the sorbents exhibit similar $\alpha$-values, once-calcined fine metamorphosed Saabar limestone should initially capture CO$_2$ at a 20% faster rate than the Riyadh sorbent, and a 70% faster rate than the
German sorbent, with the capture rate discrepancy between Riyadh and Saabar sorbent narrowing as conversion increases due to Saabar sorbent’s lower capture capacity. Considering that capture efficiency is an indicator of capture rate, Figure 3.4a reveals that the initial CO$_2$ capture rate of once-calcined fine Saabar limestone does not exceed the initial capture rate of Riyadh and German sorbents. This suggests that the Saabar sorbent’s initial carbonation rate is significantly more diffusion-controlled.

Alvarez and Abanades demonstrated that for a majority of limestone-derived sorbents, capture capacity is directly proportional to surface area and coincides with the formation of a critical product layer, ~50 nm in thickness, across the sorbent surface [81]. This observation explains the discrepancy in capture capacity between once-calcined 100-400 µm Riyadh and German limestone (see Table 3.2). Once-calcined Saabar limestone however, has the highest surface area but a relatively low capture capacity. This metamorphosed limestone-derived sorbent demonstrates further anomalous capture behavior when carbonated in BFB 2 with an influent gas composition typical of coal flue gas, 14% CO$_2$ 14% H$_2$O, 2000 ppm SO$_2$ and 3% O$_2$ in N$_2$ (see Figure 3.4a). While both unmetamorphosed limestone-derived sorbents demonstrate enhanced CO$_2$ capture efficiency and capture capacity when H$_2$O and SO$_2$ are introduced, the metamorphosed limestone-derived sorbent experiences reductions in both overall conversion and CO$_2$ capture efficiency. This anomalous behavior is better understood by examining the individual and combined effects of H$_2$O and SO$_2$ on the capture behavior of metamorphosed and unmetamorphosed limestone-derived sorbents.
3.3.2 The Influence of Gas Composition on CO₂ and SO₂ Capture Behavior

The influence of reaction atmosphere composition on the CO₂ capture performance of each of the once-calcined metamorphosed and unmetamorphosed limestones is presented in Figure 3.6. Note that all limestones were calcined at 850 °C in nitrogen for 20 minutes. Although calcination at 850 °C in N₂ is not practical for CaL systems, a literature search reveals that a bulk of CaL sorbents have been studied under these conditions [4,26,61]. Therefore, calcination under these conditions allows for baseline comparison of the limestone-derived sorbents’ morphology and capture behavior with much of the published data. The calcined limestone capture behavior was studied with BFB 2 influent gas composition varied between: (i) 12-14% CO₂, 3% O₂, (ii) 12-14% CO₂, 10-14% H₂O, 3% O₂, (iii) 12-14% CO₂, 2000 ppm SO₂, 3% O₂, and (iv) 12-14% CO₂, 10-14% H₂O, 2000 ppm SO₂, 3% O₂, with the balance N₂. Note that 12% CO₂, 3% O₂, 10% H₂O, and 2000 ppm SO₂ is within range for typical HFO-fired power plant flue gas composition.

The two once-calcined unmetamorphosed Riyadh and German limestones behave similarly when exposed to different influent gas compositions in BFB 2 (see Figures 3.6a-d). Relative to baseline conditions (CO₂ in N₂), H₂O addition positively influences the once-calcined unmetamorphosed limestones’ capture efficiency and capture capacity. Conversely, SO₂ addition reduces both capture efficiency and capture capacity. When both H₂O and SO₂ are added, the presence of H₂O has a greater influence on the combined effect. These trends are observed for fine and coarse once-
Figure 3.6. The influence of atmosphere composition on the CO$_2$ capture performance of once-calcined limestones ($\tau_o = 4.7$ mins): (a) 100-400 µm Riyadh, (b) 400-1000 µm Riyadh, (c) 100-400 µm German, (d) 400-1000 µm German, (e) 100-400 µm Saabar, and (f) 400-1000 µm Saabar.
calcined unmetamorphosed Riyadh and German limestones, for all examined space
times, and are in line with results from previous studies.

The positive influence of H\textsubscript{2}O addition on CO\textsubscript{2} capture efficiency and capacity is well-documented [70,82–86]. This phenomena has been attributed to the formation of a hydroxylated layer on the sorbent surface, which is reported to enhance surface
diffusion and reactivity with carbon dioxide [70,82–86]. The negative influence of SO\textsubscript{2}
addition has also been widely reported and is expected since sulfation and carbonation
are competitive reactions [23,26,87]. Furthermore, CaSO\textsubscript{4} has a larger molar volume
than CaCO\textsubscript{3} and can cause sorbent deactivation, seen as reduced capture capacity in
Figure 3.6, by pore blockage [23]. The stronger influence of H\textsubscript{2}O on capture capacity, in
an atmosphere containing both H\textsubscript{2}O and SO\textsubscript{2}, has also been previously reported [58,88]. The hydroxylated layer formed on the sorbent surface, in the presence of H\textsubscript{2}O, is polar
and causes pore narrowing [88]. Sorbent permeability to larger polar SO\textsubscript{2} molecules is
therefore reduced in the presence of H\textsubscript{2}O, while permeability to smaller nonpolar CO\textsubscript{2}
molecules remains undisturbed [89].

The once-calcined metamorphosed Saabar limestone behaves unexpectedly
when exposed to different influent gas compositions in BFB 2 (see Figures 3.6e-f). While
H\textsubscript{2}O addition initially enhances CO\textsubscript{2} capture efficiency, it ultimately has a negative effect
on both CO\textsubscript{2} capture efficiency and CO\textsubscript{2} capture capacity. Once-calcined fine Saabar
limestone experiences a shorter-lived positive effect due to H\textsubscript{2}O addition, and a more
sever negative effect when compared to once-calcined coarse Saabar limestone. When
SO\textsubscript{2} is added into the capture atmosphere, the impact on fine Saabar sorbent’s CO\textsubscript{2}
capture efficiency varies from negative to positive, depending on the initial space time (see Figure 3.7). Note that the impact of SO$_2$ addition is delayed, and can be seen after some CaSO$_4$ accumulation (around $X > 0.2$). SO$_2$ addition may also positively influence the CO$_2$ capture capacity of the fine Saabar sorbent. At $\tau_o = 9.3$ mins, fine Saabar sorbent experiences enhanced conversion to CaCO$_3$ in the presence of SO$_2$. Note that CaL systems typically operate at relatively high space times to ensure a sustained high
capture efficiency. Unlike the fine Saabar sorbent, once-calcined coarse Saabar limestone’s capture capacity and efficiency are not positively influenced by SO$_2$ addition, nonetheless relative to the once-calcined Riyadh and German limestones, coarse Saabar sorbent is less negatively impacted by SO$_2$ addition. Furthermore, for both fine and coarse Saabar sorbent fractions, superior CO$_2$ capture capacity and capture efficiency are achieved in a capture atmosphere containing both H$_2$O and SO$_2$ when compared to a capture atmosphere with only H$_2$O added. Limited sulfation of once-calcined Saabar limestones enhance this sorbent’s CO$_2$ capture performance.

The influence of sorbent sulfation on carbonation performance is better understood by examining the SO$_2$ capture performance of these sorbents in parallel with the CO$_2$ capture performance. Co-capture of CO$_2$ and SO$_2$ occurs during the experimental sets in which BFB 2 influent gas composition is set to either: (i) 12-14% CO$_2$, 2000 ppm SO$_2$, 3% O$_2$, or (ii) 12-14% CO$_2$, 10-14% H$_2$O, 2000 ppm SO$_2$, 3% O$_2$, with the balance N$_2$. The SO$_2$ capture performance of the once-calcined Saabar, Riyadh, and German limestones, corresponding with these experimental sets were examined. Note that the two once-calcined unmetamorphosed Riyadh and German limestones exhibit similar SO$_2$ capture performance, and therefore once-calcined Riyadh limestone is selected as a representative example of the once-calcined unmetamorphosed limestone and its SO$_2$ capture performance is discussed in more detail. Once-calcined German limestone’s SO$_2$ capture performance is presented in Figure 3.8.
Once calcined unmetamorphosed Riyadh and metamorphosed Saabar limestones exhibit similar SO$_2$ capture efficiency under H$_2$O-free conditions (see Figure 3.9). Upon H$_2$O addition, once-calcined unmetamorphosed limestones exhibit enhanced SO$_2$ capture efficiency while fine Saabar sorbent exhibits reduced SO$_2$ capture efficiency. This observed divergence in behavior between once-calcined metamorphosed and unmetamorphosed limestones is analogous to the divergence in CO$_2$ capture behavior observed upon H$_2$O addition. Under reactor conditions, where the CO$_2$ concentration is greater than the equilibrium CO$_2$ concentration, direct sulfation (Eq. 1.6) is the favored sulfation pathway [26]. Since H$_2$O addition enhances carbonation efficiency in once-calcined unmetamorphosed limestone, sulfation efficiency is also enhanced. Since H$_2$O addition reduces carbonation efficiency in once-calcined metamorphosed limestone, sulfation efficiency is also reduced. Note that for once-calcined coarse Saabar limestone, the SO$_2$ capture efficiency is initially enhanced by H$_2$O addition, and then drops at $X \approx$
0.5. \( X \approx 0.5 \) also corresponds to the point at which \( \text{H}_2\text{O} \) addition begins to negatively impact coarse Saabar sorbent carbonation (see Figure 3.6f). A relationship between \( \text{CaSO}_4 \) and \( \text{CaCO}_3 \) accumulation is revealed by comparing results from runs at different initial space times (see Figure 3.10).

**Figure 3.9.** \( \text{SO}_2 \) capture performance of once-calcined Saabar and Riyadh limestones (\( \tau_o = 4.7 \) mins). \( \text{SO}_2 \) capture efficiency for: (a) 100-400 \( \mu \text{m} \), and (b) 400-1000 \( \mu \text{m} \) sorbent.
In this study, initial space time is increased by introducing more CaO into BFB 2 without changing the influent gas flow rates. Increasing initial space time therefore leads to reduced CO$_2$ and SO$_2$ concentrations in BFB 2 during the initial fast carbonation stage, and consequently, slower carbonation and sulfation reaction rates. In BFB 2 atmospheres that do not contain SO$_2$, the once-calcined Saabar, Riyadh, and German limestones achieve a slightly higher CO$_2$ capture capacity at higher space times; capture

**Figure 3.10.** The space time effect on the relative conversion (CaSO$_4$ vs. CaCO$_3$) of 100-400 µm Riyadh sorbent in (a) H$_2$O-free, and (b) 10% H$_2$O atmospheres, and Saabar in (c) H$_2$O-free and (d) 10% H$_2$O atmospheres.
capacity is seen to increase by < 0.1 mol/mol with a tenfold increase in space time (Figure 3.11). This effect was previously reported by Manovic and Anthony, and is caused by the slower carbonation rate allowing improved surface diffusion thereby reducing the probability of CaCO₃ forming in a manner that blocks unreacted CaO [90].

![Figure 3.11](image)

**Figure 3.11.** Influence of initial space time on capture capacity. Line colors: Riyadh is black, Saabar blue, and German red. Marker shapes: fine sorbent is circle, coarse sorbent is diamond. Line style: H₂O-free capture atmosphere is solid, atmosphere containing H₂O is dashed.

In BFB atmospheres that contain SO₂, experimental results indicate that the relative average concentration of SO₂ in the BFB, \( C_{SO₂}/C_{CO₂} \), and the relative average SO₂ capture rate, \( \dot{F}_{SO₂,c}/\dot{F}_{CO₂,c} \), decrease as initial space time is increased (Figure 3.12). Consequently, the relative accumulation of CaSO₄ vs. CaCO₃ diverges for different initial space times (see Figure 3.10). For both fine and coarse metamorphosed and
Figure 3.12. (a-d) Relative average concentration of SO$_2$ in the BFB (mol SO$_2$/mol CO$_2$), and (e-h) relative average SO$_2$ capture rate (mol·s$^{-1}$ SO$_2$/mol·s$^{-1}$ CO$_2$). Top to bottom: Riyadh in an H$_2$O-free atmosphere, Riyadh in an atmosphere containing H$_2$O, Saabar in an H$_2$O-free atmosphere, Saabar in an atmosphere containing H$_2$O.
unmetamorphosed sorbents, conversion to CaCO$_3$ is favored at higher initial space time.

Note that the relatively slower accumulation of CaSO$_4$, observed at high initial space time, is correlated with enhanced carbonation efficiency and CO$_2$ capture capacity under H$_2$O-free conditions for fine Saabar sorbent (as seen in Figure 3.10). The discrepancy in relative conversion (CaSO$_4$ vs. CaCO$_3$) due to space time appears around $X > 0.2$ for fine Saabar sorbent under H$_2$O-free conditions (Figure 3.10c), and the effects on CO$_2$ capture performance can be seen in Figure 3.7 at $X > 0.2$. Both size fractions of
the once-calcined metamorphosed limestone are less susceptible to the influence of space time on relative conversion in the presence of H$_2$O. For Saabar sorbents at all examined space times, H$_2$O addition causes the sulfation reaction to slow before carbonation transitions to its slow solid-state diffusion-controlled stage (Figure 3.13). Consequently, the slow CaSO$_4$ accumulation has less of an impact on CaCO$_3$ accumulation.

![Graph](image)

**Figure 3.14.** TGA CO$_2$ capture results for once calcined 100-400 µm (a) Riyadh and (b) Saabar limestones.

The TGA runs performed in parallel with the BFB runs support the observed positive influence of H$_2$O addition on once-calcined unmetamorphosed limestone
capture capacity, and the negative influence of $\text{H}_2\text{O}$ addition on once-calcined metamorphosed limestone capture capacity (see Figure 3.14). Note that the TGA runs are executed with lower initial space times (< 0.2 mins) than the BFB runs, and in line with observations on the influence of space time: (i) once-calcined unmetamorphosed Riyadh limestone experiences a greater negative impact on $\text{CO}_2$ capture capacity due to $\text{SO}_2$ addition in the TGA vs. in the BFB, and (ii) once-calcined metamorphosed limestone experiences a negative impact on $\text{CO}_2$ capture capacity due to $\text{SO}_2$ addition in the TGA.

3.3.3 The Role of Sorbent Morphology on Capture Behavior

Pore size distributions for the once-calcined Saabar, Riyadh, and German limestones are presented in Figure 3.15, and BET surface area and other relevant textural data and elemental analysis data are summarized in Table 3.2. Elemental analysis reveals that once-calcined fine Saabar limestone and both size fractions of the two unmetamorphosed limestone-derived sorbents exhibit similar purity, 85-90% CaO on a mass basis, but once-calcined coarse Saabar limestone is only 46% CaO. Since SEM-EDS imaging (Figure 3.16) reveals that the impurities are largely nonporous, porosimetry and surface area data are reported per gram of CaO allowing comparison.

Pore size distributions for the once-calcined Saabar, Riyadh and German limestones are multimodal with an intense peak in the 50-200 nm range. The fine and coarse fractions of the metamorphosed Saabar limestone-derived sorbents have smaller peak pore diameters relative to the unmetamorphosed Riyadh and German limestone-derived sorbents. Pinheiro et al. similarly found that metamorphosed limestone-derived
Figure 3.15. Pore size distributions for once-calcined limestones: (a) 100-400 µm size fraction (b) 400-1000 µm size fraction. Dashed lines represent the cumulative intrusion, while solid lines correspond to differential pore volume.
sorbents exhibit peak pore diameters in the mesoporous range (2-50 nm), and unmetamorphosed limestones calcined once under similar conditions typically have peak pore diameters in the macroporous range (> 50 nm) [68,81]. Moreover, once-calcined fine Saabar limestone has a high surface area, and exhibits low porosity; these textural characteristics were also reported by Pinheiro et al. and appear to be typical of calcined fine metamorphosed limestones [68]. While once-calcined fine Saabar limestone’s pore size distribution is narrow and uniform with macropores contributing very little to the pore volume, a significant fraction of once-calcined coarse Saabar limestone’s pore volume is due to macropores. These textural differences are likely responsible for the different capture behavior displayed by the fine and coarse Saabar sorbents.

Once-calcined metamorphosed limestone mesopores are susceptible to pore blockage during carbonation. Alvarez and Abanades demonstrated that pore blockage is likely in “narrow pores”, defined as < 150 nm in diameter [66]. The pore blockage experienced by once-calcined fine Saabar limestone results in unreacted CaO, and therefore this sorbent’s relatively high surface area does not equate to high capture capacity when carbonated in BFB 2 with an influent gas concentration of 14% CO₂, 3% O₂ in N₂ (Figure 3.4). Once-calcined fine Riyadh limestone also experiences some pore blockage during carbonation; although it has double the surface area of once-calcined fine German limestone, once-calcined fine Riyadh limestone does not exhibit a proportionally greater capture capacity. The wider pores exhibited by once-calcined German and coarse Riyadh limestones are less susceptible to pore blockage by
carbonation. In the case of once-calcined coarse Saabar limestone, CO$_2$ capture involves gas intrusion into the macropores followed by permeation into the mesopores. Consequently, once-calcined coarse Saabar limestone is initially exposed to lower concentrations of CO$_2$ at mesopore openings. This shielding of the mesopores by the macropores reduces and postpones mesopore blockage, as seen in Figure 3.6f. While once-calcined coarse Saabar limestone’s baseline CO$_2$ capture efficiency is relatively high at $X < 0.5$, a steep drop in capture efficiency is observed at $X \approx 0.5$. It is proposed that this drop in capture efficiency coincides with the delayed mesopore blockage resulting from the macropore shielding effect.

The difference in CO$_2$ capture performance between once-calcined fine and coarse Saabar limestones when H$_2$O is added can also be attributed to the coarse Saabar sorbent’s macropores. In the case of once-calcined fine Saabar limestone, pore blockage is intensified by H$_2$O forming a hydroxylated layer on the sorbent surface. The hydroxylated layer causes further pore narrowing and enhanced CO$_2$ reactivity. Since fast carbonation rates further increase the probability of bottleneck formation, H$_2$O addition increases the fine Saabar sorbent’s susceptibility to pore blockage [90]. For once-calcined coarse Saabar limestone, H$_2$O addition does not negatively influence initial CO$_2$ capture efficiency, controlled by gas intrusion into the sorbent’s macropores. Once-calcined coarse Saabar limestone therefore initially displays capture behavior similar to macroporous once-calcined unmetamorphosed limestones, with enhanced CO$_2$ capture efficiency observed due to H$_2$O addition. The subsequent restricted permeation into the once-calcined coarse Saabar limestone’s mesopores leads to a
delayed and less intense negative impact on the sorbent’s capture capacity relative to that experienced by once-calcined fine Saabar limestone. In Figure 3.6f, the drop in once-calcined coarse Saabar limestone’s capture efficiency due to H₂O addition is seen at $X \approx 0.4$, while in a H₂O-free environment, the drop in capture efficiency is observed at $X \approx 0.5$. The once-calcined metamorphosed limestones’ mesopores appear to be the dominant textural feature controlling capture capacity in these sorbents, with H₂O addition intensifying mesopore blockage. Mesopore narrowing due to H₂O addition more significantly impacts sulfation. Larger polar SO₂ molecules experience more diffusional resistance caused by H₂O addition than the smaller nonpolar CO₂ molecules. Recall that in an atmosphere containing both H₂O and SO₂, the once-calcined metamorphosed limestones’ sulfation rate slows before the carbonation rate enters its solid-state diffusion-controlled stage. The macroporous once-calcined unmetamorphosed limestones’ capture capacity is positively influenced by H₂O addition.

The mesoporous nature and low porosity of once-calcined fine metamorphosed limestones limit SO₂ intrusion into these sorbents’ pore network and contribute to these sorbents’ reduced susceptibility to sulfation deactivation. For once-calcined fine metamorphosed limestones, sulfation likely proceeds through the “unreacted core” mode, with a CaSO₄ shell forming on the external surface of the sorbent. Since direct sulfation occurs, the CaSO₄ shell that forms is porous [91,92]. While the wider pores and higher porosity exhibited by once-calcined unmetamorphosed limestones, such as fine German, are less susceptible to pore blockage by carbonation, they exhibit less
diffusional resistance to SO$_2$ molecules, enhanced sulfation rates and pore blockage by sulfation [93]. In the case of once-calcined fine German limestone, this translates to the high sulfation deactivation seen in Figure 3.6b. Once-calcined coarse German limestone, which has a similar porosity and pore size distribution to the once-calcined fine German limestone in the < 200 µm range, experiences less sulfation deactivation than once-calcined fine German limestone. This is due to the coarse German sorbent’s > 200 µm diameter macropores, that are less susceptible to pore blockage by CaSO$_4$ formation. Similarly, once-calcined coarse Saabar limestone’s high volume of macropores in the > 200 µm range enhances this sorbent’s resistance to sulfation deactivation; relative to once-calcined Riyadh and German limestones, the coarse Saabar sorbent experiences the least sulfation deactivation (see Figure 3.6). While fine Saabar sorbent sorbent’s narrow pores influence this sorbent’s resistance to sulfation deactivation, the positive influence of SO$_2$ on fine Saabar sorbent carbonation is not explained by pore size distribution alone. SEM-EDS is used to further examine the sorbents’ morphology, and structural and compositional characteristics.

SEM images of the limestones and their calcines are presented in Figure 3.16. While the impurities in the unmetamorphosed limestones are relatively evenly distributed throughout the limestones’ matrices (see Figures 3.16e-f and h-i), the metamorphosed Saabar limestone is primarily composed of large monomineralic phases separated by clear boundaries (see Figures 3.16d and g). This marbled distribution of monomineralic phases is due to grain size growth during limestone metamorphism. The grain size growth results in metamorphic differentiation, or the redistribution of
Figure 3.16. SEM images of the (a) Saabar, (b) Riyadh, and (c) German limestones, and of the once-calcined fine (d) Saabar, (e) Riyadh, and (f) German limestones, and of the once-calcined coarse (g) Saabar, (h) Riyadh, and (i) German limestones.

White arrows indicate impurities.
chemical components within the limestone without altering the overall chemical composition [63]. Note that the degree of metamorphic differentiation is a function of metamorphic conditions. SEM further reveals that once-calcined coarse Saabar limestone macropores are largely fractures formed at phase boundaries and within the large monomineralic phases (see Figure 3.16g). This may indicate that Saabar limestone is more sensitive to thermal stress than Riyadh or German limestones. Saabar limestone’s impurities, primarily composed of quartz (SiO₂), endow a higher mechanical strength to the mineral than pure CaCO₃. After milling and sieving the limestone to obtain the 100-400 µm size fraction, large particles (> 400 µm) composed primarily of impurities are therefore excluded from the fine Saabar limestone fraction.

Fine Riyadh and Saabar limestones have a similar bulk chemical composition (Table 3.1), but their distinctive distribution of impurities along with differences in their crystalline structure might be responsible for once-calcined Saabar limestone’s distinct textural features, such as smaller pore diameters. Figures 3.16a-c show the textural quality resulting from Saabar limestone’s large CaCO₃ grains vs. Riyadh and German limestones, which have more pronounced polycrystalline structures and exhibit lower crystallinity. X-ray diffraction (XRD) analysis performed by KAUST Catalysis Center postdoc, Alla Dikhtiarenko, revealed that the structural refinements of raw limestone minerals suggest that their dominant phase is better described as calcium magnesium carbonate with a doping amount of magnesium. Moreover, the large and active monomineralic grains of metamorphosed Saabar limestone have a composition of Ca₀.₉₁Mg₀.₀₉CO₃, while Riyadh and German limestones’ contain larger amount of
magnesium and reveal compositions of Ca$_{0.85}$Mg$_{0.15}$CO$_3$, and Ca$_{0.84}$Mg$_{0.16}$CO$_3$, respectively. The higher purity, in terms of CaCO$_3$ content, of the metamorphosed limestone’s crystals may have resulted from metamorphic differentiation during the limestone’s recrystallization. The low incidence of structural defects in the metamorphosed limestone’s large structured highly crystalline relatively pure CaCO$_3$ phase, likely leads to the evolution of the once-calcined metamorphosed limestone’s uniform mesopores. Unmetamorphosed limestones’ more polycrystalline structure likely leads to the evolution of the larger macropores and wider pore size distributions seen for these once-calcined unmetamorphosed limestones.

The bulk of once-calcined fine metamorphosed limestones’ reactive surface area is only accessible after reactant diffusion through the mesopores. Therefore, once-calcined fine metamorphosed limestone’s initial carbonation rate is more diffusion-limited than unmetamorphosed limestone-derived sorbents. Moreover, the higher CaO purity of once-calcined metamorphosed limestones translates to higher surface reactivity and increased susceptibility to unreacted CaO shielding and mesopore blockage by carbonation. Recall that the once-calcined fine metamorphosed limestone’s narrow pores and low porosity limit SO$_2$ intrusion, and at high space times, this restrained sulfation improves carbonation. It is postulated that the introduction of a limited amount of impurities in the form of CaSO$_4$ pacifies sections of the highly reactive once-calcined Saabar limestone’s matrix and introduces some resistance to mesopore blockage due to fast carbonation. Sulfation may also have an effect analogous to the introduction of an inert support into the relatively pure recarbonated sorbent surface;
note that CaSO$_4$ has a higher sintering or “Tamman” temperature (861 °C) than CaCO$_3$ (533 °C) and is therefore less susceptible to sintering under carbonation condition [62,94]. The larger molar volume of CaSO$_4$ relative to CaCO$_3$ may also lead to fractures, introducing defects in the Saabar sorbent’s uniform structure. These structural defects enhance reactant access to active (1, 1, 1) oriented surfaces and reactant permeation into the particle’s core [95]. The introduction of fractures in the CaO matrix due to sulfation is discussed in greater detail in Section 3.3.4.

3.3.4 The Influence of Sorbent Cycling on Morphology and Capture Behavior

The influence of calcination/carbonation cycles, performed under practical conditions, on the textural evolution and co-capture behavior of metamorphosed and unmetamorphosed limestone-derived sorbents is examined. Fine Saabar sorbent, with its initially uniform mesoporous structure is compared to macroporous polycrystalline fine Riyadh sorbent. Sorbent cycled in a SO$_2$-free atmosphere is compared to sorbent cycled with SO$_2$ in the carbonation atmosphere. Under both conditions, sorbent is cycled in BFB 1 and calcination is performed at 900 °C in an atmosphere comprising ~ 30% CO$_2$ and 13% H$_2$O. Carbonation is performed at 650 °C in either a (i) sulfurous (2000 ppm SO$_2$), or (ii) sulfur-free, synthetic flue gas containing H$_2$O. The morphology and co-capture behavior of cycled metamorphosed and unmetamorphosed limestone-derived sorbents with activities, $X_N$, equal to about 0.1, 0.3 and 0.6 mol/mol are examined. $X_N$ is defined as the cycled sorbent’s baseline CO$_2$ capture capacity in cycle $N$, measured by recarbonating the sorbent in a 12% CO$_2$ and N$_2$ environment in the TGA
Note that $X_N \approx 0.6$ corresponds to once-calcined limestone activity, and sorbent residual activity after innumerable cycles, $X_F$, is typically $\approx 0.07$ [57]. Since sulfation, predictably, enhances both metamorphosed and unmetamorphosed limestone-derived sorbent deactivation rates, sulfated and non-sulfated sorbents at different cycle numbers but equivalent activities are compared [23]. This allows the comparison of textural changes experienced by sulfated and non-sulfated sorbents that result in similar activities but different co-capture behavior. Non-sulfated sorbents at $N = 13$ and sulfated sorbents at $N = 6$ have an activity, $X_N \approx 0.1$; non-sulfated sorbents at $N = 6$ and sulfated sorbents at $N = 3$ have an activity, $X_N \approx 0.3$.

**Figure 3.17.** BFB 1 deactivation curves. Line colors: Riyadh is black, Saabar is blue. Solid lines: cycled in a SO$_2$-free environment. Dashed lines: cycled with SO$_2$.

Figure 3.18 shows the CO$_2$ and SO$_2$ capture behavior of fine Saabar and Riyadh sorbents at different cycle numbers and activities, when the sorbents are recarbonated in BFB 2 with an influent gas composition of 12% CO$_2$, 10% H$_2$O, 2000 ppm SO$_2$, 3% O$_2$, with the balance N$_2$ (hereafter referred to as “wet synthetic flue gas”). Similar trends are
observed for all examined space times; results from $\tau_o = 4.7$ mins are presented. For the unmetamorphosed Riyadh limestone-derived sorbents, the deactivation mechanism does not significantly impact CO$_2$ capture behavior from a gas atmosphere typical of coal or heavy fuel oil power plant flue gas. The non-sulfated and sulfated Riyadh sorbents with similar activities exhibit similar CO$_2$ capture behavior (see Figure 3.18a). A slight reduction in fast stage ($X < X_{\text{max}}$) capture efficiency is observed for the sulfated Riyadh sorbent vs. the non-sulfated Riyadh sorbent with similar activity, with the

**Figure 3.18.** The influence of sorbent activity and CaSO$_4$ content on the CO$_2$ capture performance of (a) Riyadh, and (b) Saabar sorbent, and on the SO$_2$ capture performance of (c) Riyadh, and (d) Saabar sorbent. $\tau_o = 4.7$ mins.
divergence in capture efficiency growing with CaSO₄ accumulation. A slight increase in slow stage \((X > X_{max})\) capture efficiency and conversion is also observed when the Riyadh sorbent is deactivated by sulfation. This is due to the introduction of CaSO₄ impurities, which increase lattice defects in the sorbent’s matrix and in turn enhance solid-state diffusion [96]. Unmetamorphosed Riyadh limestone-derived sorbent sulfation follows a similar trend to carbonation behavior as a result of the direct sulfation pathway (see Figure 3.18c).

Sulfated metamorphosed Saabar limestone-derived sorbents outperform non-sulfated Saabar sorbents with similar activity in terms of co-capture efficiency and, in the case of \(X_N \approx 0.3\) sorbents, co-capture capacity, indicating that metamorphosed limestone sulfation significantly impacts the sorbent’s textural evolution (see Figure 3.18b). The superior slow stage capture efficiency and conversion exhibited by sulfated Saabar sorbent is analogous to that observed for sulfated Riyadh sorbent. The superior fast stage CO₂ capture efficiency exhibited by sulfated Saabar sorbents indicates that these sorbents’ capture rates are less diffusion-controlled in a carbonation environment containing H₂O than non-sulfated metamorphosed limestone-derived sorbents with similar activity. The superior co-capture capacity of sulfated Saabar sorbent with \(X_N \approx 0.3\) indicates that this sorbent is less susceptible to pore blockage in a carbonation environment containing H₂O than non-sulfated Saabar sorbent with \(X_N \approx 0.3\).

Metamorphosed Saabar limestone-derived sorbent sulfation follows a similar trend to carbonation behavior as a result of the direct sulfation pathway (see Figure 3.18d).
Figure 3.19. Pore size distributions for cycled sorbents: (a) 100-400 µm unmetamorphosed Riyadh sorbents, (b) 100-400 µm metamorphosed Saabar sorbents.

Figure 3.19 presents the evolution of the pore size distributions of cycled fine Riyadh and Saabar sorbents, and BET surface area and other relevant textural data is provided in Table 3.2. Sintering, experienced with increasing calcination/carbonation cycles, causes surface area reduction and changes to pore size distribution and porosity [61]. Contrary to Pinheiro et al.’s observations, the metamorphosed and unmetamorphosed limestone-derived sorbents are found to experience a comparable
decay in activity (Figure 3.17) and surface area [68]. Note that mild calcination conditions were employed in Pinheiro et al.’s study [68].

Porosity and pore size distributions for the sulfated and non-sulfated unmetamorphosed Riyadh limestone-derived sorbents with $X_N \approx 0.3$ are very similar. Sulfated Riyadh sorbent that has undergone the same number of calcination/carbonation cycles as the non-sulfated Riyadh sorbent, $N = 6$, is relatively more sintered; sulfated $N = 6$ sorbent has larger peak pore diameters, a smaller surface area and lower porosity than its counterpart. These textural changes are primarily due to enhanced sintering during calcination caused by the lower Tamman temperature of CaSO$_4$ (861 °C) vs. CaO (1313 °C) [94]. The enhanced sintering and CaSO$_4$ deactivation are responsible for sulfated Riyadh sorbent’s low activity at $N = 6$ ($X_{6\,w/\,SO_2} \approx 0.1$). Non-sulfated Riyadh sorbent with $X_{13} \approx 0.1$ has a similar surface area to its sulfated counterpart ($X_{6\,w/\,SO_2} = 0.1$), but lower porosity. Itskos et al. have previously reported on sulfation, especially direct sulfation, enhancing sorbent porosity [92]. While both the $X_N \approx 0.1$ sulfated and non-sulfated unmetamorphosed limestone-derived sorbent pore diameters peak at $\sim 210$ nm, the non-sulfated fraction has a secondary pore diameter peak emerging at $\sim 90$ nm (see Figure 3.19a).

The emergence of a population of small pores has been attributed to sorbent regeneration, which is experienced by sorbents subjected to an extended carbonation that surpasses the fast reaction stage and allows recarbonation of previously occluded CaO [97]. During sorbent cycling in BFB 1, the carbonator space time and residence time result in a carbonator conversion $X_{\text{carb}} \approx 0.15$. Since Riyadh sorbent $X_{12} < 0.15$, the
carbonation reaction proceeds into the solid-state diffusion-controlled stage, leading to some sorbent reactivation post-calcination. While sulfation deactivation is mainly responsible for the relatively worse co-capture performance of the sulfated Riyadh sorbent with $X_{6 \text{w/}SO_2} \approx 0.1$ compared to the non-sulfated Riyadh sorbent with $X_{13} \approx 0.1$ (Figure 3.18a), enhanced diffusional resistance to SO$_2$ molecules due to the population of narrow pores emerging in non-sulfated Riyadh sorbent with $N = 13$, and this sorbent’s lower porosity may also play a role.

For the non-sulfated metamorphosed Saabar limestone-derived sorbent with $X_{13} = 0.1$, the bimodal pore size distribution is more developed, with a large population of ~ 50 nm pores, and secondary populations of pores with diameters > 250 nm (see Figure 3.19b). While $X_{12}$ for the metamorphosed and unmetamorphosed limestone-derived sorbents is comparable, the enhanced regeneration experienced by the metamorphosed limestone-derived sorbent indicates that non-sulfated Saabar sorbent, cycled 12 times, retains its susceptibility to pore blockage in the presence of H$_2$O. This premature pore blockage lengthens the solid-state diffusion-controlled stage thereby amplifying the population of small pores that emerge post-calcination. Note that the metamorphosed limestone-derived sorbent mesopores disappear with initial cycling, and larger pore diameters evolve, peaking at ~ 110 nm for non-sulfated Saabar sorbent at $N = 6$. While non-sulfated Saabar sorbent’s pores are largely macroporous by $N = 6$, they remain < 150 nm, and are therefore susceptible to pore blockage. Additionally, non-sulfated Saabar sorbent’s negligible pore volume associated with pore diameters > 200 nm indicates that negligible fractures or defects are present in the large dense
metamorphosed limestone-derived sorbent’s monomineralic CaO structure, enhancing susceptibility to pore blockage. While once-calcined Riyadh and German limestones’ pore diameters also peak at < 150 nm, these unmetamorphosed polycrystalline limestone-derived sorbents have pores with diameters > 200 nm, have lower surface reactivity, and therefore do not experience pore blockage in the presence of H₂O.

While sulfated metamorphosed Saabar limestone-derived sorbent with
\[ X_{3\text{w/}SO_2} \approx 0.3 \]
has a similar pore size distribution and activity as non-sulfated Saabar sorbent with \( X_6 \approx 0.3 \), the sulfated Saabar sorbent’s higher porosity, and possibly its slightly lower purity, lead to reduced susceptibility to pore blockage. This translates to the higher co-capture efficiency and capacity exhibited by the sulfated Saabar sorbent when exposed to wet synthetic flue gas in BFB 2 (Figure 3.18b). Sulfated Saabar sorbent with \( X_{6\text{w/}SO_2} \approx 0.1 \) retains a higher porosity and larger average pore diameter than non-sulfated Saabar sorbent with \( X_{13} \approx 0.1 \). The sulfated Saabar sorbent’s textural quality enhances pore diffusion, causing initial fast stage carbonation to be less diffusion-controlled relative to that experienced by non-sulfated Saabar sorbent with \( X_{13} \approx 0.1 \). This is responsible for the sulfated Saabar sorbent’s superior CO₂ capture efficiency when exposed to wet synthetic flue gas in BFB 2 (Figure 3.18b). Note that the sulfated and non-sulfated metamorphosed Saabar sorbents with \( X_N \approx 0.1 \) exhibit similar capture capacity when exposed to wet synthetic flue gas in BFB 2. The emergence of large pores, > 250 nm, in the \( N = 13 \) non-sulfated metamorphosed limestone-derived sorbent reduces this sorbent’s susceptibility to pore blockage.
Sulfated metamorphosed Saabar limestone-derived sorbent at $N = 6$ also has a higher porosity than non-sulfated Saabar sorbent at $N = 6$. The higher porosity of the sulfated fraction is partially due to the emergence of large pores, $> 250$ nm, analogous to those seen for non-sulfated Saabar sorbent at $N = 13$. SEM imaging reveals that sulfation significantly enhances metamorphosed limestone-derived sorbent grain coarsening, favoring this mechanism of sintering over densification, which is seen in non-sulfated metamorphosed limestone-derived sorbent (see Figure 3.20a-b). Lattice defects introduced by sulfation have been reported to accelerate lattice diffusion, grain

Figure 3.20. SEM images of cycled metamorphosed Saabar limestone-derived sorbent.

(a) Non-sulfated with $X_{13} \approx 0.1$, (b) sulfated with $X_{6\text{w}/SO_2} \approx 0.1$, (c) recarbonated sulfated sorbent with $X_{6\text{w}/SO_2} \approx 0.1$. White arrows indicate impurities.
coarsening and pore diameter widening [98]. Grain boundary stresses due to the accelerated textural changes caused by sulfation may lead to fractures by $N = 6$. In Figure 3.20c an SEM image of recarbonated sulfated metamorphosed limestone-derived sorbent is presented, and fractures are seen to propagate from phase boundaries with sorbent impurities. These large fractures play a similar role to the once-calcined coarse metamorphosed limestone-derived sorbent macropores, thereby enhancing co-capture from flue gas containing H$_2$O. Moreover, reactivation experienced by the sulfated metamorphosed Saabar limestone-derived sorbent leads to the emergence of a secondary pore population peaking at $\sim$ 90 nm, similar to that seen for Riyadh sorbent, vs. $\sim$ 50 nm for the non-sulfated Saabar sorbent. Sulfation alters metamorphosed limestone-derived sorbent morphology leading it to more closely resemble unmetamorphosed limestone-derived sorbents. Sulfation also preserves the porosity of the metamorphosed limestone-derived sorbent, and for metamorphosed limestone-derived sorbents with initially low porosity, high surface reactivity and relatively small pore sizes, the preservation of porosity reduces susceptibility to CO$_2$ diffusional resistance and pore blockage and leads to enhanced co-capture performance in an atmosphere containing H$_2$O.

The influence of different reaction atmospheres on unmetamorphosed limestone-derived sorbents’ capture behavior is relatively well understood. Unmetamorphosed limestone-derived sorbents in early calcination/carbonation cycle stages are typically polycrystalline and macroporous. These sorbents exhibit limited pore blockage due to carbonation, enhanced capture efficiency and capture capacity in
the presence of H₂O, and deactivation and pore blockage due to sulfation. In an atmosphere containing both H₂O and SO₂, the positive influence of H₂O counteracts the negative influence of SO₂ on capture capacity by limiting SO₂ intrusion into the sorbent pores. Calcined metamorphosed limestones’ high purity CaO arranged in large structured and dense monomineralic phases, with relatively low porosity and small pores, are likely responsible for the atypical capture behavior displayed by these sorbents in response to different gas atmospheres (see Figure 3.21). It is proposed that metamorphosed limestone-derived sorbents’ small pores are susceptible to pore blockage during carbonation. H₂O addition further narrows the sorbents’ pores and increases reactivity with CO₂ enhancing pore blockage. Limited sulfation deactivates sections of the sorbents’ surface and introduces some resistance to pore blockage. In an atmosphere containing both H₂O and SO₂, limited sulfation counteracts the enhanced reactivity caused by H₂O addition and reduces its negative influence. The presence of relatively large macropores (> 200 nm) in certain metamorphosed limestone-derived sorbents dampen the influence of the smaller pores on capture behavior. Furthermore, metamorphosed limestone-derived sorbent sulfation transforms the sorbent upon subsequent recalcination leading sulfated metamorphosed limestone-derived sorbents to behave like unmetamorphosed limestone-derived sorbents (see Figure 3.22).

The different textural evolutions experienced by the unmetamorphosed Riyadh limestone vs. the metamorphosed Saabar limestone result in non-sulfated Saabar sorbent underperforming in terms of co-capture efficiency from wet synthetic flue gas when compared to non-sulfated Riyadh sorbent (see Figure 3.22a). While non-sulfated
Figure 3.21. Illustration of the influence of reaction atmosphere gas composition, and sorbent morphology and composition on capture behavior. The dashed lines indicate the relative unreacted pore volume of metamorphosed limestone-derived sorbent. Copied from [99].
Saabar sorbent retains a higher surface area with cycling, non-sulfated Saabar and Riyadh sorbents exhibit similar CO\textsubscript{2} capture capacities during co-capture from wet synthetic flue gas. The sulfated metamorphosed and unmetamorphosed limestone-derived sorbents perform similarly, with Saabar sorbent exhibiting a slightly higher CO\textsubscript{2} capture capacity and efficiency with increasing cycle number (see Figure 3.22b). This indicates that while metamorphosed limestone-derived sorbent’s susceptibility to CO\textsubscript{2} diffusional resistance and pore blockage by carbonation in the presence of H\textsubscript{2}O is carried through to sorbents with $X_N \approx 0.1$ when cycled in a SO\textsubscript{2}-free environment, sorbent sulfation counteracts these propensities.

From a practical perspective, while metamorphosed limestone may not be preferred for CO\textsubscript{2} capture from pre-scrubbed flue gas sources, this limestone can be used in CO\textsubscript{2} and SO\textsubscript{2} co-capture CaL systems. Metamorphosed limestone attrition and fragmentation rates should be considered when assessing this sorbent’s promise. Preliminary analysis indicates that Saabar sorbent may be more susceptible to both attrition and fragmentation. While little change to the particle size distributions within BFB 1 are observed for any of the cycled sorbent fractions, about 15-20% more fines were collected from the reactor cyclones when Saabar was cycled vs. Riyadh. Furthermore, while gas analyzer data indicate that the metamorphosed and unmetamorphosed limestone-derived sorbents capture the same amount of SO\textsubscript{2} during cycling, elemental analysis reveals that the metamorphosed limestone-derived sorbent has a lower CaSO\textsubscript{4} content (see Table 3.2). The CaO purity of the Saabar sorbent also decreases with cycle number. This indicates that the Saabar sorbent is more prone to
attrition than the unmetamorphosed limestone-derived sorbent, with the newly deposited surface CaSO₄ especially vulnerable to attrition. Saabar limestone’s slightly elevated attrition rate may therefore be favorable under co-capture conditions.

Figure 3.22. The influence of sorbent activity on CO₂ capture behavior from sulfurous flue gas (\(\tau_0 = 4.7\) mins). (a) Non-sulfated sorbents, and (b) sulfated sorbents. Dotted lines used for \(X_N \approx 0.6\), dashed lines for \(X_N \approx 0.3\), and solid lines for \(X_N \approx 0.1\).
3.4. Conclusions and Recommendations

This chapter reports on the CO$_2$ and SO$_2$ capture behavior of Saudi Arabian limestones. Both metamorphosed and unmetamorphosed limestone-derived sorbents were considered. The individual and combined influence of flue gas H$_2$O and SO$_2$ content on sorbent CO$_2$ and SO$_2$ capture performance is investigated. The influence of multiple calcination/carbonation cycles and of CaSO$_4$ accumulation on the limestone-derived sorbents’ textural evolution and capture behavior are also examined. While the unmetamorphosed Riyadh limestone-derived sorbents’ capture performance aligns well with previously studied limestones, the metamorphosed limestone-derived sorbent exhibits anomalous behavior. These experimental results reveal that:

1. Contrary to expectations, calcined metamorphosed limestone CO$_2$ capture performance is negatively influenced by flue gas H$_2$O content, and positively influenced by flue gas SO$_2$ content.

2. The negative impact of flue gas H$_2$O content on metamorphosed limestone-derived sorbent CO$_2$ capture performance persists for sorbents with activities ranging from 0.6 to 0.1 mol/mol, when the sorbents have been cycled in a sulfur-free flue gas.

3. Metamorphosed limestone-derived sorbent that has been cycled in sulfurous flue gas exhibits similar capture behavior to unmetamorphosed limestone-derived sorbents.

4. Space time has a significant impact on SO$_2$ and CO$_2$ co-capture performance.
Analyzing the limestone-derived sorbents using material characterization and imaging tools, it is concluded that the distribution of impurities in the metamorphosed limestone-derived sorbent matrix is ultimately responsible for the sorbent’s capture behavior. The metamorphosed limestone is primarily composed of large monomineralic phases separated by clear boundaries. The large, relatively pure, and highly crystalline monomineralic CaCO$_3$ grains in metamorphosed limestone are responsible for the evolution of relatively narrow uniform pores and high purity crystalline CaO with low overall porosity upon calcination. These morphological characteristics are likely responsible for the anomalous capture behavior of the metamorphosed limestone-derived sorbent. It is postulated that the calcined metamorphosed limestone’s high CaO purity, narrow pores and low porosity translate to higher surface reactivity and increased susceptibility to pore blockage during carbonation. As a result, flue gas H$_2$O content, known to enhance CaO reactivity with CO$_2$ and cause pore narrowing, exacerbates metamorphosed limestone-derived sorbent pore blockage. Furthermore it is proposed that the introduction of a limited amount of impurities in the form of CaSO$_4$ may pacify sections of the metamorphosed limestone-derived sorbent’s highly reactive matrix and introduce some resistance to smaller pore blockage due to fast surface carbonation. It is also reported that:

1. Cycling metamorphosed limestone in an atmosphere containing SO$_2$ preserves the sorbent’s porosity, and increase the sorbent’s grain and pore sizes, resulting in sulfated metamorphosed and unmetamorphosed limestone-derived sorbents exhibiting similar capture performance.
2. The influence of calcined metamorphosed limestones’ narrow pores on capture behavior is dampened in sorbents with a secondary population of large macropores (> 200 nm).

These findings indicate that the metamorphosed limestone may be more prone to attrition and fragmentation than the unmetamorphosed limestone. The mechanical stability of this sorbent is further addressed in Chapter 4. The influence of additional calcination/carbonation cycles and sulfation on the metamorphosed limestone-derived sorbent’s capture behavior is also further addressed in Chapter 4. The understanding gained regarding the underlying morphology that influences the anomalous capture behavior of metamorphosed limestone-derived sorbent will help guide future sorbent selection and design efforts.
Chapter 4

Derivation of a Quantitative Correlation Describing the influence of Sulfation Deactivation on Co-capture

4.1 Introduction

As briefly discussed in Chapter 3, CaO carbonation is a two-stage process characterized by an initial fast, kinetics-limited reaction stage, followed by a slow reaction stage that is solid-state diffusion limited \[22\]. From a practical standpoint, only the fast reaction stage is relevant for CaL. Consequently, sorbent capture capacity, or activity, is pragmatically defined as the maximum achievable conversion of CaO to CaCO\(_3\), \(X_N\), at the end of the fast reaction stage \[59\]. Wang and Anthony demonstrated that the decay of this maximum conversion is analogous to catalyst sintering, and Grasa and Abanades proposed the following semi-empirical model relating maximum conversion to cycle number, \(N\) \[24,57\]:

\[
X_N = \frac{1}{1/(1 - X_r) + kN} + X_r \tag{4.1}
\]

Limestone’s residual activity after countless cycles, \(X_r\), and the deactivation “constant”, \(k\), are dependent on cycling conditions, including flue gas composition and calciner and carbonator residence times, and to a lesser degree, on limestone source \[57,70\]. Most limestones, when cycled in a sulfur-free environment, exhibit comparable sintering rates
under a wide range of relevant conditions, while sulfation deactivation by SO$_2$ is strongly limestone dependent [23,57,59,87,90,91,100].

The influence of sulfation on the deactivation rate of different limestone-derived sorbents during CO$_2$ and SO$_2$ co-capture from sulfurous flue gases has been discussed qualitatively in multiple studies, but few studies have attempted to develop a quantitative correlation describing this effect [58,87,92,101,102]. In most studies assessing CaL implementation at coal-fired power plants, sulfation deactivation was either considered negligible, or modeled by assuming stoichiometric conversion of CaO to CaSO$_4$, $X_{CaSO4}$ such that [73,75,103,104]:

$$X_N = \frac{1}{1/(1 - X_r) + kN} + X_r - X_{CaSO4}$$

(4.2)

These treatments of sulfation deactivation lead to inaccurate assessments of whether or not separate FGD installations are required. Grasa et al. demonstrated that SO$_2$ can react with sorbent that is unavailable for carbonation, leading to an activity greater than that estimated by Eq. 4.2, and multiple studies have demonstrated that CaO conversion to CaSO$_4$ may cause sorbent pore blockage, reduced access to active capture sites, and reduction in sorbent activity beyond Eq. 4.2 predictions [23,87,91].

Notably, in a preliminary analysis, Romano roughly correlated the extent of sulfation of Piaseck limestone-derived sorbent per cycle to changes in $X_r$ and $k$, and concluded that CaL could reasonably eliminate the need for a separate FGD installation at coal-fired power plants [53]. However, the deactivation correlation developed by Romano assumes that sulfation deactivation is primarily influenced by the extent of
sulfation, with sulfation conditions playing an irrelevant role [53]. A sulfation
deactivation model that accounts for the influence of flue gas steam content on
deactivation, and corrects for the reactivating effect experienced by sorbents when the
carbonation reaction is allowed to proceed past the fast reaction stage and into the slow
reaction stage has not been introduced yet [105]. A quantitative correlation more
accurately describing the influence of sulfation deactivation on the overall deactivation
rate is required to adequately assess the feasibility of using a specific limestone for co-
capture from sulfurous power plant flue gas.

In this chapter a three step thermogravimetric method is proposed for
developing a quantitative correlation that describes limestone deactivation by sulfation
under conditions relevant for CO₂ and SO₂ co-capture from sulfurous power plant flue
gases. Using this method, the sulfation deactivation of the two structurally-distinct
Saudi Arabian limestones studied in Chapter 3 are modeled. The developed correlation’s
validity is verified by subsequent pilot-scale testing. A revised semi-empirical model
valid for sorbents with very distinct structure and sulfation behavior and accounting for
sulfation deactivation and the reactivating influence of slow stage carbonation is
proposed. In Chapter 5, this model is used to assess the feasibility of co-capture from
HFO power plant flue gas.

4.2. Experimental Section

The same Riyadh and Saabar Saudi Arabian limestones used in Chapter 3,
provided by UMIC in Saudi Arabia are utilized in this study. These limestones were
milled by BHS-Sonthofen GmbH and sieved by Allgaier Process Technology GmbH to a particle size distribution between 100-400 µm. The experiments described below were performed at IFK facilities.

4.2.1 Thermogravimetric Analysis

The custom STA unit equipped with a gas mixing manifold, described in Chapter 3, was used to execute controlled temperature and gas flow rate programs simulating 25 calcination/carbonation cycles per experimental run. Calcination was performed at 950 °C, in a 70% CO₂ and 30% H₂O atmosphere, simulating oxy-combustion conditions. Note that SO₂ is not introduced in the calcination purge. The relatively long temperature ramp times are not representative of typical CaL calcination times, and would lead to excessive sulfation and deactivation. Carbonation was performed at 650 °C in 12% CO₂, 3% O₂, and 10% H₂O, with SO₂ content and carbonation times varied. The experimental matrix is presented in Figure 4.1. TGA was performed on a 10 mg (± 1) sample of limestone. Total purge flow rate, carbonation to calcination temperature ramp, and calcination to carbonation cooling rate were maintained at 100 mL/min, 400 K/min and -200 K/min, respectively. Deactivation curves for Saabar and Riyadh limestones were generated using the recorded changes in sample mass.

The experimental Sets 1-3, presented in Figure 4.1 allow: (1) measuring the $k$ and $X_r$ values for each limestone when cycled under conditions relevant for CaL implementation at an HFO-fired power plant, (2) developing a quantitative correlation describing limestone deactivation due to sulfation, and (3) accounting for the influence
of extended carbonation/sulfation reaction times that extend into the solid-state diffusion-controlled capture stage.

![Graph showing SO2 Concentration vs Carbonation Time with labeled sets: Set 1, Set 2, Set 3.]

**Figure 4.1.** Experimental sets summarized.

4.2.2 Pilot-Scale Testing

Pilot-scale experiments were performed using IFK’s electrically heated 20 kWth dual fluidized bed (DFB) test facility. This facility, described in detail elsewhere, comprises interconnected bubbling fluidized bed (BFB) and circulating fluidized bed (CFB) reactors (see Figure 4.2) [106,107]. In this set of experiments the BFB is used as the carbonator and the CFB as the calciner. Briefly, sorbent is fed into the BFB, which is 150 mm in diameter and 3.5 m tall. Carbonated sorbent proceeds through an overflow pipe and is transported from the BFB, through a fluidized loop seal, the lower loop seal (LLS), to the CFB riser. The calcined sorbent is entrained through the CFB riser, which is 70 mm in diameter and 12.4 m tall, and separated from the gas stream by a cyclone. The calcined sorbent is then transported through a standpipe to second fluidized loop seal,
the upper loop seal (ULS). The flow rate of calcined sorbent into the BFB is modulated by the ULS cone valve, with the remaining sorbent recirculated to the CFB riser. Each of the CFB and BFB are equipped with a double cyclone system and candle filter for separating entrained fines from the reactor effluent before sampling by gas analyzers (a ABB Advance Optima 2020 and an X-STREAM Emerson Process Management GmbH & Co. OHG respectively) for continuous CO\(_2\), SO\(_2\), and O\(_2\) monitoring.

![Simplified schematic diagram of IFK’s 20 kW\(_{th}\) DFB CaL test facility.](image)

**Figure 4.2.** Simplified schematic diagram of IFK’s 20 kW\(_{th}\) DFB CaL test facility.
Three experimental sets (Set 4-6) were performed per limestone (Riyadh and Saabar) using the DFB system. In all experimental sets, the DFB was run under co-capture conditions with the BFB temperature set to 650 °C and influent gas composition set to 12% CO₂, 10% H₂O, 1-2% O₂ and 2000 ppm SO₂. The CFB calciner was operated at 950 °C with a fluidization velocity of 3 m/s. At the start of each experimental set, 20-25 kg of precalcined limestone was fed into the DFB. In experimental Set 4, the limestone deactivation rate when cycled without exposure to sulfation in the calciner was considered. The CFB influent gas composition was set to 69% CO₂, 29% H₂O and 2% O₂, the BFB fluidization velocity was maintained at 0.5 m/s, the sorbent recirculation rate kept constant. In experimental Set 5, the influence of sulfation in the calciner was considered, and the CFB influent gas composition was set to 68.8% CO₂, 29% H₂O, 2% O₂, and 2000 ppm SO₂. The BFB fluidization velocity was maintained at 0.5 m/s, the sorbent recirculation rate kept constant. In Set 6, the influence of variable BFB space times and sorbent recirculation rates were considered. With a CFB influent gas composition set to 68.8% CO₂, 29% H₂O, 2% O₂, and 2000 ppm SO₂, BFB fluidization velocities were varied between 0.5-1.0 m/s and looping ratios between 1 – 10 mol/mol.

Gas analyzer data in addition to relevant system operating conditions, such as influent gas flow rates and the system temperature and pressure profiles were logged. The sorbent recirculation rate, or looping rate, was measured by closing a valve downstream of the cone valve and measuring the time required for a pipe segment of known volume to fill with calcined sorbent. After each experimental run, fines were collected from the cyclones and candle filters and weighed. During experimental runs,
sorbent was intermittently sampled from the LLS and ULS. The sorbent density was measured and an elemental analysis was performed by Huffman Hazen Laboratories, CO USA. The capture capacity of the sorbent samples were measured by TGA. A Mettler Toledo TGA/DSC 1 instrument was used. Briefly, 13-mg (± 3 mg) samples were heated (20 °C/min) to 500 °C in N$_2$ and then temperature ramp rate was increased to 100 °C/min with the gas switched to CO$_2$. The sample was allowed to carbonate at 650 °C for 20 minutes. The recorded changes in sample mass were used to calculate $X_N$.

4.3. Results and Discussion

4.3.1 Semi-Empirical Model Development

During experimental Sets 1-3 carbonation persists into the slow reaction stage, allowing visualization of the inflection point between the reaction stages, and therefore measurement of $X_N$ after each cycle (see Figure 4.3). This introduces an experimental artifact by allowing solid-state diffusion controlled carbonation, which is known to reactivate the sorbent upon subsequent calcination [61]. Arias et al. demonstrated that slow stage reactivation is directly proportional to fast stage conversion, and the inclusion of a correction factor, $A$, in Eq. 4.1 eliminates the influence of reactivation on $k$ and $X_r$ [105]:

$$X_N = \left( \frac{1}{1/(1-X_r) + kN} + X_r \right) (1 + A)$$  \hspace{1cm} (4.3)

The correction factor, $A$, is a function of carbonation time, and for short carbonation time spans (< 1 hr) a linear relationship between $A$ and carbonation time can be
reasonably assumed [105]. Note that $X_N$ is calculated from the mass change measured by the TGA, and elemental analysis data such that:

$$X_N = \frac{\Delta m_{N,CO_2}}{M_{CO_2} n_{CaO,o}}$$  \hspace{1cm} (4.4)

where $\Delta m_{N,CO_2}$ is the mass change measured by the TGA due to carbonation in cycle $N$, $M_{CO_2}$ is the molar mass of $CO_2$, and $n_{CaO,o}$ is the initial molar amount of $CaO$ introduced into the TGA:

$$n_{CaO,o} = \frac{\Delta m_{0,CO_2}}{M_{CO_2}}$$ \hspace{1cm} (4.5)

Sorbent sulfation is similarly calculated using the following equation:

$$X_{CaSO_4} = \sum_{1}^{N} \frac{\Delta m_{N,SO_2}}{M_{SO_2} n_{CaO,o}}$$  \hspace{1cm} (4.6)

![Figure 4.3. Example TGA response curve.](image)

Riyadh and Saabar sorbents’ $k$ and $X_r$ values are derived from deactivation curves obtained by cycling the sorbents in a $SO_2$-free environment (experimental Set 1). The least squares method is used to fit Eq. 4.3 to each of Set 1 deactivation curves, with
the constraint that $k$ and $X_r$ are unaffected by different carbonation times while $A$ is variable. Deactivation curves for experimental Set 1 and the corresponding regressed models are presented in Figures 4.4a-b. Values for Riyadh and Saabar’s $X_r$ (0.097 and 0.087 respectively) are similar to the average $X_r$ typically reported for limestone ($\sim 0.079$) [57]. The $k$ values for Riyadh and Saabar limestone, when cycled under conditions relevant for capture from HFO power plants, are 0.84 and 0.79 respectively.

Figure 4.4. Deactivation curves for (a) Riyadh, (b) Saabar, and (c) both Riyadh and Saabar limestones when cycled in SO$_2$-free HFO flue gas. (d) Deactivation curves as predicted by Eq. 4.1, using derived $X_r$ and $k$ values. Empirical data is represented by discrete points, and solid lines depict Eq. 4.3 model fit.
Comparing experimental deactivation curves obtained under similar conditions, it would seem that Riyadh limestone is slightly less susceptible to deactivation than Saabar limestone when cycled in an SO$_2$-free atmosphere (see Figure 4.4c). However, Saabar limestone is more crystalline than Riyadh limestone, and therefore less susceptible to solid-state diffusion and reactivation [65,99]. The discrepancy between Riyadh and Saabar limestone deactivation is eliminated by removing the reactivation effect (see Figure 4.4d), and as expected, the different limestones exhibit similar deactivation rates in an SO$_2$-free environment. Note that a linear correlation between the correction factor $A$ and carbonation time was found for carbonation times between 4-15 mins.

Figure 4.5 shows the deactivation curves for limestone exposed to flue gas containing SO$_2$ (experimental Set 2). As expected, the deactivation rate increases with increasing flue gas SO$_2$ content. The solid lines in Figures 4.5a-b correspond to Eq. 4.2 deactivation predictions. As can be seen, Eq. 4.2 does not provide a good fit. The solid lines in Figures 4.5c-d correspond to the predictions made by the sulfation deactivation correlation proposed by Romano [53]. While Romano’s correlation provides a better fit than Eq. 4.2, this correlation also does not provide a good fit for flue gases with SO$_2$ content > 400 ppm. An amended co-capture deactivation semi-empirical model is proposed.

A sulfation deactivation correction factor, $B$, is proposed, accounting for the accelerated sorbent deactivation rate due to CaSO$_4$ accumulation. Since sulfation is irreversible under CaL conditions, sulfation will eventually completely deactivate the
sorbent, therefore it is assumed that \( X_r = 0 \). A second correction factor, \( A^* \), is introduced to correct for slow stage sulfation occurring during the slow carbonation stage, or slow stage sulfation. Since slow stage sulfation is expected to be additive and inversely related to sorbent activity, the proposed amended co-capture deactivation semi-empirical model is [99]:

\[
X_N = \left( \frac{1}{1 + kBN} \right) (1 + A) - NA^* \left( \frac{1}{1 - X_r + B \cdot kN} + X_r \right)
\]

(4.7)

**Figure 4.5.** Deactivation curves for the limestones when cycled in sulfurous flue gas.

Solid lines represent deactivation predictions by previously published models.
Figure 4.6 shows the deactivation curves for experimental Set 2 and the corresponding Eq. 4.7 regressions. Using the previously derived values for $k$ and $A$, Eq. 4.7 allows a better fit than previously reported deactivation models. Regressing Eq. 4.7 against experimental Set 3, we find that the reactivating influence of extended carbonation times overshadows the deactivating influence of extended sulfation (see Figure 4.7). When a 10-min carbonation time and a 400 ppm SO$_2$ influent concentration
is used, sharp sorbent deactivation is observed around $N > 16$, once $X_N < 0.05$. This deactivation is not tracked well by Eq. 4.7 but can be represented by a linear relationship if needed. Sorbent deactivation from $X_N = 0.05$ to $X_N = 0$ is assumed less consequential than initial deactivation from $X_N \approx 0.6$ to $X_N = 0.05$.

Figure 4.7. Deactivation curves for (a) Riyadh and (b) Saabar limestones when cycled in flue gas with 200 ppm SO$_2$, and (c) Riyadh and (d) Saabar limestones when cycled in flue gas with 400 ppm SO$_2$. Semi-empirical fit uses Eq. 4.7.

It should be noted that the influence of slow stage sulfation on deactivation is not proportional to increased sorbent exposure to SO$_2$ (see Figure 4.8). The influence of
slow stage sulfation deactivation plateaus, with $A^*$ remaining relatively small ($A^* < 150 \cdot A$). Note that $A^*$ plays an increasing role with cycle number.

Sorbent deactivation can be divided into two stages: “primary deactivation”, relating to the fast deactivation rate experienced during the initial calcination/carbonation cycles, and “secondary deactivation”, referring to the relatively slow linear deactivation rate experienced after the deactivation curve inflection point. The influence of slow stage sulfation deactivation on secondary deactivation is stronger, yet less consequential. Since slow stage sulfation appears to have minor influence on sorbent deactivation, and $A^*$ is dropped from the final semi-empirical model. Note that a reasonable fit is retained when $A^*$ is dropped ($0.85 < R^2 < 0.99$ for examined cases).

![Graph](image)

**Figure 4.8.** The influence of influent SO$_2$ concentration on slow stage sulfation (4 minute carbonation time).

Examining CaO sulfation per cycle number (see Figure 4.9) reveals that the increase in sorbent deactivation rate with increasing flue gas SO$_2$ content is not
proportional to the extent of sulfation per cycle. For Riyadh sorbent, CaO conversion to CaSO₄ per cycle is proportional to the total amount of SO₂ introduced into the TGA regardless of carbonation time and SO₂ concentration. However, while $X_{N,CaSO_4}$ for Riyadh sorbent exposed to 200 ppm of SO₂ for 10 minutes is higher than that for Riyadh sorbent exposed to 400 ppm of SO₂ for 4 minutes (Figure 4.9a), this higher extent of sulfation does not equate to greater deactivation (Figure 4.7a & c). As discussed in Chapter 3, metamorphosed limestone-derived Saabar sorbent’s morphology confers this sorbent with a resistance to slow stage sulfation in atmospheres containing steam. Extended carbonation times therefore play less of a role on Saabar sorbent conversion to CaSO₄ than influent SO₂ concentration, with sorbent exposed to 400 ppm of SO₂ for 10 minutes experiencing a lower extent of sulfation than sorbent exposed to 800 ppm of SO₂ for 4 minutes (Figure 4.9b)

Experimental Set 2-3 results indicate that (1) sulfation occurring during the fast carbonation stage is mainly responsible for sulfation deactivation, (2) initial slow stage sulfation involves SO₂ reacting with sorbent unavailable for carbonation and has little impact on sorbent deactivation, and (3) at later cycle numbers, once $X_N < 0.05$, allowing longer periods of slow stage sulfation eventually leads to active sorbent sulfation and enhanced deactivation. It is concluded that the mode of sulfation has a greater influence on sorbent deactivation than the extent of sulfation per cycle number. In Chapter 3 it is demonstrated that the relative extent of sulfation with respect to carbonation during the fast carbonation stage is more meaningful for predicting sorbent activity than the extent of sulfation alone (see Figure 3.10). It is therefore proposed that
the relative rate of sulfation with respect to carbonation during the fast carbonation stage may be better suited for estimating sulfation deactivation. Since SO₂ and CO₂ capture by CaO during the fast reaction stage are first order reactions with respect to SO₂ and CO₂ concentrations respectively, a correlation relating $B$ to the influent molar ratio of SO₂ to CO₂ is proposed [108,109].

![Figure 4.9](image)

**Figure 4.9.** Extent of conversion to CaSO₄ per cycle number for (a) Riyadh and (b) Saabar limestones.
Figure 4.10. Deactivation factor dependence on flue gas sulfur content.

Figure 4.10 reveals that $B$ varies linearly with the molar ratio of SO$_2$ to CO$_2$ in the influent flue gas, $r_{SO_2/CO_2}$, and that Riyadh limestone is more strongly affected by deactivation due to sulfation than Saabar limestone. The linear relationship between the sulfation deactivation factor, $B$, and the ratio of SO$_2$ to CO$_2$ in the capture environment allows the adoption of a simple methodology for characterizing sulfation deactivation by different limestones. Since most limestones have similar $X_r$ and $k$ values, a total of three TGA runs, referred to as Runs 1-3, are required to model the deactivation rate of a limestone sorbent under a range of SO$_2$ concentrations. Runs 1 and 2, performed with different carbonation times but similar SO$_2$, CO$_2$, H$_2$O and O$_2$ gas concentrations during carbonation, generate a linear correlation for $A$, which is
limestone dependent. Runs 1 and 3, performed with similar carbonation times but a
different ratio of \( \text{SO}_2 \) to \( \text{CO}_2 \) generate a linear correlation for \( B \). Correction factors \( A \) and \( B \) are determined by fitting the resulting data from Runs 1-3 to the following amended
semi-empirical model:
\[
X_N = \left( \frac{1}{1/(1 - X_r) + k BN} + X_r \right) (1 + A) \tag{4.8}
\]
The validity of this model when applied to deactivation in DFB systems is explored in
pilot scale experiments performed at IFK’s facilities.

4.3.2 Pilot-Scale Results

During the pilot scale experiments, sorbent is continuously cycled between the
calciner and carbonator and therefore cycle number determination is not
straightforward. The equivalent cycle number, or the cycle number assuming each cycle
leads to full carbonation, is calculated using the following equation:
\[
N_{eq} = \int_0^t \frac{F_{\text{CaO}} X_{\text{carb}}}{m X_N} \, dt \tag{4.9}
\]
Where \( m \) is the total mass of sorbent in the DFB system, \( F_{\text{CaO}} \) is the sorbent
recirculation rate, and \( X_{\text{carb}} \) is the extent of sorbent carbonation in the carbonator. Gas
analyzer data and a mass balance is used for calculating \( X_{\text{carb}} \) [110]:
\[
X_{\text{carb}} = \frac{\dot{F}_{\text{CO}_2,0} E_{\text{CO}_2}}{\dot{F}_{\text{CaO}}} \tag{4.10}
\]
Capture efficiency, \( E_{\text{CO}_2} \), calculated from Eq. 3.1, with TGA performed on sorbent
samples collected from the LLS was used to determine \( X_N \).
Figure 4.11. Deactivation curves for Riyadh and Saabar limestones when cycled in the DFB system with (a) no SO$_2$ in the calciner and (b) 2000 ppm SO$_2$ fed into the calciner.

Figure 4.11a displays the deactivation curves for Riyadh and Saabar limestones when cycled with SO$_2$ in the carbonator influent and no SO$_2$ in the calciner influent (experimental Set 4). These conditions are analogous to the conditions used during the derivation of the semi-empirical model presented in Section 4.3.1. Note that the concept of $N_{age}$, first introduced by Grasa et al., is used to determine the initial cycle number [111]. Grasa et al., defined the age of the sorbent, $N_{age}$, as the theoretical
number of full calcination/carbonation cycles required to achieve the $X_N$ of the sorbent. Using Eq. 4.8, $N_{age}$ is defined as [111]:

$$N_{age} = \frac{1}{kB} \left( \frac{1}{X_N - X_r} - \frac{1}{1 - X_r} \right)$$  \hspace{1cm} (4.11)

The theoretical deactivation curves for Riyadh and Saabar sorbent cycled under similar conditions are calculated using Eq. 4.8 and plotted in Figure 4.11a. The correction factor $B$ is calculated using the average inlet CO$_2$ and SO$_2$ concentration per experimental run. Since $r_{SO_2/CO_2}$ is sensitive to the inlet SO$_2$ concentration, the inlet SO$_2$ concentration is determined by solving a mass balance across the BFB such that:

$$\dot{F}_{SO_2,o} = \dot{F}_{SO_2} + \dot{F}_{CaO}(x_S - x_{S,o})$$  \hspace{1cm} (4.12)

where $\dot{F}_{SO_2}$ is the outlet molar flowrate of SO$_2$, $x_{S,o}$ and $x_S$ are the molar fractions of sulfur in the carbonator influent and effluent sorbent. Knowing the extent of sulfation of samples taken from the ULS and LLS and the effluent SO$_2$ concentrations, it was determined that the carbonator inlet SO$_2$ concentration varies from 1,800 to 2,500 ppm across the different experimental runs. With a 12% inlet CO$_2$ concentration, experimental $r_{SO_2/CO_2}$ varies between 15.0 to 20.3 mmol/mol. Calculating $B$ from these $r_{SO_2/CO_2}$ values provides a good fit for both Riyadh and Saabar sorbents, with $R^2 = 0.96$ (see Figure 4.11a). Note that the kink in the theoretical deactivation of Riyadh sorbent seen in Figure 4.11a is due to the shift from $X_{carb} > X_N$ to $X_{carb} < X_N$ and therefore the change from $A = 0$ to $A = f(t_r)$ where $f(t_r)$ refers to a linear function of sorbent residence time in the BFB carbonator. The good fits obtained for both Riyadh and
Saabar sorbents support the validity of Eq. 4.8 and the proposed quantitative correlation used for describing sulfation deactivation.

Figure 4.11b displays the experimental deactivation rates for Riyadh and Saabar sorbent cycled with ~ 2000 ppm SO\textsubscript{2} introduced into both the carbonator and calciner, corresponding to experimental Set 5. A correction factor $B^*$ is introduced into Eq. 4.8 to account for the additional deactivation due to SO\textsubscript{2} in the calciner:

$$X_N = \left( \frac{1}{1/(1 - X_r) +kB^*N + X_r} \right) (1 + A) \quad (4.13)$$

This model is regressed against the experimental data from Set 5, and the results are plotted in Figure 4.11b. While the SO\textsubscript{2} capture efficiency in the calciner is similar for both Riyadh and Saabar limestone (> 99\%), Riyadh sorbent experiences stronger deactivation due to calciner sulfation than Saabar sorbent with $C = 1.13$ for Saabar and $C = 2.03$ for Riyadh. The validity of these results are supported by experimental Set 6, presented in Figure 4.12. During experimental Set 6, Riyadh and Saabar sorbent are cycled with ~ 2000 ppm SO\textsubscript{2} introduced into both the carbonator and calciner, and the sorbent circulation rate and BFB fluidization velocity are varied such that $0.02 < X_{carb} < 0.25$. Deactivation under a range of conditions is considered and the amended semi-empirical model, Eq. 4.13, acceptably predicts the deactivation rate experienced in Set 6. While correction factor $B^*$ is a rough estimate, it once again highlights (1) the influence of limestone source on deactivation behavior, (2) the influence of sulfation mode on deactivation behavior, and (3) the disconnect between extent of sulfation and sorbent deactivation. A more considered treatment of calciner sulfation deactivation is recommended.
It should be noted that even with sorbent exposure to ~ 2000 ppm of SO\textsubscript{2} in the carbonator and calciner, and with up to 12\% sorbent sulfation achieved (see Figure 4.13), the apparent $X_r$ remains relatively high. Arias et al. similarly found high residual activities in their pilot scale studies with coal [112]. This observation is in part attributed to sorbent reactivation by extended carbonation times, which is found to play a significant role in deactivation behavior. The higher sulfation rate of more deactivated sorbent may also play a shielding role, reducing higher activity sorbent exposure to SO\textsubscript{2}. Further experiments with longer cycle times are recommended to further explore this effect.

Attrition and fragmentation rates were measured during the course of the cycling experiments, and these rates were found to be relatively slow, about 1.0 g/min and 1.3 g/min for Saabar and Riyadh respectively. For reference, limestone make up
feed rates on the order of tonnes per hour are expected [53]. Results from Chapter 3 indicate that Saabar limestone experiences more attrition and fragmentation than Riyadh limestone, but in this study the opposite behavior is observed. It is proposed that that discrepancy is due to the quick cooling and heating experienced by the sorbents between calcination and carbonation cycles in Chapter 3. Since the sorbents where regularly removed from the 900 °C reactor and exposed to room temperature, and then dropped back into the reactor at 650°C, the thermal stresses had a stronger impact on
the denser more crystalline Saabar sorbent in Chapter 3 experimental runs. When cycled continuously, the Saabar sorbent does not experience these stresses and is more resistant to fragmentation. It is also observed that without exposure to these thermal stresses, Saabar sorbent retains its resistance to sulfation deactivation. Without exposure to thermal stresses less cracks or macropores are formed in the Saabar sorbent structure, Saabar sorbent retains its structure and is less susceptible to sulfation deactivation. Finally, since Saabar likely experiences sulfation on it’s surface, with little SO\textsubscript{2} intrusion into its pores, attrition experienced by this sorbent can remove CaSO\textsubscript{4} exposing active sorbent.

4.4. Conclusions and Recommendations

Using TGA, the deactivation rates of two structurally distinct limestones were examined at conditions relevant for CO\textsubscript{2} and SO\textsubscript{2} co-capture from HFO-fired power plant flue gas. A revised semi-empirical model accounting for the influence of sulfation on limestone deactivation was developed. The validity of this model was supported by pilot-scale experiments. It was concluded that the mode of sulfation has a greater influence on sorbent deactivation than the extent of sulfation per cycle number, with slow stage sulfation minimally impacting deactivation. A sulfation deactivation factor correlated to the relative rate of sulfation with respect to carbonation during the fast carbonation stage was introduced. This deactivation factor was found to vary linearly with the ratio of SO\textsubscript{2} to CO\textsubscript{2} in the reactor influent. This finding allows the adoption of a simple three-step TGA methodology for characterizing sulfation deactivation of different
limestones under a range of SO$_2$ concentrations in the carbonator. Moreover, results from this study indicate that when not exposed to thermal stresses, the Saabar limestone retains its resistance to sulfation deactivation with cycling. Saabar limestone also appears to be slightly less susceptible to attrition and fragmentation and more resistant to sulfation deactivation in the calciner. While more work is required to better model sulfation deactivation in the calciner, using the developed semi-empirical model reasonable limits on operating parameters for CaL implementation at HFO-fired power plants can be calculated. The results of these calculations and a discussion are presented in Chapter 5.
Chapter 5

Concluding Assessment of CaL Implementation at an HFO-Fired Power Plant

Using the model developed in Chapter 4, reasonable limits on operating parameters for CaL implementation at an HFO-fired power plant can be calculated. In this chapter, a final assessment of CaL implementation at an HFO-fired power plant is made. A discussion is devoted to the influence of limestone sulfation behavior on power plant energy efficiency and on implications for power plant process design.

Regardless of sorbent deactivation, sufficient CO$_2$ capture efficiency is maintained by manipulating two process parameters: (1) the looping ratio, $LR$, and the (2) make up ratio, $MR$, respectively defined as:

$$LR = \frac{\dot{F}_{CaO}}{\dot{F}_{CO_2,o}}$$  \hspace{1cm} (5.1)

$$MR = \frac{\dot{F}_{CaO,o}}{\dot{F}_{CO_2,o}}$$  \hspace{1cm} (5.2)

Where $\dot{F}_{CaO,o}$ is the flow rate of make up CaO introduced into the system. Increasing $LR$ and/or $MR$ increases carbonator sorbent inventory activity, which in turn increases carbonator capture efficiency [59,113]. However, increasing $LR$ and/or $MR$ also increases the rate of cold material entering the calciner, which in turn increases the calcination load. Since Cal’s primary parasitic load is the calciner’s ASU, optimal CaL system operation involves reducing the energy, and hence oxygen, requirement of the calciner, while maintaining a high CO$_2$ capture efficiency [73]. For a given $MR$ and $LR$,
average sorbent activity in the carbonator, $X_{ave}$, can be calculated by solving Eq. 4.13 in parallel with a mass balance:

$$X_{ave} = \sum_{Nage=1}^{\infty} z_{Nage} X_{Nage}$$  \hspace{1cm} (5.3)$$

Where, assuming full calcination in the calciner, the fraction of particles that have been cycled $N$ times, $z_{Nage}$, is:

$$z_{Nage} = \frac{MR/LR \cdot \left(\frac{X_{carb}}{X_{ave}}\right)^{Nage-1}}{(MR/LR + X_{carb}/X_{ave})^N}$$  \hspace{1cm} (5.4)$$

Derivation of Eq. 5.4 can be found elsewhere [114]. Fitting results from Eq. 4.13 to an equation of the form of Eq. 5.5 allows the use of the Eq. 5.6 to estimate $X_{ave}$:

$$X_{Nage} = a_1 f_1^{Nage+1} + a_2 f_2^{Nage+1} + b$$  \hspace{1cm} (5.5)$$

$$X_{ave} = \dot{F}_{CaO,o} \left[ \frac{a_1 f_1^2}{\dot{F}_{CaO,o} + \dot{F}_{CaO} X_{ave} (1-f_1)} + \frac{a_2 f_2^2}{\dot{F}_{CaO,o} + \dot{F}_{CaO} X_{ave} (1-f_2)} + \frac{b}{\dot{F}_{CaO,o}} \right]$$  \hspace{1cm} (5.6)$$

Furthermore, as reported by Rodriguez et al., for any given $MR$ and $LR$, the calciner’s energy requirement, $H_{calciner}$, is [73]:


\[
\frac{H_{\text{calciner}}}{F_{\text{CO}_2,\text{in}}} = \Delta H_{\text{calc}}(X_{\text{carb}}LR + MR) \\
+ \Delta T_{\text{calc}} \left[ Cp_{\text{CaO}}LR(1 - X_{\text{carb}}) + Cp_{\text{CaCO}_3}X_{\text{carb}}LR \right] \\
+ Cp_{\text{CaSO}_4} \frac{\dot{F}_{\text{CaSO}_4}}{F_{\text{CO}_2,\text{in}}} + Cp_{\text{CaCO}_3} \Delta T_o MR 
\]

where the achievable conversion of CaO to CaCO\textsubscript{3} in the carbonator, \(X_{\text{carb}}\), is constrained by \(X_{\text{ave}}\).

This system of mass and energy balances is solved for six scenarios relevant to CaL operation at HFO-fired power plants. \(LR\) and \(MR\) are varied to map a range of possible CaL system operating conditions. Complete conversion of CaCO\textsubscript{3} to CaO in the calciner, 90% carbonator CO\textsubscript{2} capture efficiency, and 99% SO\textsubscript{2} capture efficiency are assumed. Knowing the HFO power plant’s base energy input, \(H_{\text{comb}}\), the relative calciner energy requirement is calculated as:

\[
H_{\text{rel}} = \frac{H_{\text{calciner}}}{H_{\text{comb}} + H_{\text{calciner}}} 
\]

Since CaL’s primary parasitic load is the calciner’s ASU, \(H_{\text{rel}}\) is used as an indicator of process efficiency. Note that while attrition and fragmentation rates were measured and are reported in Chapter 4, these rates were found to be relatively slow, about 1.0 g/min and 1.3 g/min for Saabar and Riyadh respectively, and are neglected in the model.

Scenario 1 assumes CO\textsubscript{2} capture from SO\textsubscript{2}-free, fully desulfurized, HFO flue gas. Since both limestones exhibit similar deactivation rates in SO\textsubscript{2}-free conditions, the energy penalty associated with this scenario is almost identical for Riyadh and Saabar.
sorbents (see Figure 5.1a). The energy penalty is reduced by operating at $X_{\text{carb}} = 0.2$ and $MR = 0.2$, but reducing the fresh limestone feed and operating at an $MR < 0.05$ is possible with a limited additional energy penalty. Relative to the minimum Scenario 1 energy penalty, hereafter referred to as the ‘base case’, operating with an $MR < 0.05$ would lead to a ~ 0.6% point drop in the overall energy efficiency of an HFO-fired power plant with integrated CaL. This calculation is made using the Aspen model described in Chapter 2 and assuming a conservative ASU SEC of 0.3 kWh per kg O$_2$ produced.

Scenario 2 addresses co-capture from pre-scrubbed HFO-fired power plant flue gas with a residual 200 ppm of SO$_2$. This scenario assumes 90% SO$_2$ removal by FGD upstream of the CaL system. Sulfur-free calciner conditions are also assumed. Under these conditions the ratio of SO$_2$ to CO$_2$, $r_{SO_2/CO_2}$, is 1.7 mmol/mol. As seen in Figure 5.1b, Saabar’s relative resistance to deactivation by sulfation translates to higher sorbent activity, and therefore the possibility of a lower energy penalty. A slight increase in minimum $H_{rel}$ is observed when comparing Scenario 2 to the SO$_2$-free case, Scenario 1. Relative to the base case, this increase in minimum $H_{rel}$ translates to a ~ 2.3% point drop in power plant efficiency for Saabar sorbent and a ~ 3.6% point drop for Riyadh sorbent. Note that under Scenario 2, an $MR$ of 0.4 is required to minimize the energy penalty. It is possible to reduce the $MR$ to about 0.2, coinciding with $LR = 22.5$, which is on the high end of acceptable operating conditions [53]. Operating at the reduced $MR$ value imparts ~ 8.1% point drop in efficiency relative to the base case scenario. Note that using a state of the art ASU system with an SEC = 0.16 kWh/kg O$_2$ only reduces this energy penalty to 7.4% points.
Figure 5.1. CaL calciner relative load when implemented at an HFO-fired plant under different scenarios.
Scenarios 3 and 4 (Figures 5.1c-d) address co-capture from 1000 ppm SO$_2$ and 2000 ppm SO$_2$ HFO-fired power plant flue gases respectively ($r_{SO_2/CO_2} = 8.4$-$16.7$ mmol/mol). As the flue gas SO$_2$ content is increased it is observed that: (1) the minimum required $H_{rel}$ and MR further increase, and (2) Saabar limestone is capable of achieving a lower $H_{rel}$ than Riyadh limestone, and does so with a slightly lower MR. Under Scenario 4, for Saabar limestone, the increase in calciner energy requirement translates to $\sim 8.5\%$ point drop in overall plant efficiency relative to the base case, while for Riyadh limestone, $\sim 12\%$ point drop is expected. Recall that utilizing a traditional limestone slurry FGD system to pre-scrub the HFO flue gas imparts a 2-4% efficiency point penalty on this system, while achieving levels of desulfurization slightly lower that that achieved during CaL co-capture [55]. From an energy penalty perspective full desulfurization by CaL co-capture is not competitive with a CaL system wherein SO$_2$ is pre-scrubbed by FGD.

It should be noted that a previous study by Romano on co-capture from coal-fired power plant flue gas, with similar SO$_2$ concentrations, concluded that co-capture is feasible and can be accomplished with an MR $< 0.05$ [53]. However, the sulfation deactivation model used by Romano is less accurate and more optimistic than the semi-empirical model developed and validated in Chapter 4. Note that the analysis performed in this chapter does not account for the higher sulfation rate of more deactivated sorbent, and the possibility that this sorbent may also play a shielding role reducing higher activity sorbent exposure to SO$_2$. Moreover, while it is concluded that SO$_2$ and CO$_2$ co-capture by CaL from untreated HFO flue gas is not advisable, from an energy
efficiency perspective, SO$_2$ and CO$_2$ co-capture by CaL may still be competitive when
compared to FGD and amine scrubbing.

The energy penalty associated with second generation CaL systems allows full
co-capture from HFO flue gas by CaL to remain competitive with FGD and amine
scrubbing from an energy efficiency perspective. More efficient novel CaL system
designs that side-step the ASU energy penalty have emerged. Providing the heat
required for sorbent regeneration by using combined CLC/CaL systems or indirect heat
transfer by means of heat pipes or a heat transfer wall can reduce the overall CaL
energy penalty by 3% points [103,115,116]. Moreover, using concentrated solar power
(CSP) for sorbent regeneration is a promising low energy penalty approach to sorbent
regeneration. A recent review by Yan et al. details the progress on CaL-CSP systems [16].
The thermochemical storage potential of CaL allows temporal uncoupling of the
calcination and carbonation processes; excess sorbent calcined at peak CSP operating
hours can be easily stored for use in a carbonator when needed. Moreover, due to the
TCES potential of CaL sorbent, the high energy demand of calcination during co-capture
can be strategically limited to periods of low power demand [117]. Finally, synergy with
industries that can use the spent limestone as feedstock further increases the
competitiveness of full co-capture with respect to amine scrubbing.

When operating an $MR > 0.2$, it is recommended that spent sorbent is used as
feedstock in other industrial processes [75,114]. Under Scenario 4, an $MR$ of about 0.55
is possible for Saabar limestone. For a 450 MW HFO-fired power plant, a 0.55 $MR$
roughly translates to a requirement of about 235 tonnes of limestone per hour
assuming an overall 95% CO₂ capture efficiency. For comparison, a 450 MW HFO-fired power plant requires a feed rate of about 100 tonnes of HFO/hour.

A more detailed analysis and a full techno-economic study is necessary to determine the optimal: (1) extent of flue gas SO₂ scrubbing or HFO desulfurization required prior to CaL, (2) the impact of CSP and TCES on the cost and energy penalty of the system, and (3) extent of synergy with industry and allowable MR. Note that CaL and FGD are synergistic processes, as spent CaL sorbent can be used as feedstock in traditional wet limestone slurry FGD. Furthermore, unlike amine-based sorbents, 99% desulfurization is not required prior to CaL.

For further discussion of the “big picture” implications associated with the findings in this manuscript, Scenario 5, like Scenario 2 addresses co-capture from pre-scrubbed HFO-fired power plant flue gas with a residual 200 ppm of SO₂. While Scenarios 1-4 and Scenario 6 calculations assume a carbonator residence time equivalent to the reaction time required to achieve \( X_{carb} \), Scenario 5 (Figures 5.1e) assumes carbonation in a BFB with extended carbonator residence time (20 minutes). The additional residence time and associated sorbent regeneration reduces the calciner energy load very slightly. Note that a greater reduction in energy penalty is observed due to regeneration when Riyadh limestone is used; recall that Riyadh is less crystalline than Saabār limestone and therefore more susceptible to regeneration.

The influence of sulfation in the calciner, assuming an influent of 2000 ppm SO₂, on the energy penalty is presented in Scenario 6 (Figure 5.1f). Under these conditions limestone choice plays a very strong role, with the energy penalty only slightly
influenced when Saabar sorbent is used, and significantly impacted when Riyadh sorbent is used. Note that the influence of sulfation in the calciner is based on a preliminary analysis and further work is required to more fully understand the influence of calciner sulfation on sorbent deactivation rates. Excessive sorbent deactivation due to calciner sulfation can be side-stepped by using a non-sulfurous fuel such as natural gas in the calciner, or by utilizing indirect heat or CSP for sorbent regeneration.
Chapter 6

Conclusions and Recommendations

This dissertation reports on high-temperature solid cycling CCS processes, CLC and CaL, and their potential for implementation at HFO-fired power plants. As presented in Chapter 2, a preliminary study performed using Aspen software indicated that while CLC is a competitive CCS technology for implementation at HFO-fired power plants when operated at high pressures, the energy penalty associated with this technology is relatively high when operated under demonstrable conditions, i.e. at atmospheric pressure. Alternatively, the energy penalty associated with CaL implementation at HFO-fired power plants was acceptable under demonstrable conditions, and therefore CaL was selected for further investigation.

Chapter 3 reports on the CO₂ and SO₂ capture behavior of Saudi Arabian metamorphosed and unmetamorphosed limestone-derived sorbents used during CaL. More specifically, this study focused on probing (1) the individual and combined influence of HFO flue gas H₂O and SO₂ content on sorbent CO₂ and SO₂ capture performance, and (2) the influence of multiple calcination/carbonation cycles and of CaSO₄ accumulation on the limestone-derived sorbents’ textural evolution and capture behavior. While the unmetamorphosed limestone-derived sorbents’ capture performance aligns well with results from previous work, the metamorphosed limestone-derived sorbent exhibits anomalous behavior. The experimental results reveal
that, contrary to expectations, calcined metamorphosed limestone CO$_2$ capture performance is negatively influenced by flue gas H$_2$O content, and positively influenced by flue gas SO$_2$ content.

Analyzing the limestone-derived sorbents using material characterization and imaging tools, it is concluded that the distribution of impurities in the metamorphosed limestone-derived sorbent matrix is ultimately responsible for the sorbent’s capture behavior. The metamorphosed limestone is primarily composed of large monomineralic phases separated by clear boundaries. The large, relatively pure, and highly crystalline monomineralic CaCO$_3$ grains in metamorphosed limestone are responsible for the evolution of relatively narrow uniform pores and high purity crystalline CaO with low overall porosity upon calcination. These morphological characteristics are likely responsible for the anomalous capture behavior of the metamorphosed limestone-derived sorbent.

It is postulated that the calcined metamorphosed limestone’s high CaO purity, narrow pores and low porosity translate to higher reactivity and increased susceptibility to pore blockage during carbonation. As a result, flue gas H$_2$O content, known to enhance CaO reactivity with CO$_2$ and cause pore narrowing, exacerbates metamorphosed limestone-derived sorbent pore blocking. Furthermore it is proposed that the introduction of a limited amount of impurities in the form of CaSO$_4$ may pacify sections of the metamorphosed limestone-derived sorbent’s highly reactive matrix and introduce some resistance to smaller pore blockage due to fast carbonation. It is also reported that the influence of calcined metamorphosed limestones’ narrow pores on
capture behavior is dampened in sorbents with a secondary population of large macropores (> 200 nm). These observations can be used to guide future sorbent selection and design efforts.

From a practical standpoint, the results outlined in Chapter 3 indicate that the unmetamorphosed Saudi Arabian limestone, referred to as Riyadh limestone, exhibits similar capture behavior to previously studied European limestones. The metamorphosed Saabar limestone displays reduced susceptibility to sulfation deactivation. In Chapter 4, the deactivation rates of Riyadh and Saabar limestones are modeled at conditions relevant for CO₂ and SO₂ co-capture from HFO-fired power plant flue gas. Using TGA, a revised semi-empirical sorbent deactivation model was developed, with a novel quantitative correlation describing the influence of sulfation deactivation on the overall deactivation rate introduced. The validity of this model is supported by subsequent pilot scale (20 kWₜₜ) experiments. Furthermore, a simple three step method allowing quick modeling of the deactivation rate of different sorbents under a range of relevant conditions is proposed.

Results from the pilot scale experiments presented in Chapter 4 indicate that metamorphosed Saabar limestone may be more promising for CO₂ and SO₂ co-capture from HFO-fired power plants. Saabar limestone (1) retains its resistance to sulfation deactivation with cycling, (2) is slightly less susceptible to attrition and fragmentation than Riyadh limestone, and (3) is more resistant to sulfation deactivation in the calciner.

Using the semi-empirical models developed in Chapter 4, reasonable limits on operating parameters for CaL implementation at HFO-fired power plants were
calculated for Riyadh and Saabar limestones, and the potential for CaL implementation and HFO-fired power plants is reassessed; this analysis is detailed in Chapter 5. While direct SO$_2$ and CO$_2$ co-capture from untreated HFO flue gas is not recommended, 99% flue gas desulfurization upstream of the CaL system is not required. A full techno-economic assessment is required to determine optimal FGD desulfurization levels. As sulfation in the calciner may have further detrimental effects on sorbent deactivation, implementation of a CaL-CSP system is proposed. Limestone-based CO$_2$ capture systems are synergistic with FGD systems, and have TCES potential. Uncovering the full potential of CaL implementation at an HFO-fired power plant requires performing techno-economic studies that explore different plant configurations with varying degrees of FGD, CSP, TCES and CaL integration. The work in this manuscript on local limestone derived sorbent characterization and modeling, and the methodology developed in Chapter 4 that allows quick screening of different limestones for co-capture promise, pave the way for these techno-economic studies.
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