
Investigating Reaction Systems for High-
Temperature Thermochemical Energy
Storage and Discharge Integrated with
Concentrated Solar Power

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Abstract

In this thesis, two distinct reversible chemical reactions were studied for thermochemical energy storage (TCES) applications with a focus on integration with concentrated solar power (CSP): the reversible hydration of calcium oxide with steam and the redox behavior of certain copper manganese mixed metal oxides. A holistic investigation approach was employed encompassing the study of reaction kinetics, reactor design, process configuration, and the performing of a techno-economic assessment.

Kinetic data for the reactions was experimentally obtained under fluidized conditions through this work as well as from recent literature to account for the potential impacts of reaction cycling stresses on the material integrity and reactive performance of the chosen material specifications.

For exploring the potential of advanced large scale technologies that allow for continuous operation, fluidized bed reactor designs were then also used for evaluating the considered systems to assess the efficiency and effectiveness of long term and high volume energy storage processes using these reactions that allow for intermittent renewable energy sources such as solar to have stable energy production outputs over extended periods of time.

Detailed flowsheet designs were then constructed and evaluated at steady-state based on hypothetical solar tower CSP plants at 120 MW_{th} scale incorporating either of the two TCES reaction systems and appropriate power generation cycles; a steam Rankine cycle and a supercritical CO₂ Brayton cycle were designed for the calcium oxide and copper manganese oxide energy discharging systems respectively.

These flowsheets were then parametrically simulated with time variation under several operating scenarios based on historical solar irradiation data for Seville as a case study location and the performance of standalone cyclic storage and discharge cycles and standalone continuous discharging modes were evaluated in terms of technical performance criteria.

Lastly a wide-ranging techno-economic assessment was performed for the two CSP-TCES plant designs by assessing their costs of energy storage and electricity generation and the variations in these figures as a result of varying operating schedules, weather, and geographical location. The overall cost estimates were then benchmarked against those of alternative clean energy storage and power generation technologies to assess the forecasted economic viability of advanced TCES plant designs while the materials and the technology both continue to steadily develop.

Declaration of originality

Herewith I declare that the content of this thesis is primarily my own work and work of others is appropriately referenced. I declare that I am the primary person responsible for the design, construction and preparation of this manuscript including the analysis of all the experimental data presented. Any work carried out as part of a collaborative work has been explicitly stated in the text.

Shiladitya Ghosh, February 2020

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“If I have seen further, it is by standing on the shoulders of giants.”

Sir Isaac Newton, in letters to Robert Hooke

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Chapter 1

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Introduction

Chapter Contents

Sections	Subsections
1. Problem Statement: The Need for Clean Energy Technologies	
2. Aims and Objectives	1. Experimental Investigation Plan 2. Computational Investigation Plan
3. Thesis Structure	

1.1 Problem Statement: The Need for Clean Energy Technologies

Over the last three decades, much research has been devoted to finding ways to mitigate the impacts of anthropogenic greenhouse gas (GHG) emissions on the environment; particularly emissions directly generated by industrial activity on a mass scale. GHG refers to a group of gases that absorb and re-emit radiation at specific wavelengths within the thermal infrared spectrum¹; the concentrations at which they are present in the Earth's lower atmosphere results in them effectively reflecting additional heat back to the surface, causing the global surface temperature to slowly increase, giving rise to 'global warming'.

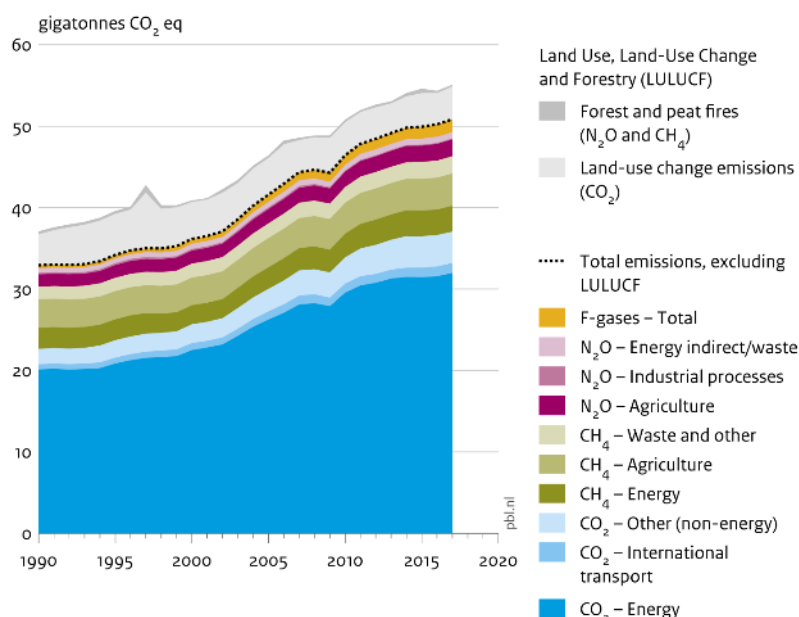


Fig. 1-1: Global GHG emissions by CO₂-equivalent weightage, 1990-2017²

CO₂ is by far the most emitted GHG globally (Fig. 1-1) and thus has been the focus of research into GHG emissions mitigation. Earlier this decade at the 21st Conference of Parties (COP 21), the Paris Agreement was adopted which agreed to reduce anthropogenic GHG emissions to a sustainable level by the end of this century.³ This landmark global legal agreement along with the growing ill-effects of global warming due to CO₂ has made the development and proliferation of renewable energy technologies all the more crucial⁴⁻⁶. However, in mid-2017 the USA officially declared its intent to withdraw⁷ from the Paris Agreement which was a significant setback as they are one of the largest producers of CO₂. This is illustrated in Fig. 1-2 where it is also seen that the annual global CO₂ emission volumes have been rising exponentially since the turn of the century, further qualifying the scale of the problem.

780 Gt of CO₂ are annually released and re-absorbed through natural processes on Earth and this is not thought to contribute towards global warming. However, industrialization activity by humans has resulted at least 30 Gt of CO₂ being additionally released to the atmosphere each year since 2010⁸; only 50% of this

is reabsorbed into the geosphere. As a result of the net increase in above-surface CO₂ inventory annually, the atmospheric CO₂ concentration has been rising by 2 ppm/year.

Calculations have shown that a 100% increase in CO₂ concentration from pre-industrial levels may result in at least a 1°C global temperature rise but secondary effects mean that the effective increase could be more than 3°C.⁹ If the status quo of emission volumes increasing annually keeps up, it is projected that by the turn of the century, the world may be facing a 5.8°C average temperature increase.¹⁰

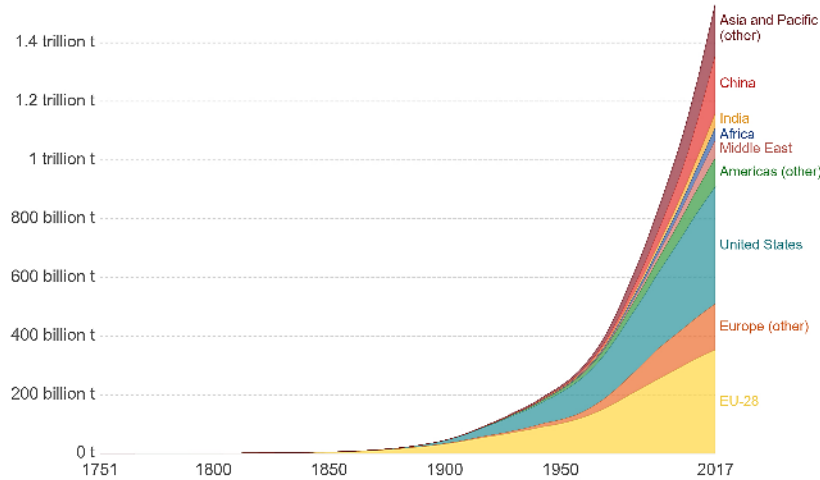


Fig. 1-2: Cumulative global CO₂ emissions over time by regions of the world¹¹

In an effort to address these concerns, a host of new technologies and ideas have been designed and developed specifically with the aim of reducing atmospheric CO₂ concentration rise by preventing its emission. The increased development of clean energy technologies (CETs) is one route, as such technologies, e.g. solar and wind, emit close to zero CO₂ after manufacture. However, they are intermittent in their generation¹² and supply chains are constrained¹³⁻¹⁵, leading to high cost of electricity and inability to provide baseload power. Nuclear energy does offer continuous power generation, albeit with steep costs and nuclear proliferation concerns.¹⁶ Recent efficiency and capacity advances have led to requirements for energy storage technologies to cost-effectively store and release electricity. For example, concentrated solar power (CSP), now has a worldwide installed capacity which has more than tripled from 1.7 GW in 2011¹⁷ to in excess of 6 GW as of 2018¹⁸; this is expected to continue growing by another 3.4 GW by 2024.¹⁹ These increases in scale and efficiency for CETs have led to an increased focus on large-scale energy storage to address intermittency issues which limit their potential for baseload power.

In the case of solar energy storage, the primary form of energy being manipulated is heat. The majority of such systems operate on one of three technologies: sensible²⁰, latent²¹, and thermochemical energy storage (TCES)²². The first technology operates by transferring heat to a single-state storage medium, the second uses heat transfer to effect phase changes in the storage medium, and the third makes use of the reaction

enthalpies of reversible chemical reactions involving the storage medium and additional species to transfer heat. Current CSP plants use latent heat storage using thermal oils or molten salts, which addresses day-to-day intermittency but not seasonal intermittency. TCES (discussed in detail in Chapter 5) is the only technology able to address both day-to-day and seasonal intermittency. While it is at the earliest stages of development, it has the highest potential for future deployment.²³ Hence, the motivation to study TCES processes is the aim of deploying them in lieu of latent heat storage and improving the inter-seasonal power generation capabilities of CSP.

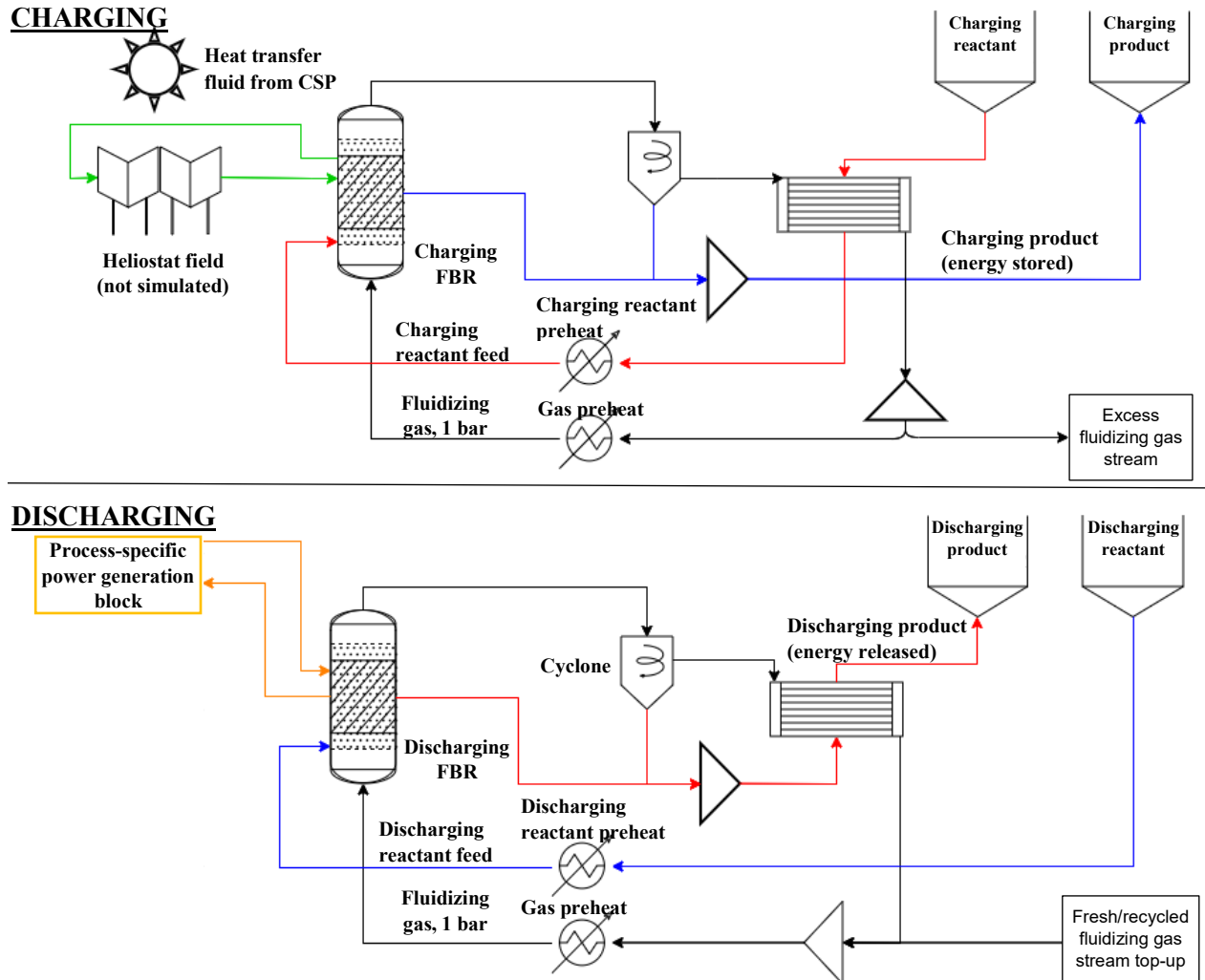


Fig. 1-3: Generic flowsheet of an FBR-based TCES process with a solar receiver and a power generation block; process specific flowsheets presented in Chapters 6 and 7

Fig. 1-3 illustrates the general approach for the integration of TCES with CSP; more detailed process flow diagrams for the TCES systems considered here are in Chapters 6 and 7. During the charging step, solar thermal energy is concentrated by the heliostat field onto a solar tower receiver, heating up a heat transfer fluid. This thermal energy is then transferred to the charging fluidized bed reactor (FBR) to drive an endothermic solid-gas reaction; the reaction products are transferred to insulated storage vessels as a means of energy storage. During the discharging step, the reaction products from the charging step are sent to the discharging FBR to operate an exothermic solid-gas reaction, regenerating material that can be reused for the charging reaction. The heat generated from this reaction is used to drive a power generation block to produce electricity. With an appropriate operating schedule for either reaction, it is thus possible to continuously generate electricity. The process conditions, thermal efficiencies, and economics of such a deployment of TCES with CSP are influenced by the choice of reaction system to be used.

CaO-based reactions are one prominent approach to TCES. Carbonation of CaO has been trialed for both energy storage and carbon capture and storage (CCS), though reaction conditions and conversions differ.²⁴ ²⁵ Hydration of CaO with steam (Eq. 1-1; discussed in detail in Chapter 2) also has potential for TCES; however its kinetics are not fully understood. The CaO hydration reaction is thus of importance for both CCS and TCES and is potentially a crucial reaction for the proliferation of clean energy technologies.



Currently, TCES processes utilise fixed beds, owing to their simplicity, low cost, ease of operation and well-characterised reactor design. However, batch-wise operation is required, including periodic shut down and replacement of ‘spent’ material. Such intermittent operation is incompatible with the requirement to produce electricity on demand, and as such limits the utility of such processes for CSP.

However, in considering continuous reaction processes developed in industry, fluidized bed reactors (FBRs) as used commonly for catalytic cracking²⁶ can also be used for running TCES reactions. Such designs are able to operate continuously (which is a reason for their use in CCS) and so if compatible, they would enable a TCES process to operate for extended periods of time. This would allow an integrated setup connected to CSP to thus discharge solar-to-electrical energy in a stable and continuous manner, greatly increasing the practicality and reliability of solar power generation.

FBRs however are technically complex and their costs tend to be prohibitive. This is due to high material stresses experienced by reacting solids leading to accelerated degradation and thus larger reaction material quantities being needed – a problem faced by the CaO hydration system. The development of supported reaction materials also has scope for application here; one such class of materials are mixed metal oxides (MMOs). Supported MMOs while typically more expensive also potentially offer additional benefits

besides their material durability. Although little success has been achieved in testing MMOs under cycled conditions relevant for TCES, a class of supported copper-manganese MMOs (henceforth CMOs) were recently demonstrated to withstand deterioration under significant high temperature cycling²⁷. The reaction temperatures of the CMO redox systems are 700-1000°C, which are higher than that of the carbonation or hydration of CaO (400-750°C) thereby offering superior thermodynamic efficiencies. This higher temperature range, while too high for current CSP technologies (as discussed in Chapter 5), is expected to be feasible for next-generation CSP technologies – as higher temperature CSP designs have been tested up to 800°C by the Next-CSP project²⁸ and further up to 1000°C by private startup Heliogen in 2019.²⁹

These factors mean that the CMO redox system is also a potential candidate for TCES in a CSP context as upcoming CSP plant designs require such a system for energy storage. Based on these considerations it is clear that there is much scope for the development of TCES to accelerate the transition to a renewable energy future. The CMO redox system and CaO hydration system are two promising candidate TCES systems on a technical basis and so an evaluation of their economic performance is needed to assess their future suitability for deployment.

1.2 Aims & Objectives

The overarching aim of this thesis is to identify and evaluate scenarios under which (i) the CaO de/rehydration system and (ii) the CMO redox system could be employed in FBR-based processes to deliver TCES systems that facilitate both inter-seasonal and baseload power generation from current or upcoming CSP capabilities. This is achieved by carrying out, with reference to Fig. 1-4:

- The study of the kinetic behavior of the CaO hydration reaction with steam in an FBR,
- The design and optimization of suitable FBR configurations to study their viability for continuously-operated TCES and discharging systems involving the candidate reactions, and
- The design and techno-economic evaluation of TCES processes incorporating FBRs and coupled with CSP plants to study their impacts on the energy storage and baseload power generation capabilities of CSP.

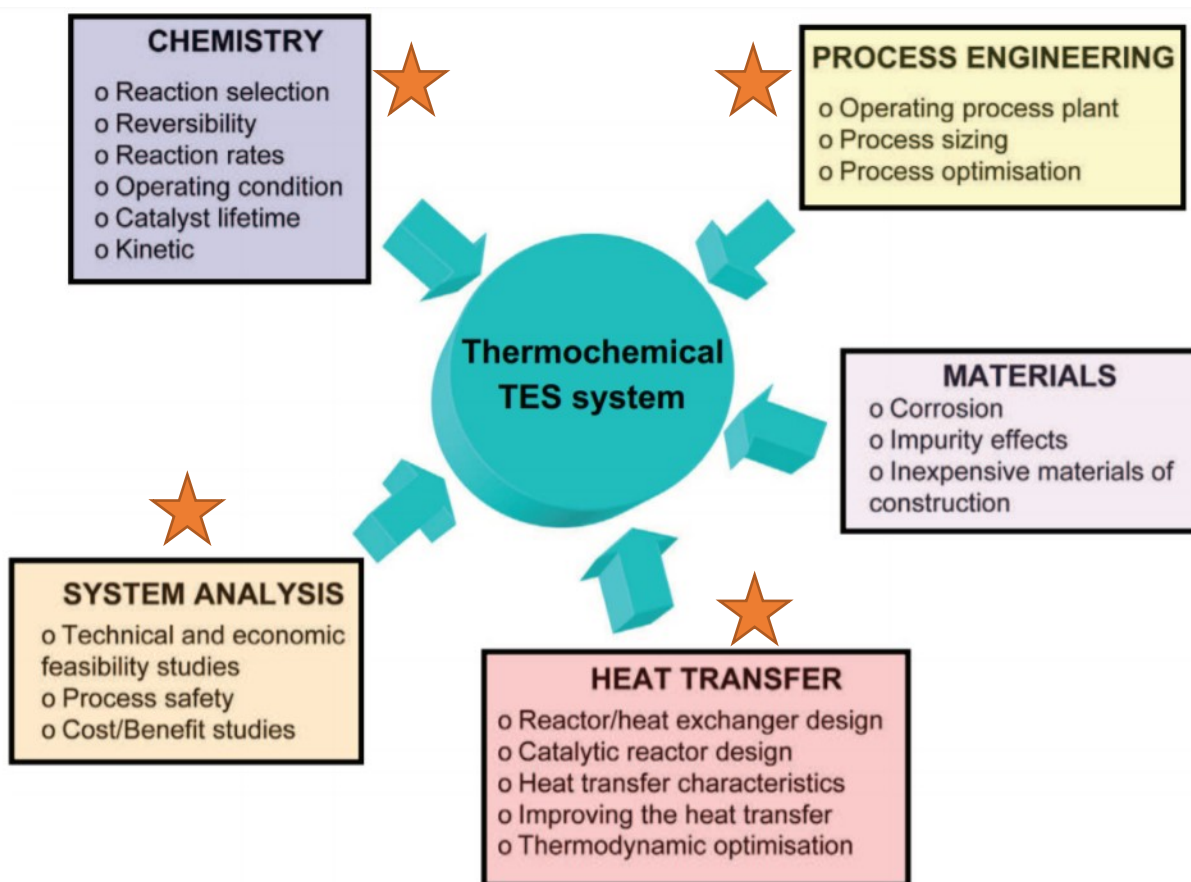


Fig. 1-4: Multi-dimensional approach for developing TCES systems³⁰; starred aspects represent areas of study addressed by work carried out in this thesis

1.2.1 Experimental Investigation Approach

Experiments were undertaken to study and model the effects of key process variables on the kinetic behavior of CaO hydration with steam – a key candidate reaction for TCES. This was to address gaps in the literature for the kinetic behavior of the CaO hydration reaction under fluidized conditions for which existing kinetic models were not accurate. The aim of this was to identify what physicochemical phenomena needed to be accounted for in subsequent computational TCES process design involving FBRs. Suitable kinetic data for the CMO redox system was already available in the literature³¹ and so no further experimental work was needed. A summary of the variables studied is presented in Table 1-1. The kinetic reaction data obtained was modelled using various state-of-the-art kinetic models as well as newly developed models presented in this work to identify what physicochemical phenomena significantly influenced reaction behavior.

Table 1-1: Selected reaction and controlled variables of interest for experimental study conducted

Controlled variables	Reaction to be investigated
Reaction temperature	CaO + H ₂ O (steam)
Particle size distribution	
Particle sintering extent	
Gas species concentration	

1.2.2 Computational Investigation Approach

After establishing the required kinetics knowledge, the energy storage system was modelled. The process and techno-economic modelling of TCES systems in a CSP context have not been studied long in the literature; the EU-based TCSPower project³² claims to have completed an initial assessment on 2015 but the results are not yet released; meanwhile a high-level economic study in 2018³³ produced early economic estimates but without great detail considered in process design. As a result, this study was among the first work conducting and reporting on such investigations using FBR-based plant designs.

The candidate reactions were first assessed in terms of the energy demands of their processes in a 120 MW_{th} TCES plant by way of steady-state process design. This analysis was carried out in process design software AspenPlus and took into account the loading duties, operating times, and frequency of demand from typical CSP heat sources in the literature. Advanced reactor designs such as FBRs were used as the basis of investigation. A techno-economic analysis of the individual scenarios was then carried out to understand the costs involved and make a comparison with latest pilot-trial developments in using sensible or latent energy storage technology for CSP plants. Current commercial CSP capabilities as well as next-generation CSP field trial results were assessed in parallel to identify what technical advancements in CSP would be required to enable the implementation of the proposed TCES plants.

The proposed TCES plants were modelled as standalone processes to obtain theoretical maximum efficiencies and suitable operating conditions based on currently known limits of conversions or cycling. Ultimately, the overall cost of power generation and energy storage through the TCES-enabled CSP plant were compared against suitable alternatives to assess the viability of the plant designs at various locations.

1.3 Thesis Structure

This first chapter introduces the scope of study and the foci of the overall investigations conducted. It presents the motivations for developing energy storage technologies such as TCES, which is expected to

significantly increase the reliability of solar heat-based energy generation technologies by allowing long-term, high-density heat storage as not yet possible through other energy storage technologies. It then outlines the investigation strategy employed to study suitable reactions for TCES at various levels. The second chapter introduces energy storage and solar power generation technologies, and identifies TCES as being the most suitable technology for energy storage for CSP. It then conducts a literature review to identify the most promising reversible reactions for TCES in CSP, which were found to be the $\text{CaO}/\text{Ca}(\text{OH})_2$ reaction and mixed metal oxide redox systems involving Cu and Mn (CMO redox). It then presents a strategy for investigating these reactions based on the aims and objectives in the first chapter.

The third chapter then conducts an experimental literature review for the kinetic study of the hydration reaction of CaO with steam. The fourth chapter builds on this by describing the experimental setup of a fluidized bed reactor system employed for further studying the kinetics of the CaO hydration reaction, the characterization of materials used, and the experimental results obtained. The fifth chapter then completes the first phase of work by performing detailed kinetic modelling of the CaO hydration reaction based on the experimental data and develops two new kinetic models with improved modelling accuracies. The sixth and seventh chapters design and simulate fluidized bed reactors and process flowsheets for the two reaction systems in a CSP-TCES context. The eighth chapter builds on this work by conducting dynamic simulations of the flowsheets based on varying weather conditions, geographical locations, and operating modes. The ninth chapter comprises a techno-economic assessment of the design cases. Chapter ten is a summary and conclusions. Table 1-2 gives a succinct chapter-wise breakdown of the thesis structure.

A significant portion of this thesis comprises of work that has already been published after peer review. Elements of chapters 3, 4, and 5 are published in:

- Ghosh, S.; Kokot-Blamey, J.; Boot-Handford, M.E.; Fennell, P.S., Kinetics Modeling, Development, and Comparison for the Reaction of Calcium Oxide with Steam. *Energy & Fuels* **2019**, 33 (6), 5505-5517

While elements of Chapters 6, 8, and 9 are published in:

- Ghosh, S.; Fennell, P.S., Design and Techno-Economic Analysis of a Fluidized Bed-based $\text{CaO}/\text{Ca}(\text{OH})_2$ Thermochemical Energy Combined Storage/Discharge Plant with Concentrated Solar Power, *25th International SolarPACES Conference Proceedings (2019)*, AIP, **2020**.

Table 1-2: Overview of thesis structure by phases of work, reaction systems studied, and focus of investigation in each chapter

Chapter	Reaction system focus	Investigation focus	Chapter title
1	-	-	Introduction
2	CaO de/hydration; CMO redox	TCES literature review	Thermochemical Energy Storage Literature Review: Applications for Solar Power
3	CaO hydration	Kinetics literature review	Experimental Literature Review: The Importance of CaO in a Clean Energy Context
4	CaO hydration	Experimental setup; kinetics study	CaO Hydration Studies: Experimental Setup, Materials, and Results
5	CaO hydration	Kinetics modelling	CaO Hydration Studies: Kinetic Modelling of CaO Hydration
6	CaO de/hydration	Reactor and process design at steady-state	CSP-TCES Plant Modelling – CaO/Ca(OH) ₂ System
7	CMO redox	Reactor and process design at steady-state	CSP-TCES Plant Modelling – CMO Redox System
8	CaO de/hydration; CMO redox	Process operation via time-varied input	Time-Varied Parametric Modelling of CSP-TCES Plants
9	CaO de/hydration; CMO redox	Techno-economic assessment	Techno-Economic Assessment of CSP-TCES Plants
10	-	-	Conclusions and Recommendations for Future Work

Chapter 2

-

Thermochemical Energy Storage (TCES) Literature Review: Applications for Solar Power

Chapter Contents

Sections	Subsections
1. The Role of Energy Storage in Solar Power	1. Characterization of Solar Energy Generation 2. Concentrated Solar Power (CSP) 3. CSP Energy Storage Options
2. Thermochemical Energy Storage (TCES)	
3. Literature Screening of Suitable Reaction Systems	
4. Selecting Systems for Investigation	1. Shortlisting of Systems 2. Calcium Oxide/Hydroxide System 3. Cu-Mn-O (CMO) Redox System
5. Investigation Approach	1. Reactor Design Choice 2. Steady-State and Time-Varied Flowsheet Simulation 3. Techno-Economic Analysis
6. Summary and Concluding Remarks	

2.1 The Role of Energy Storage in Solar Power

Over the past 50 years, a great deal of research has been undertaken to enable the utilization of solar energy, calculated to be 120 PW (or 1 million GW)³⁴. In the 1970's, solar power first started to find economically viable niches^{35, 36} with the development of photovoltaic (PV) setups for incorporating solar heating and cooling technology into buildings. Since then, solar technologies have advanced significantly and at scale to generate increasingly large volumes of renewable energy around the world. However, solar power is intermittent as a result of day/night cycles and atmospheric phenomena (cloud cover, high levels of particulates, storms, etc.). This means that solar cannot remain online beyond half a day on a continuous basis; hence solar infrastructure goes unutilized for 50% of the time on average. The incorporation of energy storage can go a long way towards combating this.

Current energy storage technologies for solar power can store energy for several hours or days and then release it at appropriate times to make up any shortfalls in generation during downtimes. For example, electrochemical batteries have been developed that connect with solar PV setups. Concurrently, thermal energy storage systems have also been developed that collect solar energy as heat, such as in concentrated solar power (CSP). Solar PV directly uses photovoltaic materials to convert solar energy to electricity while CSP systems (discussed further in Section 2.1.2) first convert solar energy to heat in an intermediate step before electricity production; this also requires specialized materials that have high thermal reflectance and high heat capacities.

2.1.1 Characterization of Solar Energy Generation

The global installed solar PV capacity exceeds 500 GW³⁷ (95% of this having come online in the last 10 years) which fulfils 3% of global electricity demand.³⁸ Global CSP implementation is at a more modest 6 GW³⁹ though this is expected to grow significantly in the near future as more CSP projects come online by 2024¹⁹. Due to technological advancements, falling costs, and a suitability for scaled deployment, solar PV is the fastest-growing renewable energy technology in terms of installed capacity⁴⁰, with many countries such as Spain and the US having GW-scale solar PV markets. However, there are several points of concern for solar PV from a technological perspective. One is that of intermittency as previously discussed. Another is that the efficiency of solar PV is fundamentally limited due to physical limitations of PV materials, offering a maximum energy conversion efficiency of solar energy to electricity of 33% due to the Shockley-Queisser Limit.⁴¹ While research is underway to identify ways to circumvent this limit, no options are currently scalable⁴² and this thus remains a drawback for large-scale energy generation through solar PV.

Batteries are the most promising way to store intermittent electricity. However, batteries are unable to store energy for long durations (< several days without significant losses) and can need regular replacing. In addition, the wide range of scales at which solar PV is deployed also means that batteries or other means of electricity storage have to be designed to accommodate constraints faced at each scale, sometimes necessitating design of separate and independent storage technologies.

Even in the present, despite solar PV capacity outweighing CSP capacity many times over as noted earlier in this section⁴³, solar PV contributes 3.0% towards the actual global electricity production mix which is only 30 times that of the contributions of CSP which was 0.1%⁴⁴. This shows that CSP deployments contribute significantly to the energy mix despite being far less widespread at the moment. The typical large-scale deployment of CSP alongside integrated energy storage make it well-suited to be further investigated for developing more reliable solar energy generation.

2.1.2 Concentrated Solar Power (CSP)

Concentrated solar power (CSP) is a solar energy technology that concentrates incident solar radiation and transfers it to a heat transfer fluid which can then be expanded in a turbine for electricity generation. Fig. 2-1 illustrates a typical plant layout⁴⁵ for the solar tower configuration showing the four major elements: the solar field, the receiver and energy storage system, the power block, and the connection to the grid.

It is a well-developed technology with significant international deployment across Spain, USA, Australia, South Africa, China, Morocco, and the Middle East, and is forecasted to contribute significantly to decarbonizing global energy production in the coming decades⁴⁶. Fig. 2-2 shows the growth in globally installed CSP capacity over the past decade; it is observed that in that time the global capacity has grown by 1200%. This is unsurprising as its capital cost requirements have dropped by 50% over the last decade⁴⁷ making it significantly more economically competitive.

Being a type of concentrating solar thermal technology, CSP plants are typically classified as either point-focus or line-focus plants which describes the solar collector and receiver setups used. Point-focus setups involve either parabolic dishes or towers/central receivers, while line-focus setups use parabolic troughs or linear Fresnel reflectors. The different setups vary in terms of, amongst other things: potential operating temperatures, concentration capabilities, and their suitability for the atmospheric conditions at any particular installation site; hence for any given design only certain TCES systems with matching reaction temperatures can be employed. Fig. 2-3(a) provides an illustration of how these designs tend to be set up.

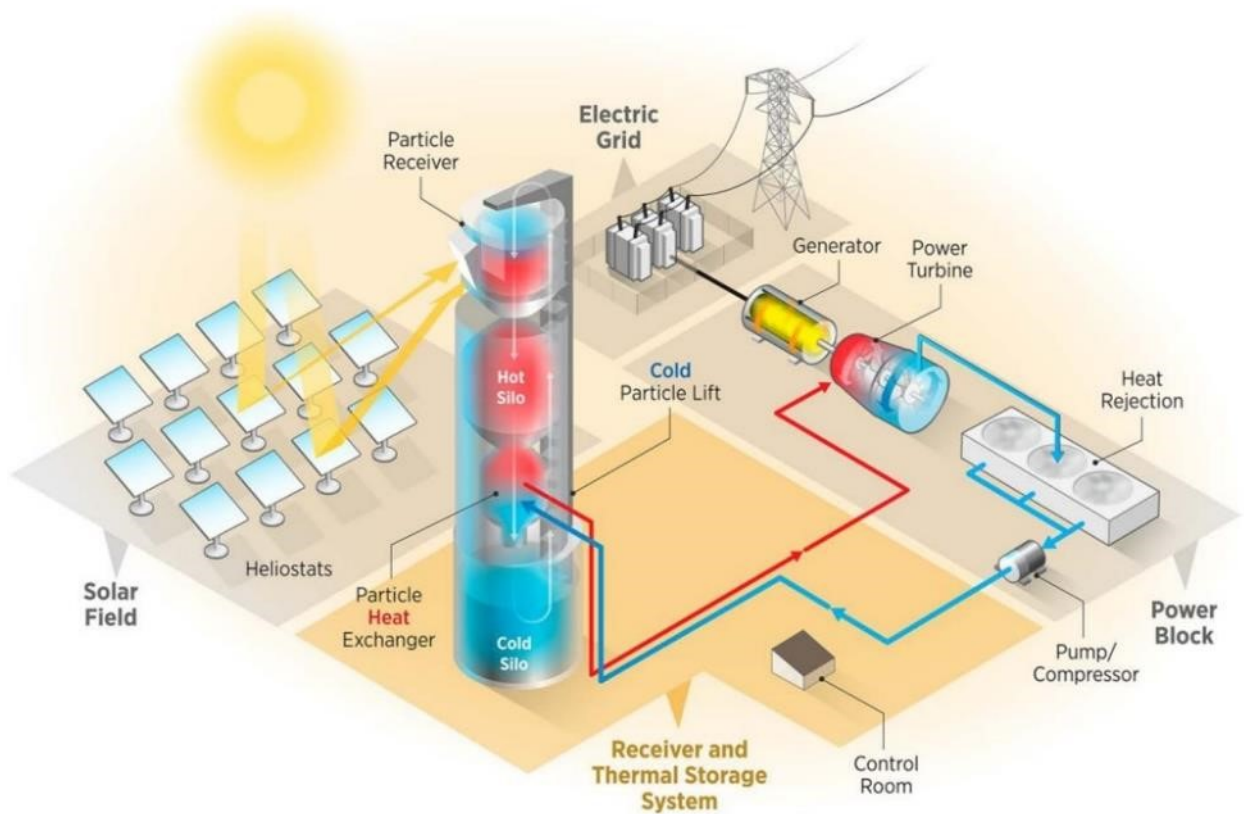


Fig. 2-1: Schematic of power generation from a solar tower CSP configuration without energy storage⁴⁸

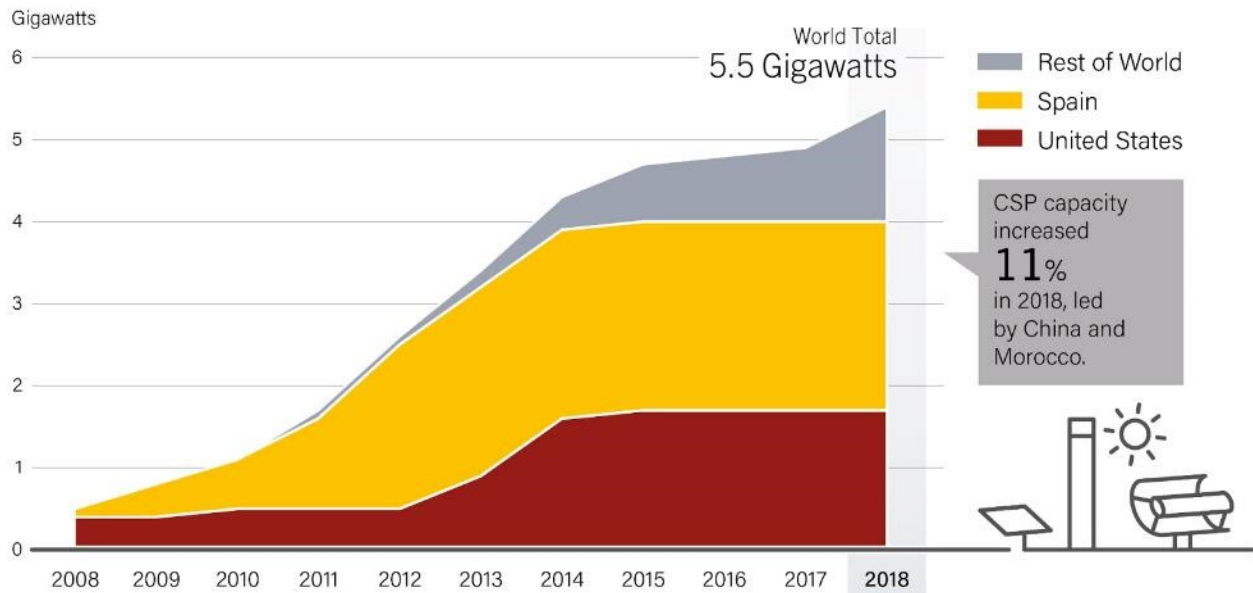


Fig. 2-2: Cumulative global installed CSP capacity broken down by region, 2008-2018¹⁸

Parabolic troughs and solar towers are the most common designs deployed and advancements in these technologies are expected to reduce costs further when downstream processes are optimized and integrated with long-term storage. This is as the high working temperatures allow for more effective thermodynamic cycles thus reducing heat wastage^{49, 50}. Key attributes of CSP plant configurations are summarised in Table 2-1. It can be surmised that parabolic trough designs which make up the vast majority of existing designs can be considered the ‘first wave’ of CSP technologies and that solar towers are now leading the ‘second wave’ by offering key technological improvements such as a far superior solar concentration ratio, higher operating temperatures, and compatibility with more common industrial power cycles.

Large-scale solar tower plants currently operate at up to 750°C. However, recent advancements in receiver designs have resulted in higher operating temperatures of 800-1500°C being achieved in pilot trials (see results of the Next-CSP project²⁸, DLR⁵¹ and Heliogen²⁹). With improvements to new receiver designs over the course of more development projects, it is possible that temperatures exceeding 1000°C will be achieved at larger scales. This means that CSP plants incorporating these designs will be able to implement a wider range of energy storage systems, including high temperature technologies investigated in this work.

Due to these reasons, the solar tower design is now examined in more detail as it is of most interest for high temperature TCES and has the most potential for development. Fig. 2-3 (a) and (b) show that it has two main components: a heliostat field for reflecting and focusing incident solar radiation, and a solar receiver tower where the radiation is focused. The heliostat field consists of large, specially designed mirrors that have high reflectivity and tend to be dynamically aligned to match the changing angle of incident radiation throughout the day. The receiver tower essentially houses a specialized heat exchanger which facilitates the transformation of the concentrated solar radiation into thermal energy by heating up a working fluid within the heat exchanger; these fluids are henceforth identified as heat transfer fluids (HTF).

Depending on the specific operating conditions of a particular CSP plant, various HTFs can be considered for use⁵²⁻⁵⁴ including liquid metals, molten salts, water or pressurized steam, air, and even streams of fluidized, granulated solids. The most common HTFs used in solar towers nowadays are nitrate-based molten salts and pressurized steam⁵⁰. The role of the HTF is to carry the concentrated thermal energy from the receiver block to the power cycle or to the energy storage step if it is present. The choice of HTF is set by the operating temperature range of the solar tower; candidate materials need to be thermally stable and have high heat capacities, low densities, and high thermal conductivities at these temperatures. Though gases are often more thermally stable, their other thermodynamic properties are weak, so liquid materials tend to be preferred. In the power generation sub-system, the thermal energy is converted into electrical energy through a thermodynamic cycle such as the Brayton, Rankine cycle (or more recently new systems using supercritical steam or CO₂, see Table 2.1).⁵⁵.

Table 2-1: Comparison of major CSP configurations along with key attributes, based on work by Xu et al.⁵⁶

	Parabolic Trough	Solar Tower	Linear Fresnel	Parabolic Dish
Capacity range (MW)	10-250	10-100	5-250	0.01-1
Operating temperature range (°C)	150-600	300-750	150-400	300-1500
Global deployment (% of total CSP)	82%	13%	4%	1%
Solar concentration ratio	50-90	600-1000	35-170	<3000
Relative cost	Low	High	Low	Very high
Power cycles used	Steam Rankine; Organic Rankine	Steam Rankine; Brayton cycle	Steam Rankine; Organic Rankine	Stirling Engine; Steam Rankine; Brayton cycle
TRL	9	7	5-7	3-4
Outlook for development	Limited	Very significant	Significant	Significant (mass production)
Advantages	Proven long-term durability and reliability; Modular design	High efficiency; Compatible with combined cycle power generation; Modular design	Easy to fabricate; Modular design; Compatible with combined cycle power generation	High efficiency; Modular design
Disadvantages	Low efficiency; Limited temperature range; Complex assembly; Large water requirements	High operating & maintenance costs; Large water requirements	Low efficiency; Limited temperature range	Low TRL; Incompatible with thermal storage

The most significant advantage of solar towers is the potential to operate at temperatures approaching 1000°C, far higher than parabolic troughs⁴⁵ thereby allowing greater thermodynamic efficiency⁵⁷. However, cost-effective fabrication materials suitable for these conditions still need to be developed. In this vein, new solar receiver designs are being investigated as noted previously – such as a volumetric air receiver design that allows temperatures >1000°C by absorbing the concentrated radiation into porous materials⁵⁸. The absorber draws in air to cool the unit and minimize radiative heat loss from the tower, while inside the absorber heat is transferred to the HTF at higher temperatures than possible previously. Such designs are at early pilot stages and so there is ample time to develop complementary TCES processes for them.

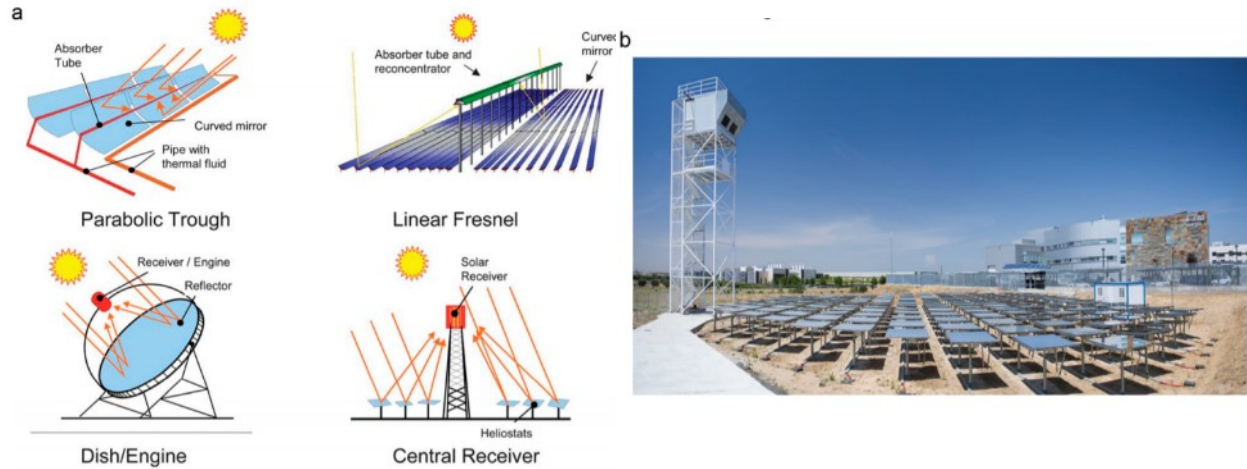


Fig. 2-3: (a) CSP optical concentrator configurations⁵⁷; (b) Image on the solar field and the tower built at IMDEA Energy Institute in Mostoles (Madrid, Spain)⁵⁹

Another key part of CSP plants is the thermal storage system. Typically using molten salts or oils, these systems often only provide short-term buffers locally within the plant. However as illustrated in Fig. 2-4, these systems are often inadequate as there still regularly remain large volumes of surplus solar energy that are generated but then lost (through radiation or other means) due to unsuitable storage systems. This is the main factor contributing to the intermittency of solar CSP, and could be overcome if longer-duration thermal storage was incorporated into CSP designs. This would enable continuous energy discharge from the plant to the grid or any direct consumers.

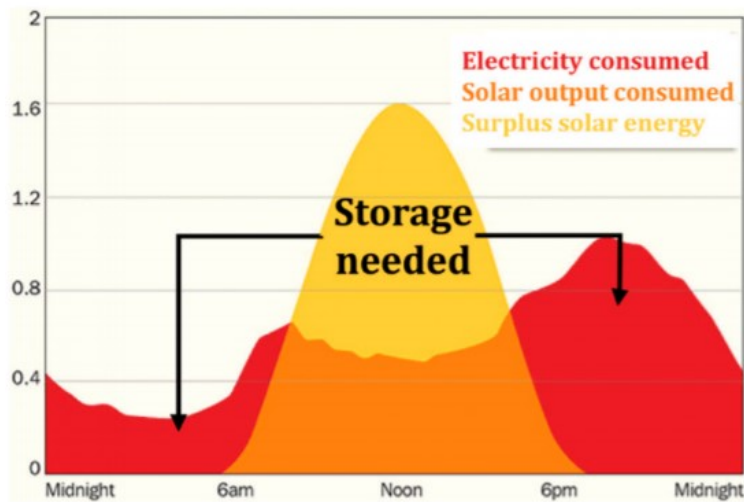


Fig. 2-4: Daily household electricity demand (kW) vs typical solar energy production in Australia⁶⁰

2.1.3 CSP Energy Storage Options

While CSP and other solar technologies are now competitive with traditional fossil fuel power generation in terms of capacity, there is a pressing need at the grid level to develop complementary energy storage systems that help assuage solar intermittency across days and even seasons. CSP is well-suited for this as it predominantly operates at large scales which means it can dispatch large volumes of electricity (on the MWh_e scale) directly to the grid on demand^{45, 52, 57}. However, CSP without energy storage currently struggles to compete on cost; research programmes by the US Department of Energy are underway to bring this cost down from \$0.21/kWh to \$0.05/kWh by 2030 by validating CSP plant designs with long-duration energy storage capabilities for baseload power generation.⁶¹

Fig. 2-4 shows that the energy volumes produced by CSP are more than adequate to fulfil the demands of the grid; the problem has been matching the solar availability to the demand trends in local communities. Thus the proposed adjustments featuring thermal energy storage (TES) generally involve storing the surplus energy collected via CSP during the solar noon periods and releasing it during periods of low solar availability (such as cloudy weather or night time) through discharging. CSP plants designed with this in mind require larger solar fields to maximize surplus energy generated for storage⁶². This may require higher upfront costs but is likely to be compensated by the revenue from selling surplus electricity to the grid; hence the economics are likely to be more favorable⁶². This is supported by calculations by Zhang et al.⁶³ estimating that TES systems would account for only 18% of the investment required for a CSP setup.

There are several options for TES which vary in their physicochemical mechanisms: sensible heat, latent heat, and thermochemical heat energy storage are the main types. For sensible heat storage systems, a solid or liquid is used as the storage medium and its high heat capacity is used to store energy by changing its temperature. Latent heat storage systems supply heat to induce a phase change in the storage material; solid-to-liquid phase changes are the most common choice. Thermochemical energy storage (TCES) systems which make use of reaction enthalpies to store and discharge energy as heat are a developing technology, offering several advantages over the sensible heat storage technologies which are currently used in the industry⁶⁴. Table 2-2 presents an overview of the three types of TES systems and further notes the systemic improvements potentially on offer through TCES. Each TES technology type is suited to different purposes based on the operating temperatures and scales of the systems they are linked to, and so in the case of large-scale CSP, TCES is very well suited particularly for solar tower designs due to their high operating temperatures. TES systems that have achieved maturity (sensible and latent heat) are lacking in energy storage density compared to electrochemical storage technologies employed by solar PV (such as Li batteries with 210 Wh/kg)⁶⁵ and if these designs persist then CSP will struggle to compete with solar PV and other renewables despite its very high potential. Hence, the development of cheaper and higher density

storage systems like TCES for CSP applications are critical for continued proliferation of CSP. Fig. 2-5 illustrates this by comparing the material volumes required to store a fixed amount of thermal energy using each TES technology as well as comparing the storage density magnitudes, suitable operating temperatures, and some example materials used for each of them.

Table 2-2: Comparison of main technologies available for energy storage

Storage mechanism	Sensible	Latent	Thermochemical
Energy density (kWh/kg)	0.02-0.03 kWh/kg	0.05-0.1 kWh/kg	0.5-1 kWh/kg
Storage scale (MW _{th})	1-2	1-10	1-200
Maturity	Industrial (TRL 9)	Pilot Scale (TRL 5)	Lab Scale (TRL 3)
Storage period	<6 h	<24 h	Effectively unlimited
Transport	Small distances	Small distances	Effectively unlimited distances
Technological complexity	Simple	Moderate	Complex
Drawbacks	Significant energy losses over time; large volumes of material needed	Significant energy losses over time; poor thermal conductivity	High cost of capital; technically complex to design and implement

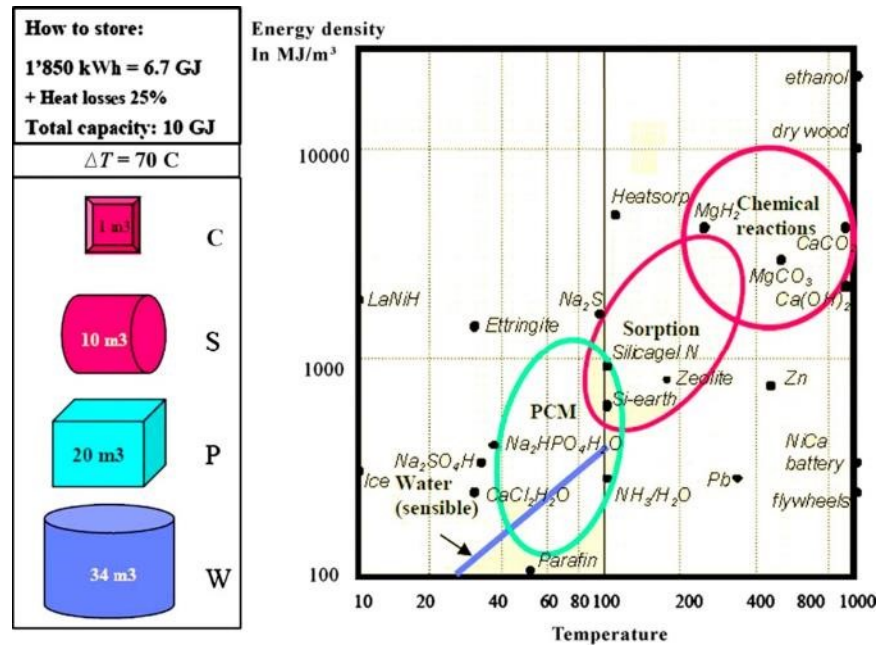


Fig. 2-5: Comparative calculation of unit energy storage requirements across TES technologies and their most suited operating conditions⁶⁶; here C is chemical reaction, S is sorption, P is phase change material, and W is water (or sensible) heat storage

2.2 Thermochemical Energy Storage

Exploration of the concept of energy storage through thermochemical means first gained traction in the 1960's when Funk and Reinstorm⁶⁷ first explored the concept of thermochemical cycles and their potential application to industrial processes. Subsequently, inspired by contemporary work involving catalytic production of hydrogen from water and its subsequent storage, Wentworth and Chen⁶⁸ proposed a method for storing solar heat energy using un-catalyzed chemical reactions as a medium. A range of chemical compounds (oxide, hydroxide, carbonate, and sulfate systems among others) were then investigated based on their effectiveness for solar energy storage between 500 – 1000°C.

Another idea being aired during this period was the possibility of using adsorption processes as a heat storage medium⁶⁹. This was based on observations made regarding a sensible heat energy storage system involving a gravel bed; its higher than expected apparent heat storage capacity was attributed to a chemical adsorption mechanism⁷⁰. It was then proposed to investigate silica gel due to its attractive adsorption capabilities however cost concerns led to the consideration of alternatives such as calcium and lithium salts.

In 1979, Shigeishi et al.⁷¹ investigated the potential use of further alternative materials including alumina (gel and activated forms), zeolites, and activated carbon specifically for use in TCES in a solar power context. It was found that a mineral zeolite/water reaction system performed the best in this preliminary study, and the subsequent body of work studying and developing mineral/water systems for TCES applications has no doubt been driven by these early results. By this point, TCES technologies were understood to offer significant improvements in aspects where existing technologies fell short (as noted in Table 2-1): storage duration, storage scale, and storage density. Furthermore, TCES also offers greater flexibility of operation and application due to a wide range of temperatures being usable, and can integrate with other industrial processes to reuse and cycle materials. It is noted that scale-up considerations and the high complexity of operations involved are the main challenges that have to be addressed before TCES can be successfully commercially implemented.

The working principle of TCES involves manipulation of a reversible chemical reaction of the form:



In Eq. 2-1, the endothermic reaction stores heat (charging) while the reverse exothermic reaction step releases the stored heat (discharging). The stored energy can then be released by adjusting process conditions to shift the equilibrium to favor the exothermic step. Often species A and B are solids or liquids while C is a gas; the heterogeneity allows for convenient separation of products and generally offers higher reaction enthalpies to take advantage of, when compared to homogeneous reversible chemical reactions.

Furthermore the high material densities of solids and liquids allow for ease of storage at ambient temperatures with little maintenance or processing required. This processing simplification is especially pertinent for CSP as the reactions will be cycled several times a day with significant downtimes in between.

Eq. 2-2 describes the energy stored in the system:

$$Q = n_A t \Delta H_r \quad (2-2)$$

Where Q is the stored thermal energy (kWh), n_A is the moles of species A reacting per unit time (mol/s), t is the duration of reaction (s) and ΔH_r is the endothermic reaction enthalpy (kWh mol⁻¹). Two other metrics are also crucial in assessing and comparing reactions for TCES: the gravimetric and volumetric energy densities. These can be expressed through Eq. 2-3 and 2-4:

$$D_m = \frac{Q}{m} \quad (2-3)$$

$$D_V = \frac{Q}{V} \quad (2-4)$$

Where Q is the stored thermal energy (kWh), m is the mass of storage material (kg), V is the volume of storage material (m³), D_m is the mass energy density (kWh kg⁻¹), and D_V is the volumetric energy density (kWh m⁻³). In the case of solid-gas systems, the pressure and temperatures at which the properties of gases are studied must be specified. For solids, it is important to distinguish on which volume basis D_V is calculated: the apparent density, the true density, or the bulk density. Apparent density is the average density of the material inclusive of pore volumes within the solid particles, true density accounts for the material density only while discounting the volume of pores, and bulk density only considers the overall density of the packed bed of particles, inclusive of pore volumes and inter-particle voidage.

In a TCES set-up configured for CSP, HTFs transfer both the heat energy from the solar receiver to the endothermic reactor and the heat energy released in the exothermic reactor to the power generation system downstream. Fig. 2-6⁷² illustrates the pathways involved during the two main modes of operation of TCES – thermal charging (on-sun hours) and thermal discharging (off-sun hours).

TCES systems can be classified by the phases of the reactant and product chemicals involved; most commonly gas-gas, gas-liquid, and gas-solid systems have been the subject of study^{73, 74}. Among gas-gas systems, ammonia dissociation and steam methane reforming have been the most commonly studied as they are reactions familiar to industry⁷⁵. Meanwhile, solid-gas systems are usually identified by the solid reactant, such as oxides, carbonates, and hydroxides. As many solids react with the same gaseous species (such as CO₂, steam, O₂, or air), studies exist for a wide range of solid-gas systems.

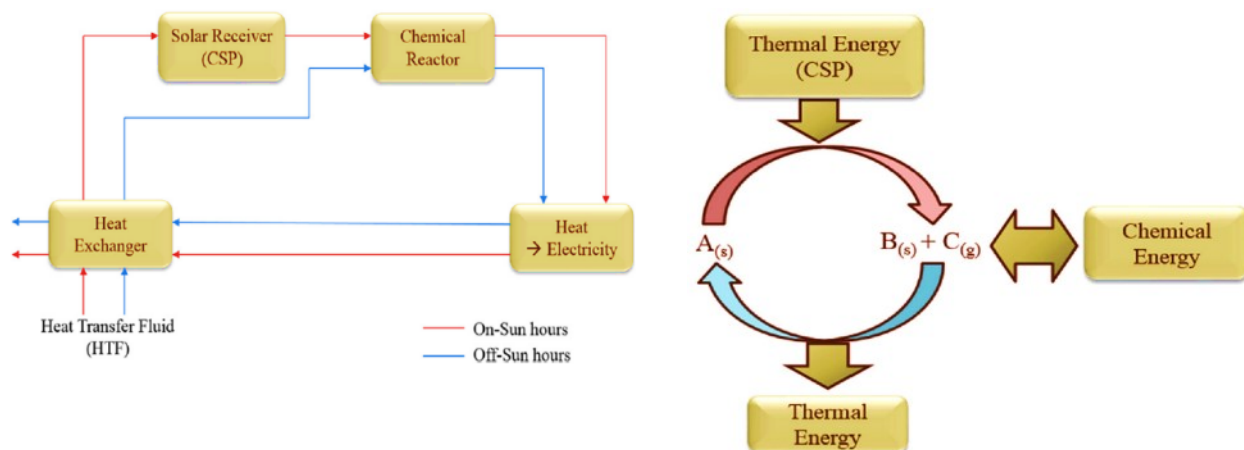


Fig. 2-6: (left) Process pathways for heat transfer in TCES system for a CSP application; (right) operating principles of chemical reactor system in TCES system

Such solid-gas systems can be either open or closed systems⁷⁵, where in open systems the reacting gas is not isolated and stored but is instead released to the atmosphere, while in closed systems the gaseous product is separated downstream and stored within the process. For closed systems, condensable gases can be stored and regenerated from reservoirs while non-condensable gases require pressurized storage and equipment for re-evaporation which can drive up costs compared to open systems. In this work only closed systems are considered as few open systems can reach the temperatures needed for CSP applications⁷⁶.

The selection of a power generation process accompanying a TCES system is influenced by the operating conditions of the TCES reaction. For instance, a system with $\sim 1000^\circ\text{C}$ exothermic reactions is better suited for an air Brayton cycle than a Rankine cycle. High reaction pressures pose additional challenges; for instance, ammonia-based TCES requires storage at pressures of 120 – 300 bar which increases costs and process complexity.

Material properties also require consideration where solid reactants are involved. Cycling stability is of particular importance as energy storage and discharge processes last for hours at a time and cycle several times daily. Hence, cycling of reversible reactions will impact particle morphology through physicochemical phenomena such as attrition and sintering. For solids, this can adversely impact their bulk energy storage capacity by increasing intra-particle diffusional resistances and reducing available surface areas for reaction, making them unsuitable for large-scale TCES. In metal oxides, distinct solid phases can form through cycling, segregating the material and affecting its overall thermodynamic properties. Hence for solid-gas TCES, reaction cycling stability has often been the focus of research. The scope of this subsequent literature review is to assess candidate reactions for their suitability for high temperature TCES for CSP and identify candidates for subsequent techno-economic study.

2.3 Literature Screening of Suitable Reaction Systems

The vast majority of heterogeneous reversible reactions involve extreme operating conditions, complex processes or other unfavorable attributes. To this end, the criteria established by Wentworth and Chen⁶⁸ (Table 2-3) serves as a guideline in identifying suitable reactions for TCES. Fig. 2-7 presents reaction families previously investigated according to these guidelines. Among these, systems involving metallic hydrides, ammonia, and other organics all possess low operating temperature ranges and/or present more considerable handling challenges and so are discounted from subsequent review. Building on this, Andre et al.⁷² conducted a thermodynamic assessment of carbonates, hydroxides, sulfates, and redox systems by estimating their reaction enthalpies and turning temperatures (the temperature at which the standard Gibbs free enthalpy of the system is zero). Pertinent analysis from their work is summarized in Appendix A-13.

Table 2-3: Overview of TCES reaction criteria proposed by Wentworth and Chen⁶⁸

Criteria	Rationale
The endothermic reaction for storing heat should take place below 1273 K	At very high temperatures, heat loss can be excessive and limit thermal efficiencies
The exothermic reaction step to release stored heat should take place above 673 K	Minimizing the temperature difference between steps improves thermal efficiency
The storage material should have high molar densities (~500 kWh/m ³) and large reaction enthalpy values (>40 kJ/mol)	Maximizing the volumetric energy storage capacity of the system can offer improved storage economics due to potential lower capital costs
The reactions should be completely reversible with no side reactions or byproducts	Minimizing the presence of additional species in process streams allows for simpler process design
The storage material should have high conversions and cycling stability	Longevity of the reacting materials improves process economics
The reactions should have fast kinetics (achieving completion within minutes)	Fast kinetics allow the system to be responsive to solar intermittency and varying grid demand
The materials and HTFs should be easy to process	Easily-handled working materials allow for simpler process design
The materials should have long-term chemical and mechanical stability	Long-term stability is required for long-term (inter-seasonal) storage mechanisms
The materials should not have negative environmental impacts or pose handling hazards	These factors would add to the economic cost of the system and are hence undesirable
The reactions should be supported by a good body of experimental studies	Having a fundamental understanding of the reactions allow for more effective process design
The reaction systems should have low process complexity and use inexpensive materials	Low complexity and inexpensive materials can make scale-up designs more cost-competitive

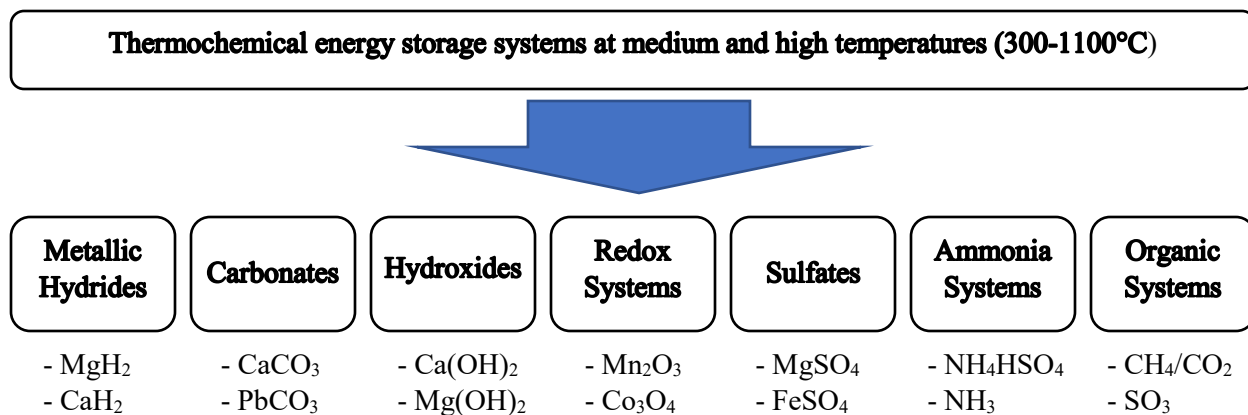


Fig. 2-7: Shortlisted reaction families with example systems for HT Solar TCES, adapted⁷⁷

2.4 Selecting Systems for Investigation

Upon establishing a shortlist of reaction systems to consider, more priority can be given to the factor of the availability of kinetic data as this is the largest barrier to being able to computationally investigate these systems further. Additional considerations can also be made for selecting systems that would have good applicability across CSP designs.

2.4.1 Shortlisting of Systems

Revisiting the material selection guidelines discussed in Section 2.3, the prescribed filters were applied to ascertain which specific systems among the reaction families were suitable for further investigation:

- Due to toxicity concerns, lead, cadmium, beryllium and uranium compounds were discounted.
- Due to low process temperatures, Cr_2O_{12} , Li_2O_2 , MgO_2 , Sb_2O_5 , ZnCO_3 , Mn(OH)_2 , Ni(OH)_2 , Zn(OH)_2 were not considered further in this study.
- Due to current raw material and processing costs, PtO_2 , Rh_2O_3 , Sr(OH)_2 were deemed not suitable for further investigation at time of writing.
- V_2O_5 (690°C) and BaO_2 (450°C) have melting points too close to their proposed operating range which would increase the complexity of their systems; they were not considered any further.

Of the remaining candidates, CaCO_3 , Ca(OH)_2 , MgCO_3 , Mg(OH)_2 , Co_3O_4 , Mn_2O_3 , and mixed metal oxides (MMOs) were longlisted. Upon further consideration, the MgCO_3 and Mg(OH)_2 systems were removed from consideration as their operating temperature ranges are potentially too low and they exhibit similar kinetic behavior to their Ca-based analogues; hence it would be superfluous to study both sets of systems. There has been relatively little interest in Mg-based systems for TCES for the above reasons thus the Ca-based systems presented a stronger case for remaining in consideration.

For Ca-based systems, both literature and industrial efforts have placed more attention on the CaCO_3 system. However, the hydroxide system operates at different temperatures and exhibits distinctly different thermodynamic and physicochemical properties meaning that it offers unique advantages for certain CSP plant designs. Hence the Ca(OH)_2 system was chosen for further consideration. Co_3O_4 is a controversial material for which much of the literature involved development of the most suitable physical preparation of the material. This suggested that the material formulation was still at an early stage and further study might be premature as improved and safer forms of the material are developed. This led to the removal of Co_3O_4 from consideration. When considering Mn_2O_3 , it was further noted that MMOs studied for TCES are all derivatives of Mn oxides and offer improved chemical and mechanical stability over the pure oxide form. Hence pure Mn_2O_3 was no longer considered.

Among MMOs, Mn oxides mixed with Co, Fe, and Cu were the main variants assessed in the literature. Based on the reports in Appendix A-13, it was apparent that the addition of Co did not yield any improvements and so Co-Mn MMOs were discarded from further consideration. Fe-Mn MMOs demonstrated some improvements in kinetics and reactivity but faced significant sintering issues in the course of cycling. As this would be a major drawback for a scaled-up process, this material was also discounted from consideration and hence only CMOs were chosen for further investigation.

2.4.2 Calcium Oxide/Hydroxide System

In the CaO hydration system, the dehydration of Ca(OH)_2 is the endothermic reaction that can store energy captured by the solar receiver, while the hydration of CaO is the exothermic reaction that releases the stored heat for use in a power block to generate electricity. With a turning temperature of 515°C , the likely suitable operating temperature range for TCES is around $400\text{--}500^\circ\text{C}$ for the energy discharging step, and $530\text{--}600^\circ\text{C}$ for the energy storage step, subject to the gas concentrations and reaction pressures used. This makes it well-suited for solar tower CSP based on current technologies that usually do not exceed 700°C . The high gravimetric energy storage density of 1352 kJ/kg means that only moderate masses of the CaO and Ca(OH)_2 materials will need to be stored which is a positive consideration when looking ahead to the economics of the overall system. Requiring only a steam environment also means a simpler process design.

2.4.3 Cu-Mn-O (CMO) Redox System

Patzschke et al.⁷⁸ synthesized a series of copper manganese spinel oxides (CMOs) with varying Cu:Mn ratios between 1:1 to 1:2 that were subjected to stringent cycling within both TGA and fluidized bed setups at a bench scale over 50 redox cycles. These were developed originally for CLC applications where very similar process conditions and reactor designs are used compared to potential large-scale TCES processes.

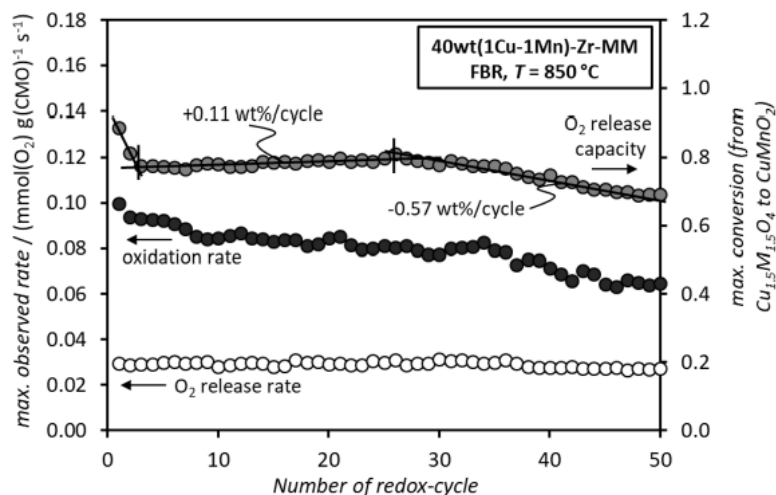


Fig. 2-8: O_2 release capacity (●), observed oxidation rate (■) and O_2 release rate (○) over 50 redox-cycles for 1Cu:1Mn mechanically mixed CMOs (40 wt%) supported with ZrO_2 , measured in a fluidized bed reactor at $850^\circ C$ with oxidation under 10 vol% $O_2 + N_2$ and reduction under pure N_2 from Patzschke²⁷

They tested both supported (with ZrO_2 and TiO_2) and unsupported materials at pilot scales and reported that the supported materials showed stable oxidation and reduction kinetics over 50 cycles (with oxidation/reduction temperatures of $850^\circ C$) as seen in Fig. 2-8 although they experienced a gradual drop in final conversions due to inter-particle physicochemical phenomenon such as grain coalescence. They also found that an equimolar ratio of Cu:Mn yielded the best reduction kinetics in the unsupported form.

These results were significant as these CMOs were mechanically stable enough to face negligible attritional effects through cycled experiments in a fluidized bed and retained their kinetic availability through cycling as well – both of which are significant material development challenges for designing materials for scaled-up testing. Within the relatively small body of literature surrounding the long-term cycling stability and mechanical durability of the complex materials that MMOs are, these CMO materials produced by Patzschke et al.⁷⁸ have shown good potential for applications in TCES processes from a technological perspective; however it remains to be seen whether they are economically viable at large scales.

The CMO materials described in the literature were designed and synthesized originally for chemical looping applications. However, their properties also make them well-suited to TCES. Through testing carried out in the literature, it was seen that a 1:1 ratio of Cu to Mn (giving a material formula of $Cu_{1.5}Mn_{1.5}O_4$) showed the best performance for long-term cycling and reaction activity. Hence this material was chosen for further consideration and is the only one referred to (in its supported form) as a CMO henceforth. There does however remain plenty of scope for varying Cu:Mn ratios to see the sensitivity of the performance of the material to the molar proportions present.

The expected densities of the supported and unsupported CMO materials are between 4300-5200 kg/m³ depending on the method of preparation and can vary significantly⁷⁸. This range is 1.5-2 times that of the materials in the Ca(OH)₂ system (2200-3300 kg/m³) and so may significantly impact the techno-economics of the plant. The operating temperature range of 850°C/950°C means that it is suitable for future designs of solar tower CSP that can reliably reach 1000°C. This is not an issue for the current study as there remain significant challenges in producing bulk quantities of CMOs in an economically-viable manner. These are likely to be resolved by the time future solar tower CSP plant designs also become commercially viable.

With both the Ca(OH)₂ and CMO systems being suitable for solar tower designs, a comparative study involving these systems allows for comparing their suitability for TCES applications now and in the future. Effectively, it can be an assessment of the trade-off between a cheaper and simpler process (using Ca(OH)₂) and a more thermodynamically effective process (using CMOs).

2.5 Investigation Approach

The chosen investigation aspects of reactor design, scaled-up flowsheet simulation, and techno-economic performance seek to address both immediate and future considerations and challenges associated with the large scale deployment of TCES systems in general. It is expected that through studying these aspects, key findings and conclusions can be drawn regarding what work needs to be done to make either TCES system technologically and economically viable at large scales when coupled with CSP, and so more informed guidance can be provided regarding suitable directions of work for further study.

2.5.1 Reactor Design Choice

Due to the operating conditions for each process, specialized reactor design is crucial in improving their operating performances. Only a few studies concerning the design of a CaL/metal redox reactor system for CSP applications exist in the literature. Most experimental data is from TGA setups which do not always accurately reproduce scaled-up reaction conditions in terms of phenomena such as diffusion and heat transfer. The extent to which these are accounted for has significant impacts on the assessment of the reactions.

In industry, fluidized beds and rotary kiln reactor designs are considered most suitable for gas-solid reactions due to superior heat and mass transfer performance; they have thus been proposed for consideration for CSP TCES⁷⁹⁻⁸⁶. In Table 2-4, these reactor designs are compared to alternatives that could be used for scaled-up TCES systems. When operating at large scales, factors such as heat and mass transfer and continuous operation are important; these are best facilitated in a fluidized bed reactor design.

Table 2-4: Comparison of reactor configurations considered for solid-gas TCES systems, adapted⁸⁷

Type of reactor	Advantages	Disadvantages	Refs
Fixed/packed bed	- Low cost - Easy to fabricate, operate, and computationally simulate	- Poor heat and mass transfer - High pressure drop - Risk of bulk expansion and shrinkage of bed	Cited from various sources ⁸⁸⁻⁹¹
Moving bed	- Direct gas-solid heat transfer - Good heat transfer coefficient - Adjustable residence time of gas-solid reaction - Smaller influence of temperature gradients	- High pressure drop under high velocities of gases or solids - Difficulties to integrate with solar reactors - Non-uniform irradiance distributions on the particle flow	Cited from various sources ^{88, 91}
Gravity-driven	- Low pressure drop - No energy penalty for the flow of particles	- Difficulties in controlling the distribution and residence time of particles - Risk of fluid bypass and insufficient heat transfer	Cited from Zsembinski et al. ⁹¹
Rotary kiln	- Improved particle mixing - High reaction conversions due to good heat and mass transfer - Reduced attrition - Continuous operation possible - Multipurpose reactors	- High energy penalty for parasitic equipment - Higher maintenance costs of rotary parts under high temperature	Cited from various sources ^{85, 92, 93}
Fluidized bed	- High heat and mass transfer - Continuous operation possible - Reduced risk of hot spots and thermal instability	- Complex system and difficult to model - Increased energy penalty for gas fluidization - Attrition of materials	Cited from various sources ^{80, 84, 94}

Several studies have investigated solar-driven fluidized bed reactor designs for TCES⁹⁵⁻⁹⁹ through both simulation and experimental work. In these studies it was explored whether integrating solar receivers into the immediate body of the reactor allowed for improved heat uptake by the system; both direct (solar energy absorbed directly by reactants in the fluidized bed) and indirect (solar energy transferred to reactants via heat transfer fluid) solar receivers were studied for this application and designs are still being refined conceptually with much work to be done for their application in TCES systems^{96, 100-103}.

One bench-scale study of a fluidized bed-based system was conducted in Japan using a direct solar receiver, a parabolic concentrator, a fluidized bed reactor, and an air compressor; initial results suggested that within the 950-1100°C temperature range, fluidization was achievable and sustainable⁹⁹. While this is a promising start, there is more complexity that needs to be accounted for in terms of mechanical design of a larger reactor, connections for additional downstream processes such as cyclones and storage tanks, and various control system considerations. Critically, the design of TCES reactors are at a low TRL and thus there is still much scope for intensive design and development of suitable reactor designs for these systems. The aforementioned considerations led to the decision to produce fluidized bed reactor designs. For this, Chapters 3 to 5 focus on obtaining relevant kinetic data, while Chapters 6 and 7 are dedicated in part to the design and optimization of fluidized bed reactors at large scales for both of the chosen reaction systems.

2.5.2 Steady-State and Time-Varied Flowsheet Simulation

There have been few efforts to analytically model FBRs for TCES in this way as the literature focuses on fixed bed designs or pilot-scale model validation; however Criado et al.¹⁰⁴ notably produced a steady-state FBR model for the $\text{Ca}(\text{OH})_2$ system in this specific context and obtained process insights relating the heat duty of the reactor to the required residence times. Meanwhile work by Pardo et al.¹⁰⁵ produced a bubbling bed model based on experimental results from a pilot scale fluidized bed.

It is important to note that both studies only yielded minimal information as to the physical design criteria of the proposed reactors, such as aspect ratio, required dimensions, internal heat exchanger designs, and so on. All of these design factors influence the progress of the reactions on a particle level thereby impacting the viability of the design. Furthermore, analytical models typically struggle to account for thermodynamic and physicochemical phenomena in large-scale operations. For instance in a fluidized bed setup the elutriation phenomenon is a notorious issue but it is not well-described, and hence elutriation correlations have been industrially obtained. The choice of correlation can significantly influence the specification of the designed reactor and thus incorporating this into reactor design would be greatly beneficial.

Incorporating the fluidized bed into the rest of the flowsheet is the next step that allows for the high-level process optimization required of a large-scale TCES plant. Such studies have been conducted before for related processes such as for the CaCO_3 system by Chacartegui et al.¹⁰⁶ and can yield useful insights as to the sensitivity of the performance of the system to specification changes of individual unit operations. It was thus determined that detailed steady-state study of FBRs and the design of TCES processes incorporating them would be the first step. This would produce high-level process insights for the two systems as an early forecast for their potential while the material challenges are independently tackled through research efforts elsewhere. These studies are the focus of Chapters 6 and 7.

Due to solar intermittency, a steady-state analysis performed at peak sunlight levels would overestimate the true average performance of the TCES system. It was not apparent whether any previous TCES studies had identified an approach for tackling this modelling consideration. However, Patschke et al.¹⁰⁷ recently presented a time-varied parametric (TVP) simulation of a large scale solar-driven process pertaining to CCS which sought to account for solar intermittency. Based on their work, a framework for conducting appropriate TVP simulation studies as part of this work was identified. It was noted that the choice of site for the CSP-TCES plants could also significantly impact the performance of the energy storage processes. Hence it was also planned that TVP simulation studies would be performed for a variety of locations to investigate their influence on the viability of CSP-TCES plants; these are covered in Chapter 8.

2.5.3 *Techno-Economic Analysis*

As noted in Section 2.5.1, techno-economic analyses pertaining to TCES systems at large scales have been scarce. Notable work by Peng et al.⁶⁰ investigated purely gaseous systems for TCES (steam reforming of methane and synthesis of ammonia) coupled with CSP and reported that the use of large volumes of gas in this manner resulted in high costs and large energy requirements for compression and on-site storage.

For solid-gas systems, an extensive study was conducted by Bayon et al.³³ for the carbonate, hydroxide, and redox families, benchmarking them against molten salts. They also considered chemical looping processes involving methane combustion as an additional section of study involving reactions with redox cycles. Their key conclusions and findings are seen in Fig. 2-9 where they reported estimated energy storage costs and also recommended the most suitable power cycles for each system. These recommendations are critical in realistically assessing each process and were employed in subsequent work in Chapters 6 – 9.

Some important observations can be made in the case of Mn-based systems where the Mn-redox system and Mn-CLC system have significantly different energy storage costs, operating temperatures, and corresponding power cycle recommendations. Further; Mn-based systems with Fe-doping (the $(\text{Mn}_{0.8}\text{Fe}_{0.2})_2\text{O}_3/(\text{Mn}_{0.8}\text{Fe}_{0.2})_3\text{O}_4$ system) also yield more specific power cycle recommendations. Among the other systems considered, the most promising reactions for Rankine steam cycles for power generation were those based on the hydroxides - $\text{Ca}(\text{OH})_2$ (energy storage cost: \$4.78/MJ), $\text{Sr}(\text{OH})_2$ (\$7.09/MJ) and $\text{Ba}(\text{OH})_2$ (\$8.28/MJ).³³ For temperatures where supercritical CO_2 cycles were deemed most feasible, the CaCO_3/CaO (\$15.09/MJ) and BaO_2/BaO (\$23.93/MJ) reactions were reported to be the most economically attractive, whereas for air Brayton or combined cycle power generation, the carbonate system SrCO_3/SrO (\$22.74/MJ) was found to offer the best performance. Certain CLC systems using methane such as $\text{Fe}_3\text{O}_4/\text{FeO}$ (\$18.87/MJ) and NiO/Ni (\$24.01/MJ) were also studied in the same work although their use would not strictly be considered a form of clean energy since fossil fuel usage is directly involved.

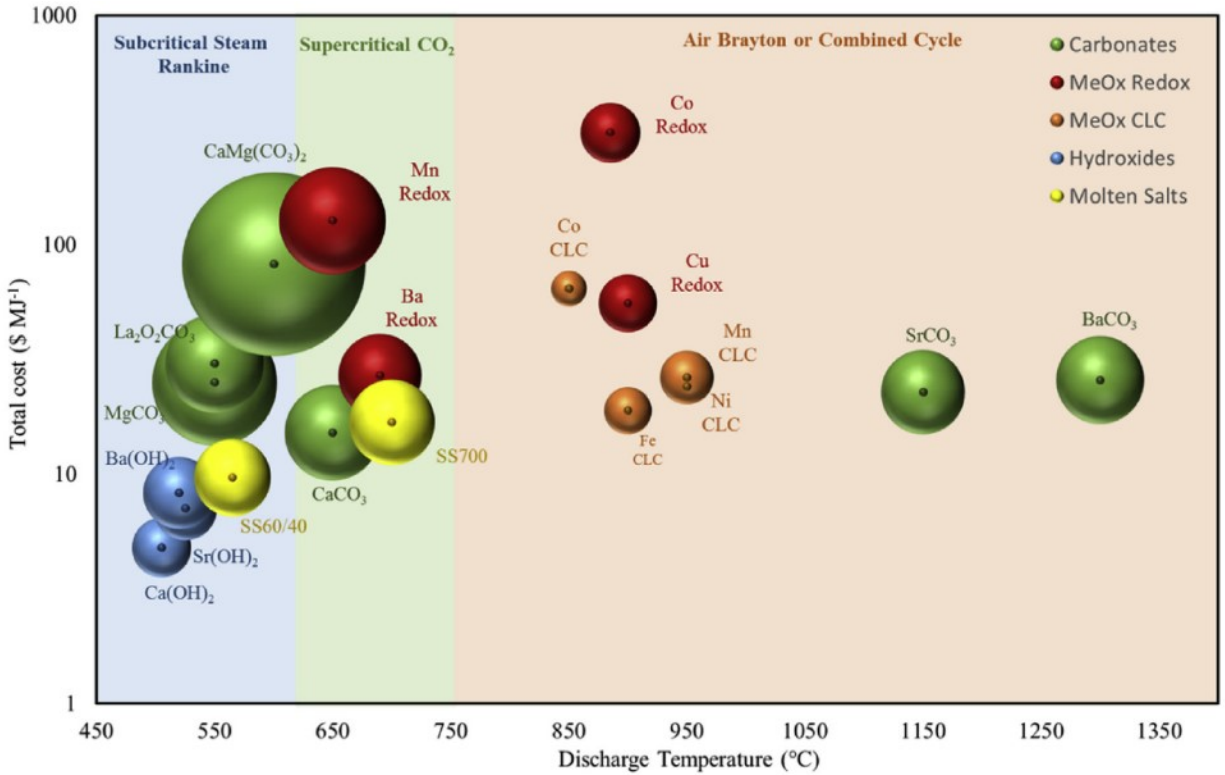


Fig. 2-9: Comparison of energy storage costs and energy discharge temperatures for various TCES candidate reactions, and recommendation of appropriate power cycles, by Bayon et al.³³

However, this study by Bayon et al.³³ paved the way for considering newer materials such as the Cu-Mn-O system. It is noted that the aforementioned studies were conducted for steady-state simulations, often used fixed or moving bed reactors, and involved assumptions of 100% reaction conversion and no material deterioration/replenishment costs. This means that these estimates are not only inapplicable to more complex reactor designs such as fluidized beds, but also do not paint an accurate picture of a dynamically-operated plant. As such, it was determined that the reactor design and TVP flowsheet simulation results produced in Chapters 6 – 8 would be used to conduct high level techno-economic analyses.

2.6 Summary and Concluding Remarks

In Chapter 2 CSP plant designs were identified and characterized; it was noted that parabolic trough designs which have a low operating temperature range and high complexity constitute over 80% of current CSP designs as they were the first generation of CSP technologies to achieve maturity. In contrast, solar tower CSP designs were identified to be the most promising for the next wave of maturing designs with operating temperatures approaching 1000°C; this much higher temperature limit means that higher thermal efficiencies can be achieved in CSP plants. Improvements in energy storage capacities and durations would significantly increase the availability of power generated through CSP, making the technology much more

commercially viable and suitable for implementing on a large scale as it was noted that energy storage infrastructure would only account for less than 20% of the total investment required for a CSP plant⁶³.

The characteristics and setups of TCES systems involving chemical reaction were then examined. It was determined that solid-gas systems were of most interest as the energy would be stored in the solid material and solids typically require the least complex handling and storage processes compared to liquids or gases, and offer much higher volumetric energy storage densities thus being more economical.

The thermodynamic properties of the reactions were also noted to have significant impacts on their suitability for TCES in terms of process design such as the reaction temperatures, pressures and enthalpies. Based on these considerations and by utilizing additional recommendations made by Wentworth and Chen⁶⁸, a thorough literature screening of reaction systems was performed for TCES applications, following which further screening was done to identify those most suitable in a CSP context in particular. Since the focus was on solid-gas reaction systems and a high operating temperature range was desired, only a few types of reaction systems were reviewed— carbonates, hydroxides, and redox systems.

Upon reviewing shortlisted reaction systems, techno-economic factors such as phase transition temperatures, material costs, and hazard levels led to consideration of hydroxides and carbonates of Ca and Mg, as well as MMOs. It was further identified that Mg compounds exhibited very similar reactions to Ca compounds which offered better thermodynamic properties as well; hence Mg compounds were not considered further. Between CaCO_3 and Ca(OH)_2 , the hydroxide system was found to offer greater flexibility due to its temperature range being suitable for several power cycles and CSP plant designs, and as research efforts elsewhere are already focused on CaCO_3 , coupled with the detailed kinetic study conducted earlier in this work it was decided that Ca(OH)_2 possessed sufficient advantageous traits to warrant detailed process design in this phase of work. Meanwhile among redox systems, CMOs were found to offer the best performance in terms of cycling stability while also satisfying all the other requirements for effective TCES and so were chosen as the second system to be considered for scale-up.

A three-pronged approach for continuing the study of TCES systems in this work was devised: performing detailed design for large-scale fluidized bed reactors for these reactions, conducting steady-state and dynamic simulations of the high level processes in conjunction with CSP systems, and a techno-economic forecasting of the commercial viability of these systems at large scales. As a result, these areas of investigation are the focus of Chapters 6 – 9. For detailed reactor design, suitable kinetic data for the CaO hydration system was needed and so this is first addressed in Chapters 3 – 5.

Chapter 3

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Literature Review: The Kinetics of CaO Hydration

Chapter Contents

Sections	Subsections
1. Sorbent Hydration Reaction	
2. Kinetics of CaO Hydration	1. Previous Kinetics Studies of CaO Hydration in the Context of CCS and Calcium Looping 2. Previous Kinetics Studies of CaO Hydration in the Context of Energy Storage 3. Potential Areas for Investigation
3. Conclusions from the Experimental Literature Review	

3.1 Sorbent Hydration Reaction

Initial studies of the hydration of CaO by Glasson et al.¹⁰⁸ involved using X-ray diffraction to examine the sorption of water vapour onto solid sorbent at 22°C across a range of concentrations and specific surface areas (1-100 m²/g). Here it was demonstrated that CaO hydration is a two-stage process; the first forming a pseudo-CaO complex structure and the second being the fully-reacted Ca(OH)₂ structure. Under certain conditions it was found that material with a high surface area underwent the second stage of the reaction at a faster rate than it did for the first stage, noticeably influencing the time-dependent behaviour of the reaction and the resulting particulate structures observed as summarised in Table 3-1.

Table 3-1: Observations of hydration reaction with particles of different average surface areas¹⁰⁹

Surface area (m ² /g)	Hydration activity	Physical changes due to hydration	Secondary comments
20-100	Most Active	Loss of surface area Caused by agglomeration of the grains and growth of crystallite size.	More pronounced at higher vapour pressures & when hydration was continued
5-20	Moderately Active	Formation of greater surface area (x1.54) Increase corresponded to the theoretical increase in molar volume from lime to slaked lime.	Crystallite size has been observed to be independent of vapour pressure
1-5	Least Active	Formation of greater surface area. (> x1.54) Increase in the number of crystallites. A decrease in the average size of crystallites.	Formation of cracks leads to greater surface area caused by erratic rates of reaction.

Subsequently, further work by Beruto et al.¹¹⁰ studied the final physical surfaces of the Ca(OH)₂ products formed by hydrating CaO with water vapour. SEM imagery results indicated that the external surface of the CaO particles was minimally impacted by the hydration reaction, however if water vapour exposure was further sustained, the smoothness of the crystals of the Ca(OH)₂ particles was reduced. This seemed to indicate that the particles tended to possess any and all of the following properties: (i) a low degree of crystallinity, (ii) the abundance of small and scattered crystallites, and (iii) the lingering presence of inter-crystal physical strains. Despite the value of these observations, a quantitative understanding of the CaO hydration reaction was yet to emerge.

3.2 Kinetics of CaO Hydration

The advantage of using steam instead of liquid water is that the energy efficiency of the process is increased – this has been attributed to be due to the greater potential storage of energy with a hydration enthalpy of -

104 kJ/mol (steam) versus -62 kJ/mol (liquid water hydration) under standard conditions¹¹¹. The higher temperatures necessitated also allow for better heat recovery when considering the industrial suitability of the Ca-looping process and hence most kinetic investigations only consider using steam. Having a precise understanding of the kinetics of the reaction and what factors enhance or hinder it under various environments allows for improved control and optimization in operating the process at large scales which can have significant thermodynamic as well as economic benefits. However due to the wide range of applications of this reaction system, the reported kinetic mechanics have varied drastically under different conditions; the most pertinent findings are summarized in this section.

3.2.1 Previous Kinetics Studies for CaO Hydration in the context of CCS and Calcium Looping

For industrial operation, sub-atmospheric pressure operation including the maintenance of operation is expensive and difficult to equilibrate. As a result work has also been done for atmospheric pressure steam hydration systems. However, most of the calcium looping literature for systems operating at temperatures greater than 100°C, do not go much into detail on the hydration kinetics or behaviour. For example, Materic et al.¹¹² examined samples that when through multiple cycles of carbonation (900°C, N₂, 10 min) and calcination (650°C, CO₂, 25 min) and their implication on hydration (110°C, water, 60 min) using a TGA. They described the hydration as “complete in all experiments”. Maciel-Camacho et al.¹¹³ examined the kinetics of quicklime at sub-steam temperatures (<100°C) and sub-atmosphere pressures (1.2 – 3.6 kPa). Creating synthetic powdered pellets that were sintered and calcined at varying temperatures (750, 850, 1010, 1100°C) they discovered a well-defined interface between the slaked lime product layer and the unreacted core. With envelope densities of 1155 – 1450 kg/m³ and porosities of 0.65-0.54 they found that the rate of hydration reaction increased for decreasing calcined temperatures, increasing water vapour pressure and increasing hydration temperature at the cost of considerable crack formation in the pellet.

They also developed an unreacted shrinking core model which considered the effects of gas-film diffusion, product layer diffusion with an assumption of unimolecular counter-diffusion, and interfacial chemical reaction with first order kinetics. Despite the assumptions made, the model fit with the data with deviations for particles that cracked. They did further work¹¹⁴ into the effect of carbonation on pellets for hydration reactions and found that crack formation increased for pellets that had deeper carbonation layers and for samples calcined at higher temperatures. As a result a further term was added to consider such resistances.

Serris et al.¹¹⁵ performed a range of experiments in the range of 70-420°C, 0.5-16 kPa on two types of quicklime (soft-burned and hard-burned quicklime). They reported that the rate of reaction increased with increasing vapour pressure and decreasing temperature of hydration and described that as anti-Arrhenius

behaviour. They hypothesised that this was caused by a solid-state diffusion mechanism that considered surface nucleation and subsequent nuclei growth and developed a reaction rate equation that linked the growth in the reaction surface area of the sorbent to the equilibrium constants for each step in the mechanism. It should be noted that the equation did not consider the pore-diffusion effects or the size of the grains used.

Blamey^{116, 117} investigated the hydration behaviour of Havelock limestone (500-710 μm) for the use in CO_2 capture. They examined samples that were calcined 0, 2, 6 and 13 times in a fluidised bed reactor. It was observed that the sorbents had a surface area varying between 2.88-16.17 m^2/g and pore volumes between 0.027-0.118 cm^3/g . The samples were hydrated using a TGA under 75% steam and at 483, 578 & 678 K. It was found that when increasing the hydration temperature the maximum rate of reaction increased for 20 minutes and after that time the rate of reaction would decrease. This result contradicts the work done by Serris et al.¹¹⁵ as Blamey et al.¹¹⁸ illustrated the Arrhenius-type behaviour expected of such reactions.

Blamey¹¹⁶ described the blockage effect defined by Serris et al.¹¹⁵ as pore blockage accelerated by sintering of the slaked lime layer formed. They also observed that the maximum rate of reaction and total conversion of slaked lime for each cycle decreased and concluded it was due to larger sintering extents. It should be noted that the authors did not examine operating conditions representative of industrial flue gas generation.

The effect of temperature on the extent of hydration can be explained by two major effects; the reaction rate and the diffusion rate. The former is an Arrhenius-type rate where the intrinsic rate of reaction increases with an increase in temperature whilst controlling all other variables. The latter is an anti-Arrhenius-type rate where the rate of reaction is dependent on the solid-state diffusion of $\text{Ca}(\text{OH})_2$ through the CaO .

Due to rapid pore closure at higher temperatures it is important to maintain a balance between the extents of sintering (caused by a rapid formation of an external layer of $\text{Ca}(\text{OH})_2$) and the conversion of CaO to $\text{Ca}(\text{OH})_2$ (caused by slower rates of reaction that allow steam to diffuse further into the porous structure). Furthermore, both works operated at different time scales: 20 hours¹¹⁹ and 20 minutes^{116, 117}. It is possible that there is a shift from a kinetic-control regimen to a diffusion-controlled regimen across these time periods. Both works however illustrate the importance of a large reaction surface area by creating quicklime using lower-bound calcination conditions with an optimized steam pressure. This is also observed in earlier works such as by Shearer et al.¹²⁰ where they show that optimization of steam pressure can significantly improve the reaction kinetics and conversions at high partial pressures of steam, although the limestone used was partially sulphated in a fluidized bed combustor prior to hydration.

3.2.2 Previous Kinetics Studies for CaO Hydration in the context of Energy Storage

As the application of the CaO hydration reaction to TCES has only received significant attention in recent years, there is a relatively smaller body of work studying its kinetics under conditions relevant to this application¹²¹⁻¹²⁹. Within this, some instances focus on the reaction behaviour under theoretically optimized conditions that may not be suitable for scaled up applications and thus become limited in their scope.

Recent work done by Schaube et al.¹²⁷ investigated the kinetics for both the hydration and dehydration reactions through cycling and using high partial pressures of steam (up to 95.6 kPa) and found that the CaO material did not undergo any significant degradation in the course of 100 such cycles. For the kinetics they used different empirical models for individual reaction steps further depending on the reaction temperature during hydration and also depending on the equilibrium dehydration conversion; this approach suggested that the models used could not account for the fundamental phenomena influencing the reaction consistently.

A cycled investigation of the kinetics for the CaO hydration/Ca(OH)₂ decomposition reaction was also recently carried out by Lin et al. and Wang et al.^{125, 128, 130} with reactions at high temperatures (550-710°C) and using high steam concentrations (0.67-2.33 MPa during hydration in atmospheres of 1-3.5 MPa). The high reaction temperatures and pressures involved in this study for evaluating the reaction kinetics are outside the feasible range for an energy storage system involving this reaction; particularly the pressure range considered which would require operating highly pressurized fluidized bed reactor designs that pose significant technical and operational challenges and face high fabrication, operating, and maintenance costs.

While considering more moderate temperatures, Irabien et al.¹²⁴ used the random pore model as a basis to study the dehydration of Ca(OH)₂ in the 330-450°C temperature range, and proposed a derived pseudo-homogeneous kinetic model for the behaviour of Ca(OH)₂ during dehydration. However they also noted that the design of the experimental setup used in their study made it difficult to avoid the influence of particle diffusion effects and external mass transfer, meaning that the veracity of their proposed model was not verifiable. Some additional investigations into hydration kinetics involving liquid water^{123, 129} in place of steam as suggested by Irabien et al. in another work were not considered relevant for energy storage processes due to reasons discussed earlier in this chapter.

In their study of the Ca(OH)₂ dehydration reaction, Galwey et al.¹²² used a miniature fixed bed design by performing the reaction using 10-28 mg particles of Ca(OH)₂ within a glass vacuum apparatus connected to a TGA. They found the dehydration reaction rates to be influenced by the extent of dispersion of the reactant particles within the glass vacuum tube used for reaction as a representation of an ideal fixed bed reactor design. A first order rate equation was found to provide the best fit to their reaction data however

complex reaction models were not considered in this assessment. In successive cycles of hydration and dehydration reactions they noted reaction rates to increase for both reactions due to the disintegration of the original material, producing increasingly smaller particles which facilitated the faster reaction rates.

Work carried out by Matsuda et al.¹²⁶ studying the $\text{CaO}/\text{Ca}(\text{OH})_2$ reversible reaction specifically for energy storage applications used a wide temperature range of 83–450°C and mild steam concentrations of 1.5–15.7 vol% and found a first order rate equation reflected both reactions. While these conditions were conducive for studying kinetics, the steam concentrations were significantly lower than what would be expected in a scaled-up energy storage process where a concentrated steam flow would reduce the total volumetric flowrate required and also contribute to reducing the reactor cross-sectional area for any given gas velocity.

3.2.3 Potential Areas for Investigation

The literature investigating the kinetics of CaO hydration have almost exclusively involved the use of thermogravimetric analysers where reactions tend to experience significant diffusional limitations – with one notable exception being the EU stoRRre project investigating the use of fluidized beds¹³¹; the results of which have been included in this review. However for the most part it has not been assessed whether the outcomes of these studies also successfully describe the reaction behaviour and specific factors influencing the reaction in a fluidized bed setup which significantly mitigates the diffusional resistances encountered in a thermogravimetric analyser and more importantly, is closer in terms of reactor design to the manner in which this reaction is often performed in scaled-up applications and thus allows better recreation of the associated physicochemical and mechanical particle-reactant phenomena pertinent at that scale.

TCES literature has usually considered fixed bed reactors for both reactions.^{132–137} However, fixed beds are inherently limited as they have low heat transfer effectiveness. The low thermal conductivity of stationary solids in these cases necessitates a very large total heat transfer surface area from which the large amount of thermal power required for a large-scale storage system could be extracted and transferred. Moreover, high pressure drops in the reacting gas streams (steam during hydration; air during dehydration) would be required in the fixed bed to contact the fine particles with the reacting (hydration) or purge (dehydration) gases – resulting in unnecessary engineering complexity. If large pellets or particle sizes are used to mitigate these effects in a fixed bed design, the reaction kinetics can become significantly slower and mechanical stresses experienced during the prolonged reaction times may lead to increased pellet or particle breakage.

In looking to upgrade reactor designs, fluidized bed reactor systems using CaO particles (potentially with an inert and easy-to-fluidize ceramic support) are an alternative option for carrying out both hydration and dehydration reactions. Fluidized bed systems offer additional advantages as they can operate in continuous mode (whereas fixed beds require batch-wise operation) and the heat transfer coefficients to internal

surfaces in the reactor are very high due to inter-phase mixing and far greater reaction surface areas, which means that the heat transfer area requirements in fluidized beds are considerably reduced. Also, upstream and downstream process operations such as the separation of gases and solids, the feeding or extraction of solids and their handling and transport to and from the storage silos can draw on the industrial expertise and knowhow of many similar systems in the chemical and energy industry that employ such processes.

Historically, the possibility of utilizing fluidized beds for the hydration/dehydration of $\text{CaO}/\text{Ca}(\text{OH})_2$ had been recognized as feasible in studies by Ervin^{73, 138} and Rosemary et al.¹³⁹ almost 50 years ago. However, little further progress has been made in the development of these reactor concepts for this reaction system.

3.3 Conclusions from the Experimental Literature Review

The $\text{CaO}/\text{Ca}(\text{OH})_2$ system was identified to have wide-ranging applications for TCES due to an operating temperature range of 400-550°C, and supported by the fact that the gas involved is steam which can be handled, stored, and generated easily. A design for a TCES facility coupled with CSP was found to be feasible as well under certain conditions. Early studies of the CaO hydration reaction suggested that the available reaction surface area influenced the post-reaction morphology of the resultant $\text{Ca}(\text{OH})_2$ material due to increases in size; when reversing the reaction this transformed morphology was deduced to contribute to a reduced degradation of the material. While the mechanical behaviour of the CaO material is important, greater importance was placed on learning more about how the kinetics of the hydration system behave. The most suitable reaction models were identified as certain variants of the random pore model, a version of a catalyst model called the grain catalyst model, and the fundamental unreacted shrinking core model.

These studies were almost always performed using TGA setups where diffusional resistances are prominent, though steps were often reported to have been taken to mitigate such issues. Furthermore, for scaled-up applications the hydration process was noted to have historically employed fixed bed reactors. However, the next generation of reactor designs are expected to be fluidized bed reactors, which offer significant heat and mass transfer improvements and thus improved technical and thermodynamic performance. It was noted that there were few reports of hydration kinetics or kinetic models for such environments. This was identified as a crucial gap in the literature. Through the study and modelling of the hydration of CaO under fluidized conditions, advancements in understanding could be made possible for performing the reaction on large scales, thereby contributing to efforts to improve the cycling stability of natural CaO materials.

Chapter 4

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CaO Hydration Studies: Experimental Setup, Materials, and Results

Chapter Contents

Sections	Subsections
1. Fluidized Bed Reactor System	1. Design of New Reactor 2. Relative Humidity Probe 3. Design of Steam Generation System 4. Rotameters
2. Thermogravimetric Analysis Set-up	1. Horizontal Tube Furnace 2. Thermogravimetric Analysis Unit (TGA)
3. Nitrogen Adsorption and Desorption Background	
4. Material Characterization and Preparation	1. Materials Used 2. Limestone Calcination 3. Thermogravimetric Characterization of Calcined Limestone 4. N ₂ Porosimetry of Calcined Limestone
5. Experimental Preparation	1. Experimental Reproducibility
6. Experimental Scheme	1. Standard Hydration Reaction Experiments 2. Conditions Tested
7. Experimental Results	1. Varying Particle Size 2. Varying Steam Concentration 3. Varying Hydration Temperature 4. Kinetic Parameter Estimation
8. Chapter Summary and Concluding Remarks	

4.1 Fluidized Bed Reactor System

As noted in Chapter 1, experiments were planned to obtain an improved understanding of the CaO-steam hydration reaction under fluidized conditions – as detailed in Section 4.6. Reaction models were then developed to identify physicochemical phenomena that accurately described the observed reaction behavior – as discussed in Chapter 5. A bench-scale atmospheric fluidized bed reactor (AFBR) setup was assembled for conducting the kinetic experiments; this section specifies major components of the overall setup.

4.1.1 Design of New Reactor

The body of the reactor is a 330 mm incoloy 800HT pipe schedule 80 with an OD of 33.4 mm and an ID of 26.0 mm; this encases a quartz liner which is the functional reaction vessel (ID of 21.0 mm and length of 500 mm). A sintered disc made of quartz is positioned ~200 mm from the base of the liner and serves to support the fluidized bed during operation as well as function as a catchment area for non-fluidized particles (during start up and shut down of the system).

Associated with the reactor are two copper electrodes secured around the reactor body, to which are connected ten copper welding cables (35 mm² cross-sectional area each) supplying power through a transformer (1600 A, 2 V). Due to the high temperatures involved in operation, a water cooling network was installed around the individual welding cables using coils of 1/6" copper tubing; this serves to prevent oxidation and deterioration of performance of the cables. Superwool® 607 Max Blanket insulating material was used to thermally insulate the electrodes and reactor body to reduce heat losses to the environment and for safety when handling the reactor. The reactor support structure is presented in Appendix A.4. Fluidization calculations relevant to this setup are included in Appendix A.15.

To control and automate the heating of the furnace, a bespoke reaction control programme was operated in Agilent VEE™ Pro. The programme continuously monitored $T_1 - T_5$ (Fig. 4-1) and the temperature and humidity measured by the RH probe through Type-K thermocouples. These thermocouples have a measurement accuracy of $\pm 0.004 \cdot |T|$ up to 1100°C and have an incoloy 600 sheath which helps to guard against damage from the regular cycles of heating and cooling.

The control programme continuously output graphical data and converted the humidity signal from the RH probe into a steam concentration reading. A PID controller was also embedded to ensure control over bed temperature (T_1) even during disturbances as the quartz liner was regularly disengaged to replenish material. Separately, heating control boxes were used to maintain the gas pre-heating system temperatures with automatically-tuned PID control systems. These were connected to the gas lines by wrapping heating tapes beneath the Superwool® encasements of these lines alongside the thermocouples.

4.1.2 Relative Humidity Probe

A HMT338 Relative Humidity (RH) probe supplied by Vaisala™ (Fig. 4-2) was used to indirectly measure the steam concentration at the outlet of the AFBR. The sintered tip of the probe measures the electrical conductivity of the gas flowing around it and outputs a voltage signal. By controlling the gas composition and recording the corresponding voltages, a calibration was derived and the voltage converted into a measurement of steam concentration (%). It was found that the sensitivity of the probe fluctuated with changes in gas temperature and the corresponding P_e of steam, thus affecting the accuracy of concentration readings. It was not possible to adjust this in the programme so post-experimental data corrections using Antoine's law were applied.

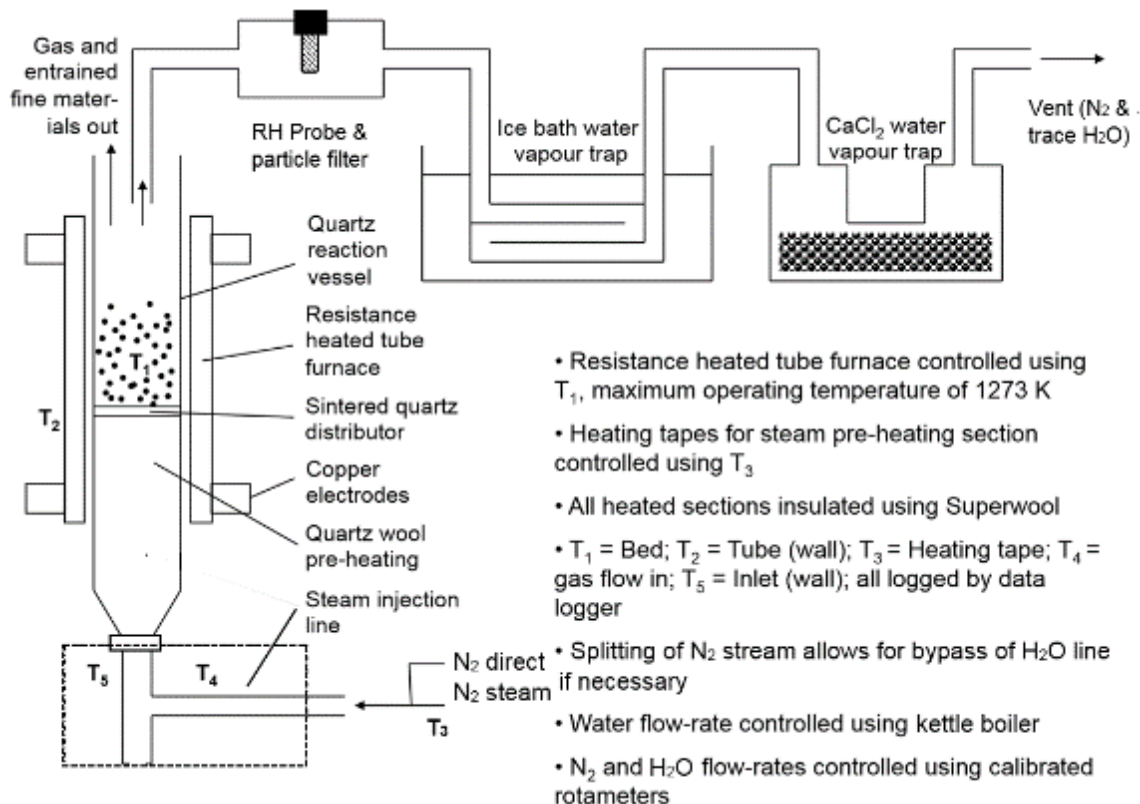


Fig. 4-1: Annotated schematic of lab-scale AFBR setup, adapted¹¹⁶



Fig. 4-2: Positioning and schematic of RH probe downstream of AFBR

4.1.3 Design of Steam Generation System

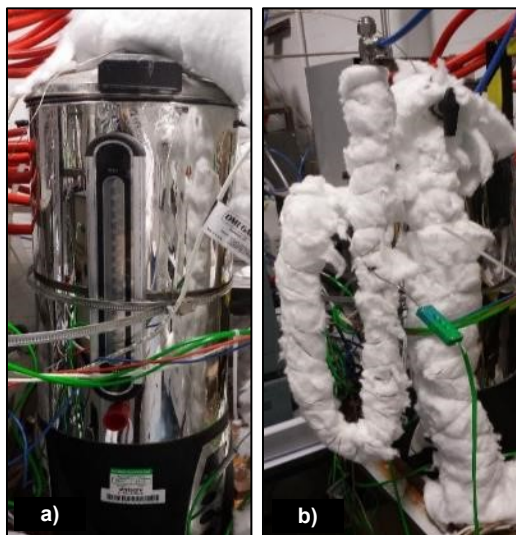


Fig. 4-3: (a) steam generator and (b) bypass line for the AFBR setup

An in-house steam generating system (Fig. 4-3(a)) built around a 5.0 L water boiler with temperature control was repurposed as a water bath housing a 0.2 L stainless steel bubbler vessel with the control system reconfigured to take inputs from a heating controller unit. The bubbler vessel produced steady flowrates of steam subject to constant bath temperature and periodical topping up of water content (every 5 hours of operation). Piping routed N_2 through the bubbler to carry out steam with the gas stream and recombine with the direct N_2 line (Fig. 4-4). For this study, a section of heated piping (Fig. 4-3(b)) was installed to allow bypassing of the generator and directly injecting a flow of water into the system for RH probe calibration. This was to simplify the calibration sequence as an accurate RH probe reading was needed to calibrate the heating set-points for the bath to generate steam. Due to heat losses, the bath temperature could not exceed 80°C so gas flowrates were adjusted based on this. During operation, the volume of liquid in the bath was maintained through controlled drip-feeding of deionized water using a HPLC pump.

To recover the excess steam downstream of the AFBR, a two-stage water trap was built. The first stage consisted of an Incoloy vessel with an internal volume of 40 cm^3 fixed within an ice bath followed by a coil of piping with $\frac{1}{4}$ -inch diameter, with the increased path length allowing the post-reaction gases to cool down and condense within the cylinder. A T-junction and gate valve were incorporated upstream of the cylinder to allow for it to be emptied after each experimental run. The second stage was a CaCl_2 -based vapour trap consisting of a 50 cm^3 , $\frac{1}{2}$ -inch diameter length of piping capped with cross-overs to $\frac{1}{4}$ -inch tubing in either end. The trap contained dry CaCl_2 granules bookended by quantities of glass wool to trap fine debris in either direction and secure the granules in place. The caps were easily re-sealable allowing for periodic replenishment of granules prior to experimental runs.

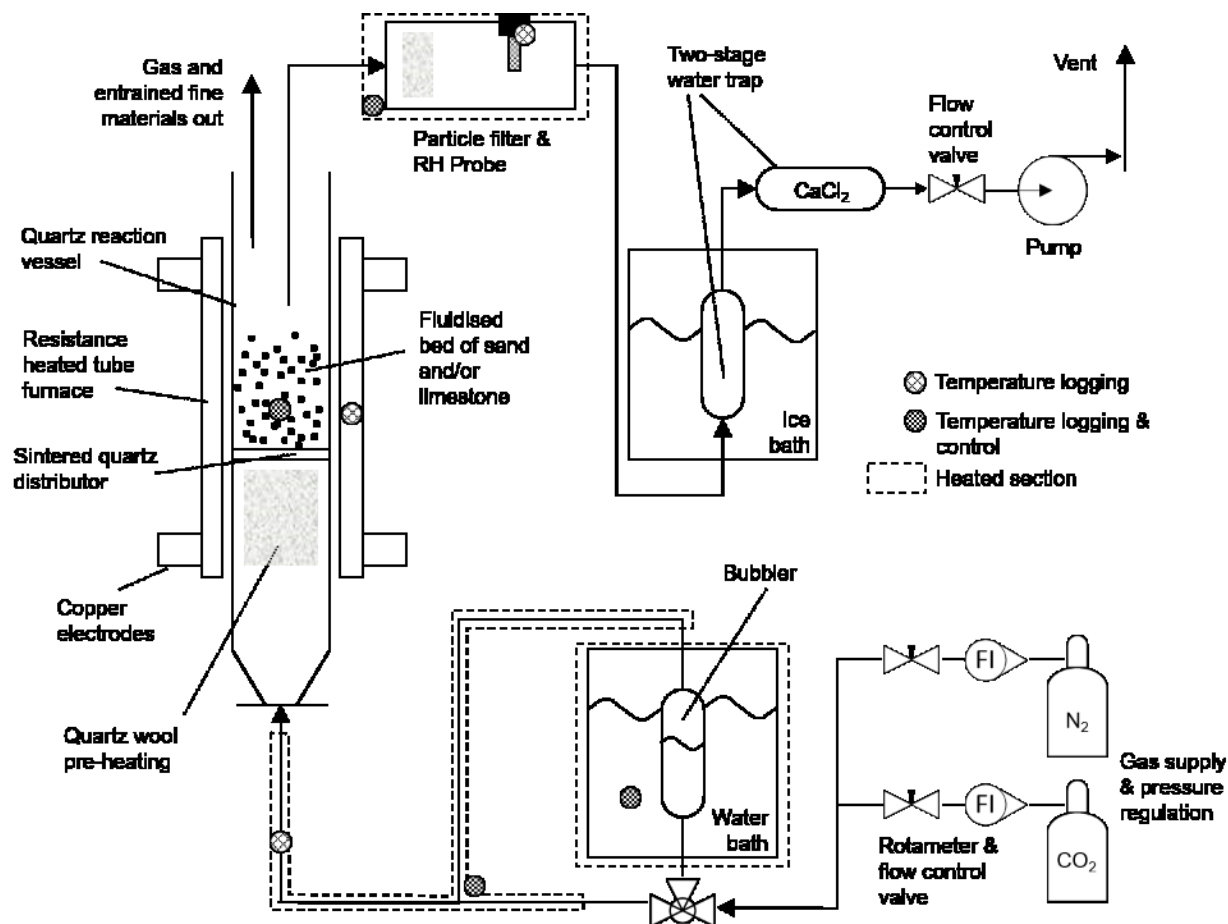


Fig. 4-4: Extended schematic of AFBR inflows and outflows, valves, logging and control sites

4.1.4 Rotameters

Rotameters (Fig. 4-5) were used to control N₂ flow through to the system via either a direct route or via the bubbler as a carrying gas before reaching the AFBR. Calibration curves are provided in Appendix A.2.



Fig. 4-5: Direct and indirect N₂ rotameters connected to the AFBR setup

4.2 Thermogravimetric Analysis Set-up

To obtain the calcium oxide material for the experimental study, natural limestone was sourced and calcined under controlled conditions to obtain the reactive material. This was preferred to purchasing synthetic or pre-prepared calcium oxide as though they would potentially offer a superior kinetic and/or mechanical performance, they are also currently significantly more expensive and thus any scaled-up deployment of the hydration reaction will likely use naturally produced material for economic reasons. As such, obtaining kinetic data for calcined limestone would be of more practical interest in the short term and thus this approach was used. As a result of this decision, limestone was purchased externally and the calcination and characterization were both conducted in-house as discussed in the following sub-sections.

4.2.1 Horizontal Tube Furnace

Batches of limestone were subjected to controlled calcination in a CarboliteTM horizontal tube furnace (Fig. 4-6) through a heating programme under constant N₂ flow. The unit is rated to 1600°C and was chosen for its fast heating rate. Based on the temperature profile of the heating chamber, samples had to be positioned exactly midway (50 cm) along the alumina furnace liner (100 cm total length, 5 cm ID); crucibles constructed from wire gauze were used to contain the samples instead of ceramic boats to allow unobstructed gas flow and more even heating on all sides. The constant flow of pure N₂ gas, which is inert, ensured that no unwanted reactions took place and that any released gas species via calcination (such as CO₂) were removed to prevent re-carbonation while the reacting material cooled down.

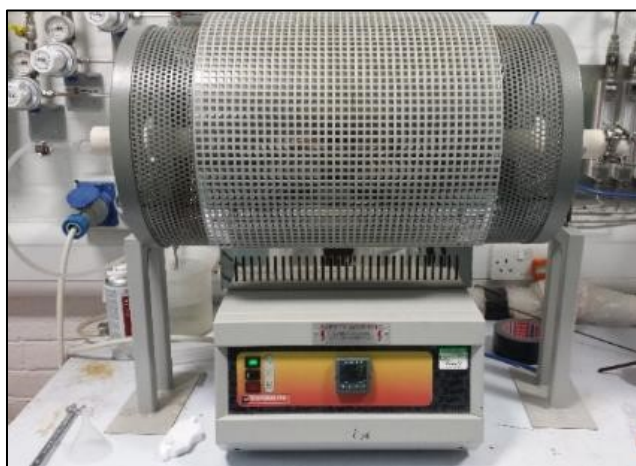


Fig. 4-6: CarboliteTM horizontal tube furnace used for limestone calcination

4.2.2 Thermogravimetric Analysis Unit (TGA)

The extents of hydration and carbonation present in individual batches of calcined limestone were determined using a TA Instruments Q5000® TGA unit (Fig. 4-7); this was selected due to its very high

precision, sensitivity, and programmability up to over 1000°C. For this, samples were placed in platinum pans (10 mm diameter) and heated under N₂ while weight changes were recorded over the duration of the programme which, based on temperature, allowed for quantification of H₂O and CO₂ lost from the samples. It was noted that the unit was very sensitive to external disturbances such as closing doors or heavy contact with the bench and readings can be thrown off due to these, so careful handling was needed to minimise noise in the data through such factors.

In essence, the TGA was used to conduct controlled dehydration and calcination reactions for the pre-calcined materials in very small quantities. Many studies in the literature have used analogous setups to conduct extensive kinetics studies of such materials and thus their suitability for the task is well established.

A three-stage procedure was followed: (1) heating to and holding at 383 K to remove moisture from samples; (2) heating to and holding at 673 K – a temperature at which dehydration and calcination both occur with dehydration occurring at much faster rates; and (3) heating to and holding at 1173 K for complete calcination of the samples. As illustrated in Fig. 4-8, by recording the sample masses at the end of each stage (m_0 , m_h and m_f respectively), the quantities of released moisture, chemically released H₂O, and chemically released CO₂ were calculated which allowed for calculating the extents of conversion of CaO to CaCO₃ and to Ca(OH)₂ in each sample through Eq. 4-1 – 4-2.



Fig. 4-7: TGA unit in operation for characterizing calcined limestone

$$X_{Ca(OH)_2} = \left(\frac{m_0 - m_h}{M_{H_2O}} \right) / \left(\frac{m_f F_{CaO}}{M_{CaO}} \right) \quad (4-1)$$

$$X_{CaCO_3} = \left(\frac{m_h - m_f}{M_{CO_2}} \right) / \left(\frac{m_f F_{CaO}}{M_{CaO}} \right) \quad (4-2)$$

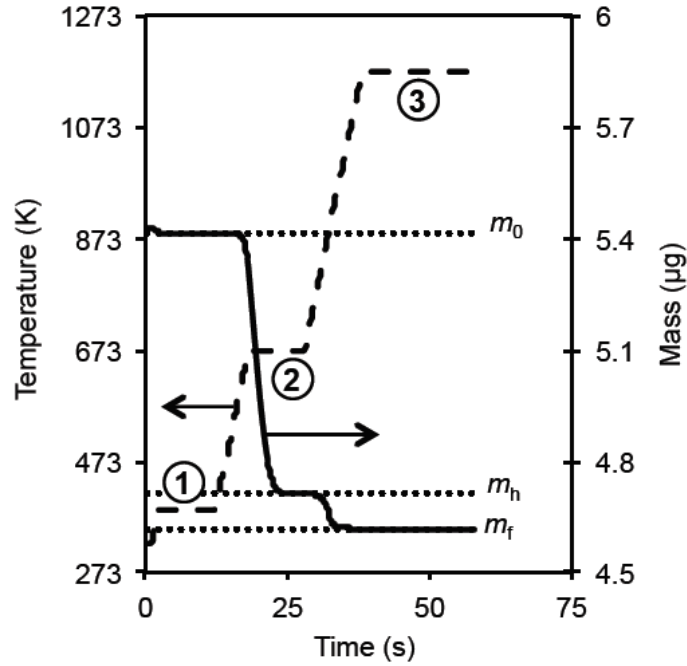


Fig. 4-8: Example results from TGA experiment to quantify hydration and carbonation extents in a pre-calcined limestone sample¹¹⁶

4.3 Nitrogen Adsorption and Desorption Background

The characterisation of calcined limestone samples in terms of their pore volumes, porosities, and pore surface areas was performed using a Micromeritics Tristar™ 3000 N₂ sorption analyser unit. This was done by controlled adsorption of N₂ onto the surface and pores of samples at -196°C at which temperature N₂ liquefies under atmosphere.

The rates of adsorption were interpreted through BET (Brunauer, Emmett, and Teller) theory to estimate cumulative pore surface areas, and BJH (Barrett, Joyner, and Helenda) theory to estimate pore size and volume distributions. Employing this approach allowed direct comparison of the materials used with other work done in the literature as N₂ adsorption/desorption characterization techniques are commonly used for calcined limestone analysis. These approaches are detailed further in Appendices A.7-A.9.

4.4 Material Characterization and Preparation

To produce the CaO sorbent, the composition of the source limestone was first analyzed for impurities. Next, small batches of limestone were calcined to produce CaO, considered as calcined limestone at this point. These were subjected to thermogravimetric analysis to determine the extents of calcination and hydration present, and also to N₂ porosimetry to characterize their surface areas and pore volumes.

4.4.1 Materials Used

Limestone from Longcliffe Quarries Ltd henceforth referred to as ‘LC’ was used throughout the work in 3 different particle size ranges obtained through mechanical sieving: 212-355 μm , 355-425 μm , and 500-710 μm . According to X-Ray Fluorescence (XRF) data (Table 4-1), limestone batches were characterised to be 98% CaO by mass in terms of mineral content after calcination. Here LOI refers to any material that is lost on ignition of the samples; typically loose particulate and/or carbonaceous material such as CO_2 evolved from calcination. The results match up with the specification quoted by the quarry in Table 4-2.

Table 4-1: XRF data for untreated Longcliffe limestone

Element	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	SrO	LOI	Others
Mass %	0.216	0.065	0.069	0.22	55.101	0.023	44.23	<0.076

Table 4-2: Physical properties of Longcliffe limestone as quoted by Longcliffe Quarries Ltd

Moisture Content (wt%)	% Ca in form of CaCO ₃ (mass %)	Bulk Density (tonne/m ³)	Specific Gravity (g/cm ³)
0.05	98.25	1.38	2.65

Sand (SiO₂) was used as an inert and heat-stable thermal ballast to add volume and dilution to the fluidized beds of calcined limestone and to facilitate inter-particle heat transfer. For consistency, the material was solely obtained from David Ball Group, plc. Table 4-3 presents some relevant properties of the specification and grade utilized in this work. All sand was heated at 900°C for at least 2 hours under air to completely dry the material and remove any carbonaceous material that may cause unevenness in particle weight.

Table 4-3: Sand (SiO₂) specification used in this work

Characteristic Particle Shape	Bulk Density (kg/m ³)	Particle size range (μm)
Quasi-spherical	2650	355-425

4.4.2 Limestone Calcination

The Carbolite tube furnace was used to prepare all batches of calcined limestone. A temperature ramp rate of 20°C/min was used though faster rates were possible, so as to reduce thermal stresses on the furnace liner. The calcination was then controlled at either 850 or 950°C for 60 min after which the heating would stop and the material would be allowed to cool to ambient conditions under constant N₂ flow. After several trials of calcined batches being checked through thermogravimetric analysis, a maximum batch size of 5 g was found that could reproducibly be calcined to a sufficiently high extent as seen in Table 4-4.

Table 4-4: Average calcination extents of limestone batches calcined at different temperatures

Limestone batch size (g)	Average mol fraction of Ca as CaO – 850°C	Average mol fraction of Ca as CaO – 950°C
3.0	0.94	0.95
5.0	0.92	0.92
7.0	0.81	0.79
10.0	0.69	0.71

4.4.3 Thermogravimetric Characterization of Calcined Limestone

Table 4-5: TGA-derived data for calcined limestone

Batch ID (Calcination T, min. particle size)	Total CaO (mol fraction of total Ca)	Free CaO (mol fraction of total Ca)
850.212	0.87	0.78
850.355	0.94	0.83
850.500	0.98	0.87
950.212	0.89	0.82
950.355	0.93	0.86
950.500	0.93	0.88

Table 4-6: Composition of calcined limestone broken down by compounds of Ca present as a proportion of total Ca, determined through decomposition analysis in a TGA

Particle size, calcination T (µm, °C)	Mol fraction of Ca as Ca(OH) ₂	Mol fraction of Ca as CaCO ₃	Mol fraction of Ca as CaO
212, 850	0.05	0.03	0.92
355, 850	0.03	0.06	0.91
500, 850	0.02	0.05	0.93
212, 950	0.05	0.03	0.92
355, 950	0.05	0.03	0.92
500, 950	0.04	0.02	0.94

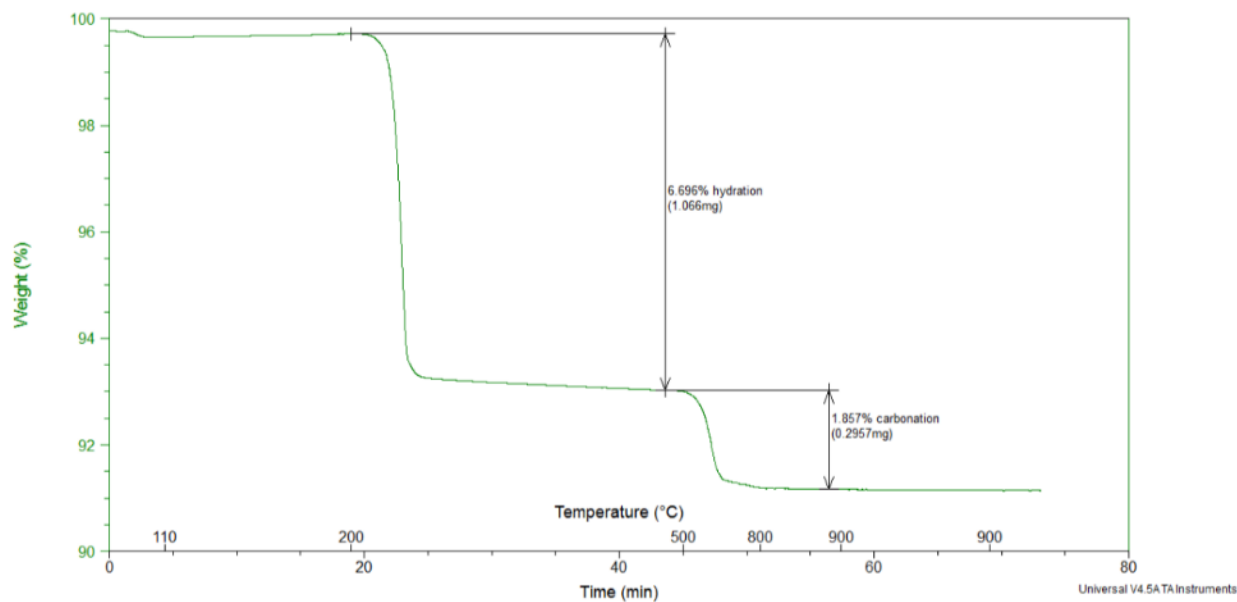


Fig. 4-9: TGA data quantifying hydration and carbonation extents of limestone calcined at 850°C of size fraction 500-710 μm

Table 4-5 and 4-6 show processed TGA data of calcined Longcliffe limestone batches (notation is calcination temperature followed by the lower bound of particle size). The ‘free CaO’ quantity indirectly indicates the extents of ambient hydration prior to reaction; the availability of free CaO was observed to decrease with both decreasing particle size and decreasing calcination temperature. Re-hydration was noted to occur upon handling as the calcined material contacts with moisture in air; efforts to reduce exposure were made through storage in desiccators and appropriately sealed vials.

A sample of the raw data obtained from the TGA analysis is shown in Fig. 4-9 which can be interpreted following the guidance provided in Section 4.2.2. In this case the sample had 91% of its total Ca content available as free CaO which was reasonable for the purposes of this work.

4.4.4 N_2 Porosimetry of Calcined Limestone

Table 4-7 contains data produced by the N_2 porosimetry unit and subsequently calculated porosities for each batch of calcined material based on the ratio of estimated void space volumes (pores) to the bulk volume of the samples. Between 0.15 g and 0.25 g of the samples were degassed under N_2 at 120 °C for at least 2 h and then loaded into the TriStar inside sample flasks. After the evacuation of the sample flasks, the pressure was gradually increased by introducing N_2 at 77 K into the flasks. Following the procedure described in Section 4.3, estimates for the BET surface areas were obtained.

Table 4-7: Porosimetry data and calculated porosities of calcined limestone measured by N_2 porosimetry

Particle size, calcination T (μm , $^{\circ}\text{C}$)	BET Surface Area (m^2/g)	BJH Pore Volume (cm^3/g)	BJH Pore Size (nm)	Density- based ϵ
212, 850	29	0.20	28	0.54
212, 950	12	0.13	29	0.42
355, 850	31	0.22	28	0.54
355, 950	10	0.14	26	0.44
500, 850	30	0.22	29	0.57
500, 950	12	0.14	29	0.45

Subsequently, the adsorption isotherms were used to calculate the specific surface area of the pores and the cumulative pore volume of pores with a diameter between 1.7 nm and 300 nm using the BJH method. It is noted that the calculated values deviate slightly from the true ones, due to the suboptimal filling of pores, which is a result of imperfect molecular packing caused by different pore sizes and irregular pore shapes.¹⁴⁰

It was observed that the measured BET surface area and BJH pore volumes significantly decreased with an increase in calcination temperature at all particle sizes; this is consistent with expected behavior due to sintering at these temperatures¹⁴¹. It is also noted that the BJH average pore size was not affected by particle size or calcination conditions, indicating the consistency in particulate pore size distribution (PSD) of the Longcliff material. The calculated particle porosities were found to decrease with an increase in calcination temperature; also an expected result based on sintering behavior. These quantities were subsequently used for fitting the investigated reaction models to experimental data as discussed in Chapter 5.

4.5 Experimental Preparation

Before experimentation, the AFBR setup and the data collection setup were tested rigorously to quantify the reliability of subsequent reaction data. In this case, several steps were taken: first, the response time of the system to any change was measured and quantified for deconvoluting subsequent data (detailed in Appendix A.16); second, the reactor system as a whole was subject to test experiments for commissioning (detailed in Appendix A.17); and lastly, repeated test experiments to check that the system allowed for performing of consistent and repeatable experiments and that data was logged accurately. The subsequent subsection goes into detail regarding experimental reproducibility.

4.5.1 Experimental Reproducibility

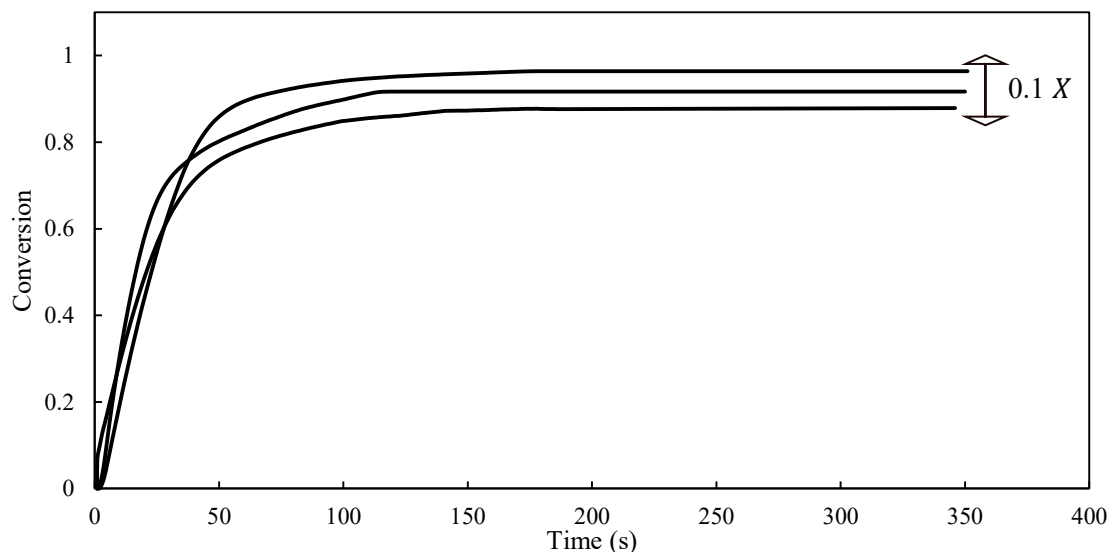


Fig. 4-10: Conversion profiles for reproducibility experiments with 20% steam, 500-710 μm LC calcined at 850°C, $T_{rxn}=300^\circ\text{C}$

The set of repeated hydration experiments conducted for commissioning gave conversions reproducible to a difference of $\pm 5\%$ of the final value (Fig. 4-10). When checking the subsequent data sets, 85% of them were found to fall within this margin of deviation. As this demonstrated good consistency given the real-time variability of concentration and temperature data from the setup, it was accepted as a margin of experimental error. Subsequently, data for each set of experiments were averaged for trend analysis and model fitting. All subsequent data sets presented are the average of 3 experimental runs under identical conditions and it was noted that no set of conditions produced runs that deviated from this conversion range.

Upon further inspection of the 15% of data sets that exhibited greater deviation, it was noted that smaller particle sizes and higher steam concentrations were frequently involved. As smaller particles are likely to undergo a greater degree of attrition due to physical impacts with the bed sand and quartz liner walls, and as the steam generator faced a higher rate of heat loss to the surroundings at set-points corresponding to higher steam concentrations, it was assumed that the uncertainties introduced through this contributed towards accounting for these discrepancies.

As the commissioning and reproducibility experiments demonstrated that the AFBR setup was fit for purpose, the main experimental work was subsequently undertaken. For the subsequent sections of this chapter, only a subset of experimental results are presented for illustrative purposes. The trends highlighted pertaining to these results are consistently observed in the remainder of the data sets – the complete set of experimental results are available along with modelling results in a prior publication.¹⁴²

4.6 Hydration Experimental Scheme

In completing the previous tests, the AFBR setup was quantitatively characterized so as to allow accurate processing of any obtained data from conducted experiments. This section now describes in detail how the hydration experiments were performed and what reaction conditions were tested.

4.6.1 Standard Hydration Reaction Experiments

Small batches of calcined material (0.5 g) were subjected to hydration experiments at 300°C for 180 s in the AFBR set-up coupled with the bubbler system producing steam concentrations of 10-20 mol% with balance N₂ with total flowrates of 47.5 cm³/s giving $u/u_{mf} > 3$. A mass of 12 g of sand (355-425 µm) was used as an inert diluent for the bed to mitigate inter-particle exothermic heating effects over the course of reaction, resulting in negligible (~3%) bed temperature fluctuations such as in Fig. 4-11 which shows the temperature profile of a reaction run that commenced at $t=0$ s. For hydration experiments, the reaction vessel containing sand as a bed diluent was first equilibrated at the desired reaction temperature under pure N₂. The heating and temperature control for the overall system was by means of a custom control interface configured in Agilent VEETM Pro based on a prior design by Blamey¹¹⁶. The bubbler system was then equilibrated at temperatures of 51-68°C (characteristic to this specific setup) corresponding to steam flowrates that would produce the desired steam concentration. The steam supply to the reactor was then switched on, whilst monitored through an RH probe at the reactor exit; the humidity reading was converted through a calibration curve to give real-time measurements of the steam concentration in the exit stream.

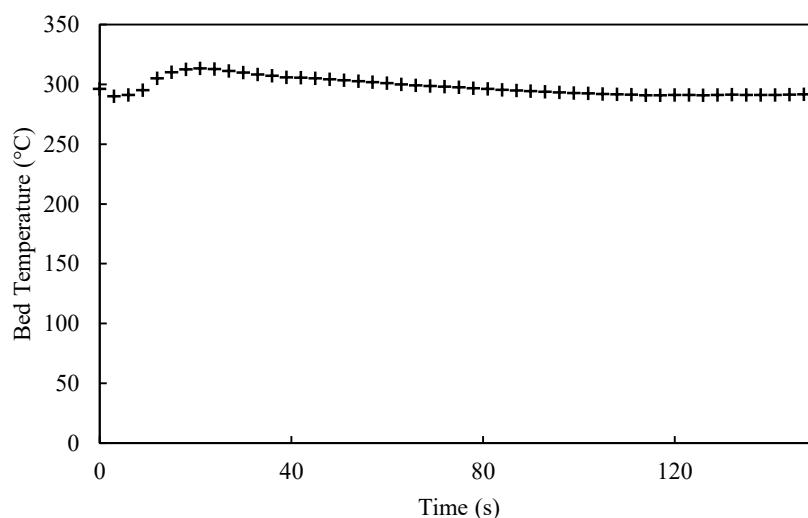


Fig. 4-11: Plot of bed temperature data over time for 500-710 µm LC particles, $T_{rxn}=300^{\circ}\text{C}$, 20% steam

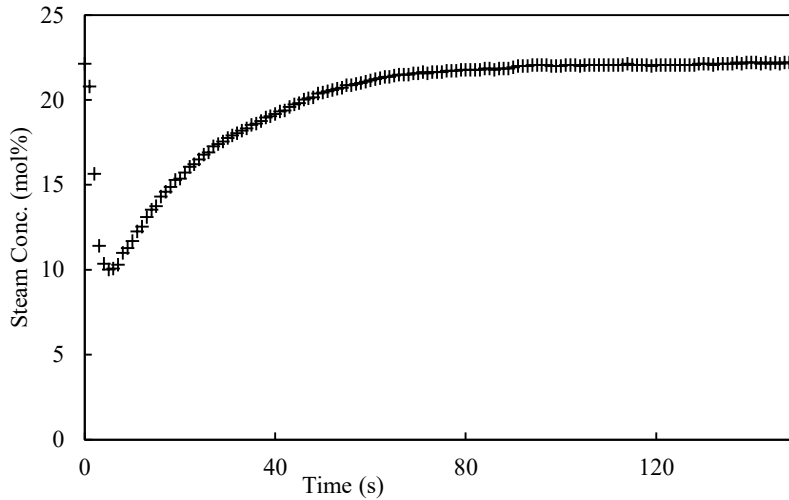


Fig. 4-12: Plot of steam concentration over time for 500-710 μm LC particles, $T_{\text{rxn}}=300^\circ\text{C}$, 20% steam

Batches of calcined material were then directly injected at the top opening of the reaction vessel. The resulting humidity vs time data over 180 s from the RH probe for each run (a sample is shown in Fig. 4-12) was then processed according to Eq. 4-3 using sorbent characterisation data to produce conversion vs time plots for each experiment. The calibration on the RH probe was checked prior to each experiment and the mass balance for steam across the system was consistently $\geq 95\%$, which made for satisfactorily precise measurements. A sample of the measured data and intermediate calculations is provided in Table 4-8.

$$X_t = \frac{c_{\text{steam},0} - \left(\frac{(Q_{N_2} * 100)}{100 - c_{\text{steam},t}} - Q_{N_2} \right) + \sum_{k=0}^{t-1} X_t}{m_{\text{CaO},\text{sample}}} \quad (4-3)$$

Table 4-8: Sample of raw and processed data for hydration of 500-710 μm LC particles under 20% steam

T_{rxn} ($^\circ\text{C}$)		XRF purity		N_2 flow (mol/s)		CaO mass (g)	
300		0.97		0.00181		0.4984	
Time (s)	Relative humidity (%)	T_{probe} ($^\circ\text{C}$)	$P_{\text{w,s}}$ at T_{probe} (kPa)	Steam Conc. (%)	Total molar flow (mol/s)	Cumulative moles of steam reacted (mol)	Conversion to $\text{Ca}(\text{OH})_2$
0	15.33	110.53	146.2	22.13	0.00233	0.00000	0.000
1	14.40	110.53	146.2	20.79	0.00229	0.00004	0.004
2	10.84	110.53	146.2	15.65	0.00215	0.00022	0.025
3	7.91	110.53	146.2	11.42	0.00205	0.00050	0.056
4	7.18	110.53	146.2	10.36	0.00202	0.00081	0.091
5	6.93	110.53	146.2	10.01	0.00201	0.00112	0.126
6	6.98	110.53	146.2	10.08	0.00202	0.00143	0.161
7	7.13	110.53	146.2	10.29	0.00202	0.00174	0.195
8	7.62	110.53	146.2	11.00	0.00204	0.00203	0.228
9	7.81	110.53	146.2	11.28	0.00204	0.00231	0.260

4.6.2 Conditions Tested

Experiments were performed to study the effects of varying particle size (212-355 μm , 355-425 μm , and 500-710 μm), calcination temperature (850°C and 950°C), and steam concentration (5%, 10%, and 20%) on the effectiveness of the various kinetic models considered. Several experiments were also performed at 400°C to assess how the models would hold up for conditions close to those likely used in a scaled-up process. Under the conditions tested, the reactions occurred too fast (<120 s) for reliable kinetics measurements using traditional TGA setups hence only data from the AFBR was used.

4.7 Experimental Results

4 variables were tested (particle size, steam concentration, calcination temperature, and hydration temperature). The effect of calcination temperature is inherently presented in each set of data presented.

4.7.1 Varying Particle Size

By controlling steam concentrations and varying the size of particles, the influence of particle size on reaction behaviour was studied as evidenced in Fig. 4-13. As particle sizes were increased, lower rates of reaction were observed meaning that reactions took longer to proceed to equilibrium. Conversely smaller particles reacted under a kinetics-controlled regime for greater extents of reaction compared to larger particles. The effect, though small, was definite and was found to be more pronounced for the more sintered materials, again due to their measured surface areas and porosities.

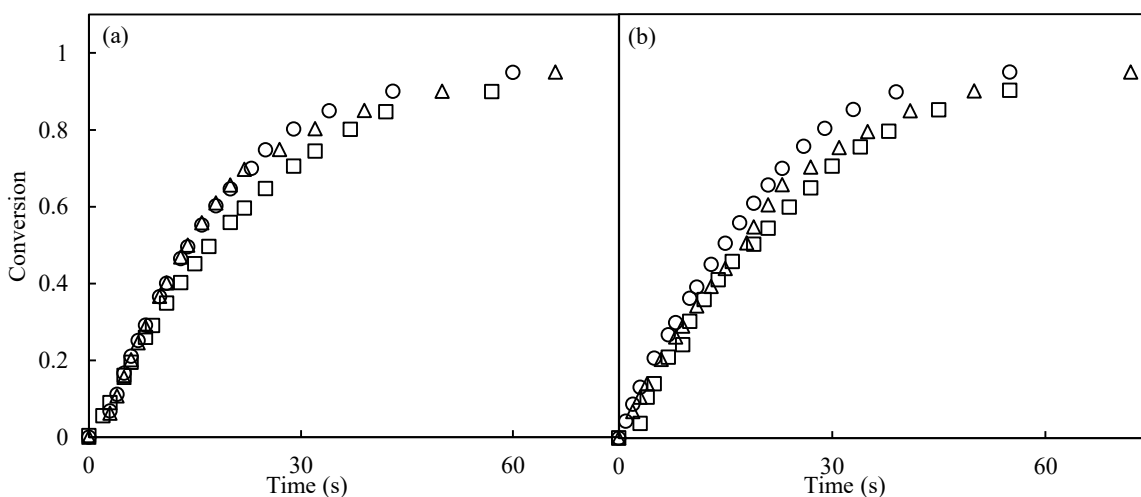


Fig. 4-13: Experimental hydration data under 20% steam, for 212-355 (O), 355-425 (Δ), and 500-710 ($\square$) μm LC particle sizes calcined at (a) 850°C and (b) 950°C, $T_{\text{rxn}}=300^\circ\text{C}$

4.7.2 Varying Steam Concentration

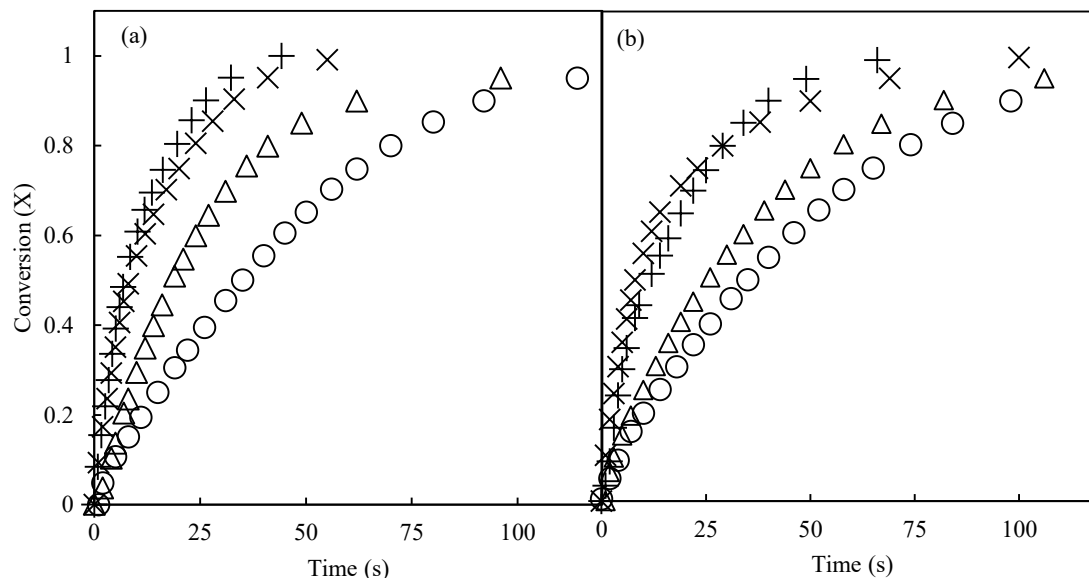


Fig. 4-14: Experimental data for 500-710 μm LC particles calcined at (a) 850°C and (b) 950°C, and then hydrated under 10% (O), 15% (Δ), and 20% ($\square$) steam, $T_{\text{rxn}}=300^\circ\text{C}$

Fig. 4-14 shows relevant data for the effects of steam concentration upon reaction behaviour for one size fraction of particles; however the same relationships were observed for the other sizes. At both sintering temperatures, an increase in steam concentration resulted in shorter reaction times to achieve final conversions. At lower concentrations, the maximum rates of reaction occurred earlier in the reaction.

For the more sintered particles, the total reaction times were longer and the measured maximum reaction rates were noticeably lower; consistent with their significantly smaller measured surface areas and lower porosities. From the reaction rates it was observed that the more sintered particles also experienced mass transfer control for greater extents of reaction as observed in Section 4.7.1; the additional data considered here shows that this trend also applied regardless of steam concentration.

4.7.3 Varying Hydration Temperature

Subsequently, several further experiments were carried out at 400°C to assess the impact of reaction temperature on the kinetic behaviour of the reaction; Fig. 4-15 shows this data only for the largest particle size range as using 355-425 μm and 212-355 μm particles resulted in reactions too fast to study with precision, reaching their final conversions within 30 s. The same considerations resulted in limiting the steam concentration to a maximum of 15% at this temperature.

In contrast to the reaction rates at 300°C, the maximum and average reaction rates at 400°C are both evidently much higher throughout, regardless of steam concentration or calcination temperature, as would be expected based on the thermodynamics of the system. Going much higher than this temperature would likely see a reduction in rates of reaction as the reverse (dehydration) reaction rate becomes significantly faster above 450°C under these partial pressures.

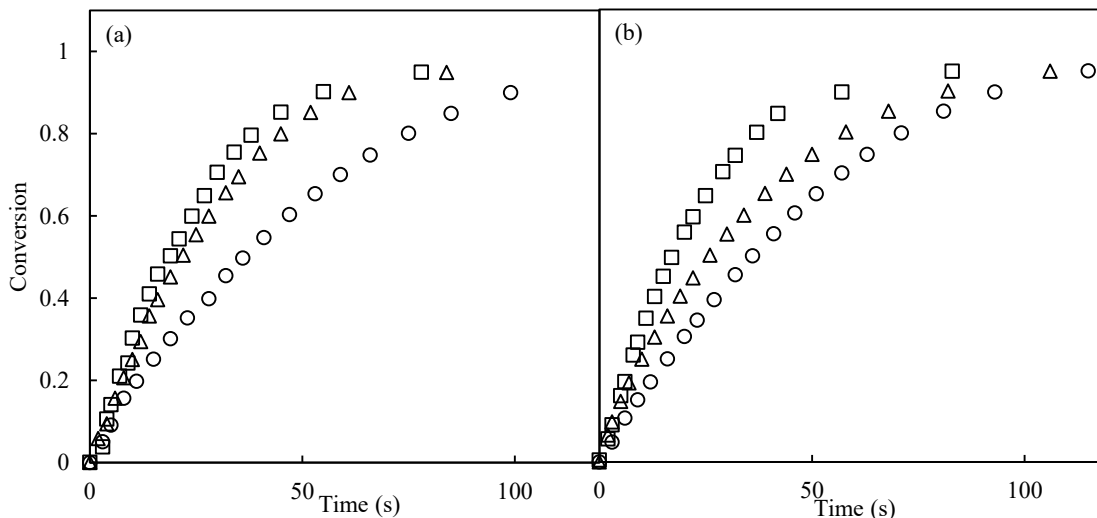


Fig. 4-15: Experimental data for 500-710 μm LC particles calcined at (a) 850°C and (b) 950°C, and then hydrated under 10% (O) and 15% (Δ) steam, $T_{\text{rxn}}=300^\circ\text{C}$ and 10% (x) and 15% (+) steam, $T_{\text{rxn}}=400^\circ\text{C}$

For particles calcined at 950°C and hydrated at 400°C, there is a noticeable kink in the conversion slope not apparent under other studied conditions; this is expected to be due to an abrupt switch over from a kinetics-controlled reaction regime to a diffusion-controlled one. This may have such prominence under these conditions due to the kinetic rate being significantly faster than the intra-particle diffusion rate, meaning that the gaseous steam quickly runs out of available reaction surface area on more accessible pores and needs more time to diffuse within the particles to reach smaller or more occluded pores.

4.7.4 Kinetic Parameter Estimation

To obtain estimates of the activation energy of the reaction, the procedure in Section 4.6.1 was adapted to facilitate additional reactions at 250 and 350°C using 500-710 μm LC particles; here a lower temperature and larger particles were chosen to facilitate slower reactions which allowed more data points to be collected while the reaction is slow enough to measure reliably. The experimental data was processed assuming first-order kinetics and Arrhenius' equation (Eq. 4-4) being applicable. Fig. 4-16 shows the result of the fitting.

$$k_s(T) = A e^{-\frac{E_a}{RT}} \quad (4-4)$$

It was estimated that $A = 3.51 \times 10^{-6} \text{ s}^{-1}$ and $E_a = -51 \text{ kJ/mol}$. The pre-exponential factor fell within the $2.5\text{--}4 \times 10^{-6}$ range reported elsewhere^{111, 118}; meanwhile the activation energy also fell within commonly referenced estimates of -50 to -84 kJ/mol ^{118, 143}. Upon considering the AFBR system and particle sizes used, it was identified that these values could be slight underestimates due to the potential for intra-particle diffusional resistances masking more accurate measurement of the true kinetic rate; however further attention was not devoted to refining these estimates as they did not prove to have a significant impact in the reaction modelling work subsequently done in Chapter 5.

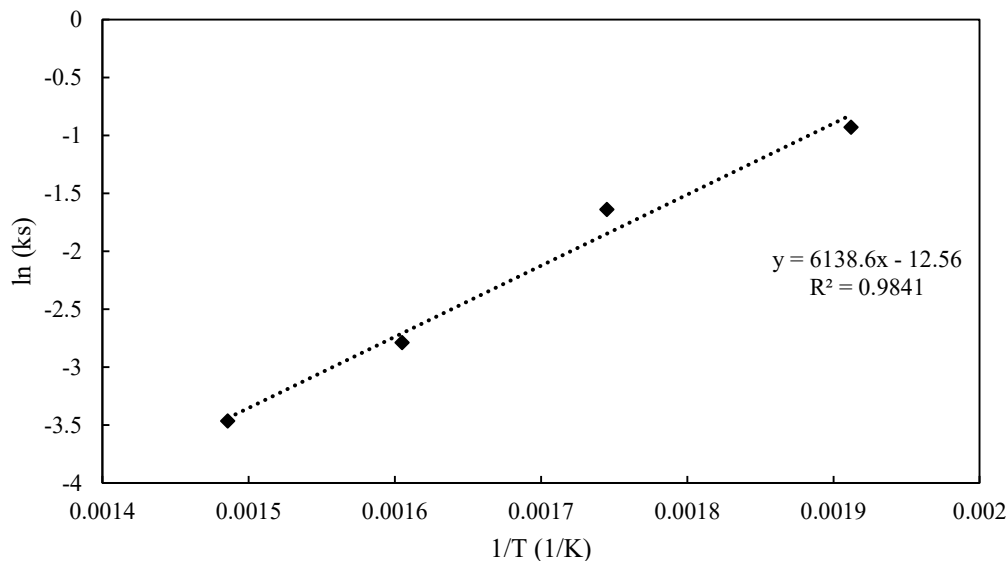


Fig. 4-16: Fitting of hydration kinetic data to the first-order Arrhenius equation

4.8 Chapter Summary and Concluding Remarks

This chapter involved conducting hydration kinetics experiments to obtain conversion data based on the 4 controlled variables: reactant calcination temperature, hydration reaction temperature, steam concentration, and reactant particle size. It was observed that larger particles underwent slower maximum rates of reaction due to greater intra-particle diffusional resistances. It was also found that smaller particles experienced a kinetics-driven regime for larger extents of the reaction. In addition, the porosity of particles –observed to be loosely correlated with particle size – did not appear to have an effect on the conversion behavior.

The effect of varying steam concentration was done by keeping particle sizes and reaction temperature constant while running experiments at the three concentrations established as reproducible by the steam generation system: 5%, 10%, and 20% with the balance being N_2 gas. A higher steam concentration was consistently found to yield higher maximum and average rates of reaction resulting in shorter overall reaction times. The maximum reaction rate was observed to be lower also for more sintered particles which is an expected result due to their resultant smaller surface areas and lower porosities. Across steam

concentrations, the more sintered particles also faced mass transfer controlled reactions for greater extents of the reaction regime; something also observed across particle size ranges.

The influence of varying the hydration reaction temperature was assessed by keeping particle sizes and steam concentrations constant while conducting experiments at both 300°C and 400°C. It was found that only the lower steam concentrations of 10% and 15% and the largest particle size range of 500-710 μm offered reactions slow enough at 400°C to allow for precise kinetics measurements. The higher reaction temperature resulted in much higher maximum and average reaction rates throughout the entirety of reactions; however it was noted that going to temperatures higher than this would see a drop in reaction rate under these conditions as the dehydration reaction rate increases quickly in that temperature range.

Several separate experiments were conducted at 250°C, 300°C, and 350°C for the purposes of estimating the activation energy and the Arrhenius pre-exponential factor to allow for comparison with literature values studying the same reaction under other conditions. The obtained estimates of $A = 6.45 \times 10^{-6} \text{ s}^{-1}$ and $E_a = -52 \text{ kJ/mol}$ fell in line with reported estimates in the broader literature suggesting that the AFBR was suited for conducting accurate kinetics experiments when compared to other setups used elsewhere.

Chapter 5

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CaO Hydration Studies: Kinetic Modelling

Chapter Contents

Sections	Subsections
1. Modelling Introduction	1. Shrinking Core Model (SCM) 2. Random Pore Model (RPM) 3. Grain Catalyst Model (GCM) 4. Comparison of Models
2. Modelling Results at 300°C	1. Shrinking Core Model (SCM) 2. Random Pore Model (RPM) 3. Grain Catalyst Model (GCM)
3. Developing the SCM and GCM	1. Theoretical Development for the SCM (D-SCM) 2. D-SCM Modelling Results 3. Theoretical Development for the GCM (D-GCM) 4. D-GCM Modelling Results
4. Additional Testing of the Developed Models	1. Modelling Results at 400°C 2. Modelling of Literature Data
5. Comparison of Modelling Results	1. χ^2 Goodness of Fit Test 2. Statistical Testing Results
6. Chapter Summary and Concluding Remarks	

5.1 Modelling Introduction

The reaction models chosen for study have been demonstrated to describe certain gas-solid reactions in the literature. However, the most closely-related applications of these models have been either for CaO hydration in a TGA setup, or instead for the CaO carbonation reaction. Hence the novelty of this work is in establishing the suitability of these kinetic models for CaO hydration in a fluidized bed setup, as well as developing new forms of these models better suited for this application. The identification and analysis of the most consistent and accurate models will allow the specification of accurate reaction kinetics in a fluidized bed setup when designing the corresponding TCES flowsheet in Chapter 6.

5.1.1 Shrinking Core Model

The SCM (Fig. 5-1) was first proposed by Yagi and Kunii¹⁴⁴ as a generalized and parameterized reaction model for fluid-solid reactions while considering kinetic control and film diffusion resistances considered in series and can be applied to model a wide variety of gas-solid reaction systems (Eq. 5-1). In its basic form it considers particle density (ρ_B), mass transfer (k_g), reactant concentration (C_A), and changing radii of the particle shell (r_s) and its unreacted core (r_c) to predict conversion extents at various time intervals.

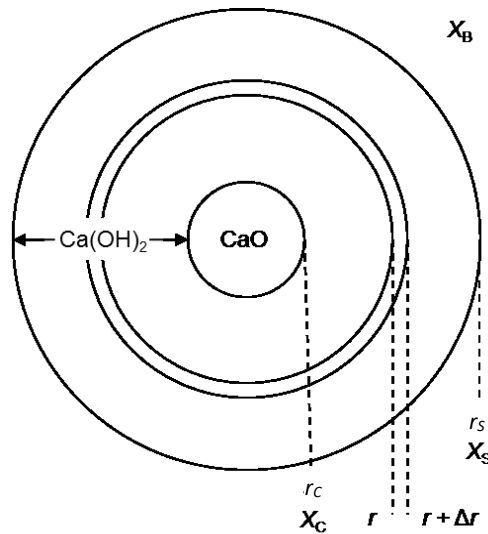


Fig. 5-1: Schematic of SCM¹¹⁶

$$t = \frac{\rho_B R}{3k_g C_A} \left(1 - \left(\frac{r_c}{r_s} \right)^3 \right) \quad (5-1)$$

Recently Criado et al.¹¹¹ investigated this model for the hydration of CaO through a linear fitting of the maximum rate of reaction (hydration) against the inverse of the average particle diameter. They

demonstrated that it could be effectively applied to the reaction under a limited range of conditions, with the assumption of equimolar counter-diffusion. Blamey et al.¹⁴⁵ further developed the SCM (henceforth alluded to as D-SCM) while removing this assumption using Eq. 5-2 – 5-6. However, all investigations thus far have assumed that there is no change in particle size during the reaction; this is known to be untrue as CaO particles expand upon hydration.^{112, 146}

$$\frac{dX_{Ca(OH)_2}}{dt} = \frac{-3}{r_s} (1 - X_{Ca(OH)_2})^{2/3} \frac{M_{CaO} W_{H_2O, r_C}}{\rho_{CaO} (1 - \varepsilon_{CaO})} \quad (5-2)$$

$$W_{H_2O, r_C} = \frac{-CD_e \ln\left[\frac{(1-x_S)}{(1-x_C)}\right]}{r_s \left(\left(\frac{r_C}{r_s} \right)^2 - \frac{r_C}{r_s} \right)} \quad (5-3)$$

$$-k_g (X_B - X_S) = \frac{-D_e \ln\left[\frac{(1-x_S)}{(1-x_C)}\right]}{r_s \left(1 - \frac{1}{(r_C/r_s)} \right)} \quad (5-4)$$

$$k_a = \frac{dX_{Ca(OH)_2}}{dt} \frac{\rho_{CaO} (1 - \varepsilon_{CaO})}{(1 - X_{Ca(OH)_2}) M_{CaO} S_0 C (x_C - x_E)} \quad (5-5)$$

$$X_{Ca(OH)_2} = 1 - \left(\frac{r_C}{r_s} \right)^3 \quad (5-6)$$

Eq. 5-2 calculates the rate of reaction as a function of Eq. 5-2 – 5-6, as well as the molar weight, density, and voidage ε_{CaO} of the sorbent. Eq. 5-3 describes the molar flux of steam W_{H_2O} at the interface between the core and product layers of the particle to describe mass transfer across this layer by way of non-equimolar counter-diffusion; this incorporates D_e to account for intra-particle diffusivity. Eq. 5-5 gives the rate constant k_A assuming first-order kinetics, and needs to be calculated iteratively along with Eq. 5-4 – this allows for Eq. 5-2 to be fully evaluated. Eq. 5-6 models the extent of the reaction using a basic shrinking core expression.

A more detailed discussion of the terms and assumptions involved is provided in the original text¹⁴⁵. The SCM is considered in this study as it is a significantly specialized reaction model that has been widely applied in the literature to this system; however it has not been tested on setups involving a fluidized bed. Hence it is of interest to ascertain whether it is suitable to be adapted for such a setup and also quantitatively compare its performance to the other selected models.

5.1.2 Random Pore Model

The RPM illustrated in Fig. 5-2 was introduced by Bhatia & Perlmutter¹⁴⁷ for improved modelling of fluid-solid reactions. It considers the overall pore size distribution of a material while acknowledging that many particles do not exhibit a regular distribution of pores. In practice it is known to deal more accurately with a wider range of reactions that exhibit more complex behaviour than those predicted well by the SCM. The RPM was found to provide a good fit for the carbonation of CaO^{148, 149}. Eq. 5-7 – 5-10 describe the general (kinetics-controlled) RPM.

$$\frac{dX}{dt} = k_a e^{-\frac{E_a}{RT}} (1 - X) [1 - \Psi_K \ln(1 - X)]^{\frac{1}{2}} \quad (5-7)$$

$$\Psi_K = \frac{4\pi L_o}{\rho S_o^2} \quad (5-8)$$

$$S_o = 2 \int_0^\infty \frac{v_o(r)}{r} dr \quad (5-9)$$

$$L_o = \frac{1}{\pi} \int_0^\infty \frac{v_o(r)}{r^2} dr \quad (5-10)$$

Eq. 5-7 describes the rate of reaction using Eq. 5-8 – 5-10 which calculates the pore structure parameter for the kinetics-controlled model Ψ_K , reaction surface area S_o , and the total overlapping pore length L_o in the system respectively as inputs to Eq. 5-7, as a means to approximate a random distribution of pores. All of these parameters depend on v_o , the pore volume distribution of the material which has to be physically measured via porosimetry from the sample material prior to running experiments. Upon measuring v_o , Eq. 5-9 – 5-10 are computed to then calculate Ψ via Eq. 5-8. Morales-Florez et al.¹⁵⁰ performed a follow-up study investigating the applicability of the diffusion-controlled RPM to the CaO hydration reaction and obtained a good fit with a modification (Eq. 5-11 – 5-13) of the fundamental RPM for diffusion control. However, for their study, the experiments were conducted over extended time scales (300-600 h) and under ambient conditions, meaning that the reaction durations and conditions are significantly different compared to those used in CaL and so its suitability for calcium oxide hydration under CaL conditions has yet to be assessed in the literature. Here an additional term is required to calculate the pore structure parameter for the diffusion-controlled model Ψ_D (Eq. 5-12) - porosity ε_o (Eq. 5-13). This calculated pore structure parameter is used in Eq. 5 which describes the conversion of the reactant, along with ω and θ , which are fitting parameters that have to be iterated to produce a conversion versus time profile from the model.

$$X_B(t) = 1 - \Psi_D e^{-\omega(\sqrt{t} + \theta)^2} \quad (5-11)$$

$$\Psi_D = \frac{4\pi L_o(1-\varepsilon_o)}{S_o^2} \quad (5-12)$$

$$\varepsilon_o = \int_0^\infty v_o(r) dr \quad (5-13)$$

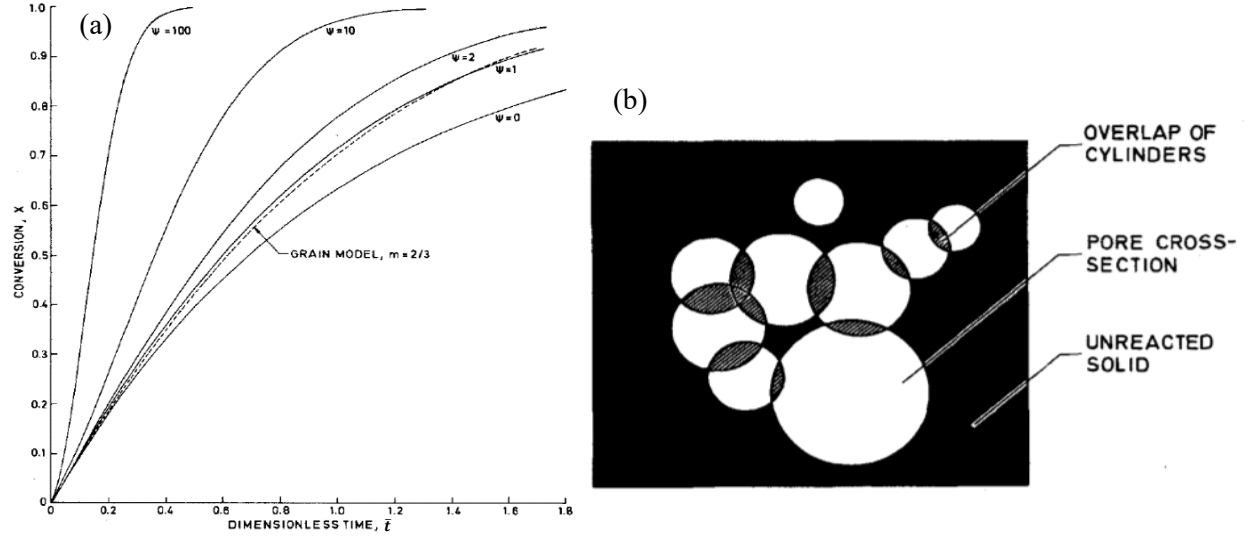


Fig. 5-2: (a) Effect of Ψ on RPM profile;¹⁴⁷ (b) illustration of particle surface with randomly-sized pores¹⁴⁷

The fitting parameters are characteristic to each system and are thus expected to be consistent across experiments from a particular setup. Importantly, as this version of the model is diffusion-controlled, the reaction kinetics do not directly influence the fitting parameters hence the rate of reaction described in Eq. 5-7 is not considered for Eq. 5-11. Overall, the RPM is a reaction model with wide-ranging applicability from which more specialized models have been developed. Hence it is included in this study to quantify its suitability for the considered reaction and to compare this with the performance of more advanced models.

5.1.3 Grain Catalyst Model

CaO hydration kinetics have also been investigated from the perspective of a heat pump/energy storage system¹⁵¹, where Zhang and Ogura noted that previous gas-solid models such as the RPM did not adequately account for heat/mass transfer resistances, changes in pore sizes, and volumetric expansion of the particles, which meant that in many applications the predictions from those models would significantly overestimate the rate of conversion at later stages of reaction as well as the final equilibrium conversions. This led to the introduction of the GCM (Fig. 5-3) which makes use of a fundamental catalyst model as a starting point to obtain Eq. 5-14 – 5-18.

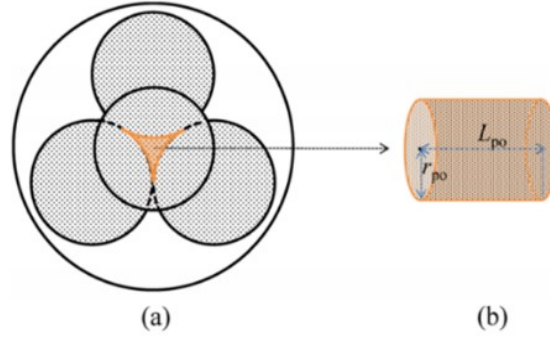


Fig. 5-3: Schematic of GCM pore & grains¹⁵¹

$$\left(\frac{dX_B}{dt}\right)_a = 3E_f \frac{k_1}{1+\left(\frac{k_2}{k_3}\right)} \Delta P_h (1 - X_{hyd})^{\frac{2}{3}} \quad (5-14)$$

$$E_f = \frac{1}{\Phi} \left(\frac{1}{\tanh(3\Phi)} - \frac{1}{3\Phi} \right) \quad (5-15)$$

$$\Phi_X = \frac{r(X)}{3} \sqrt{\frac{k_a \rho(X)}{D_e(X)}} \quad (5-16)$$

$$D_e = 3.067 \frac{\varepsilon}{\tau} r_{po} \sqrt{\frac{T_S}{M_{mg}}} \quad (5-17)$$

$$\Delta P_h = (P_w - P_p)/P_0 \quad (5-18)$$

$$k_1 = 51.1 e^{\frac{-1.096 \times 10^4}{RT}} \quad (5-19)$$

$$\frac{k_2}{k_3} = 5.25 \times 10^4 e^{\frac{-4.81 \times 10^4}{RT}} \quad (5-20)$$

This model considers each CaO particle to be made up of multiple grains and thus performs calculations based on individual grains rather than the overall particle. It was developed by Zhang and Ogura based on hydration experiments conducted in a thermogravimetric analyzer at atmospheric pressure and a range of particle sizes (45-1000 μm) and reaction temperatures (161-288°C). The significance of this study and the resulting model is that they demonstrated the increasing influence of intra-particle mass-transfer resistance with increasing particle size, and accounted for changing the particle size during the reaction.

Eq. 5-14 calculates the actual rate of reaction by accounting for the catalyst effectiveness factor E_f (Eq. 5-15), the characteristic reaction rate constant functions (Eq. 5-19 – 5-20), the pressure gradient across the sorbent particle ΔP_h (Eq. 5-18), and the reaction conversion. The catalyst effectiveness factor is used to account for changes in pore size within the particle over the course of the reaction, and is dependent on the Thiele modulus Φ_X (Eq. 5-16) - a dimensionless quantity dependent on the ratio of the reaction rate to the

effective diffusivity. The effective diffusivity coefficient D_e (Eq. 5-17) accounts for both Knudsen diffusion and effective bulk diffusion phenomenon and is needed for evaluating the Thiele modulus.

The initial inputs into the model are the initial measured average pore radius r_{po} , calculated initial density $\rho(0)$, and calculated initial grain radius $r(0)$, all used to evaluate the effective diffusivity, Thiele modulus, and effectiveness factor at the start of the reaction and then calculate the initial rate of reaction, as the pressure gradient is assumed constant. The initial rate is then used to calculate the new grain density and grain radius, resulting in an iterative calculation procedure that ultimately produces a reaction rate versus time profile for the reaction while accounting for changes in particle and pore sizes along with heat and mass-transfer effects. This last point is one of the main motivations for examining the GCM in this study, as other models in the literature that attempt to describe this system do not consider changes in particle or pore size, hence it is of interest to ascertain if this proves helpful for improving modelling accuracy.

5.1.4 Model Comparison

The model developed by Blamey et al.¹⁴⁵ was considered as the most detailed version of the SCM that had been applied to the reaction and was compared against the predictions returned by the RPM developed by Morales-Florez et al.¹⁵⁰ and the GCM developed by Ogura & Zhang¹⁵¹. While all three models were developed based on diffusion-controlled conditions in TGA setups or open-air systems, their suitability was instead assessed here with kinetics-controlled conditions of industrial setups with an AFBR system.

5.2 Modelling Results at 300°C

Each model was applied to all data sets collected in Chapter 4 for experiments conducted at 300°C to allow for an objective comparison of their modelling performance. The trends in modelling accuracy observed were found to be consistent across particle size ranges; as a result the modelling results presented in this section only show the effect of calcination temperature and steam concentration for brevity as both of those parameters are linked to important attributes of the considered models. Modelling of data sets for 500-710 μm particles are shown as they experienced the slowest reactions which allow for more data points for modelling and hence clearer assessment of the capabilities of each model. The modelling work carried out here only considered the reaction behaviour for the hydration of freshly calcined material. Cycled pure CaO material results in progressively finer powdery substances instead of retaining its original particle size. Such a powder would have significantly different particle size distributions, pore size distributions, and physical durability compared to freshly calcined material.

Studying the kinetics of cycled pure CaO would not be of interest for TCES using fluidized beds at all, as employing fine powders in FBRs presents considerable operational challenges. However, the ideal novel material (as may be developed elsewhere) will, upon cycling, retain the reactivity and physical stability of the uncycled CaO material. Hence, for the time being, studying the kinetics of the uncycled CaO offered new insight into physicochemical phenomena relevant for FBR design – which may remain relevant in the consideration of materials developed in future. It is suggested that these kinetic models be revisited when durable supported/composite CaO materials are successfully tested through cycling in pilot scale FBRs.

5.2.1 Shrinking Core Model

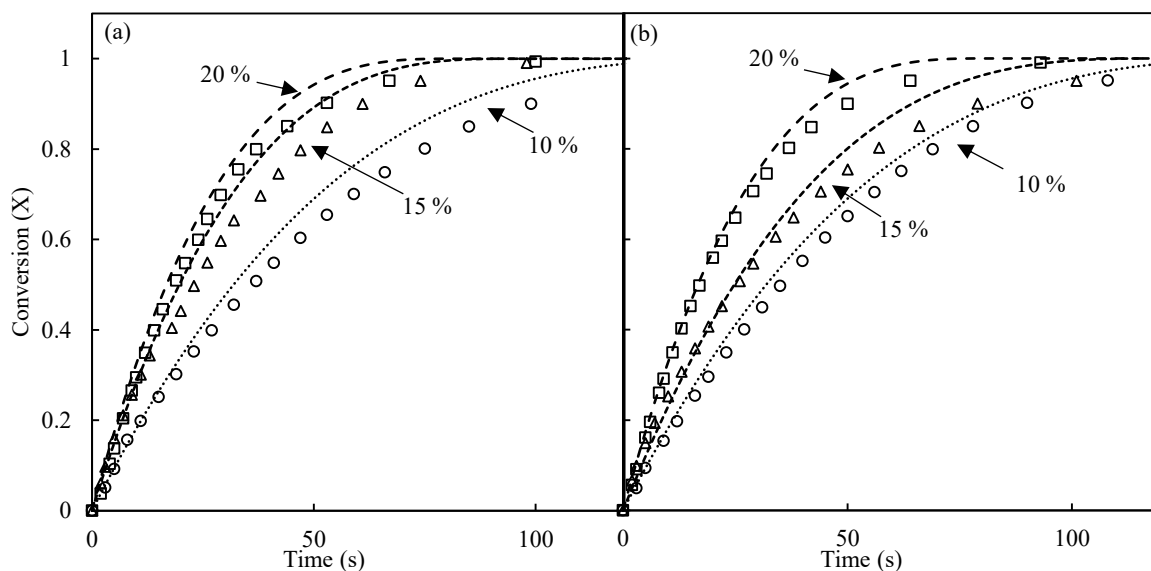


Fig. 5-4: Application of the shrinking core model (SCM) applied to data using 500-710 μm LC particles calcined at (a) 850°C and (b) 950°C, hydrated under 10% (O), 15% (Δ), and 20% ($\square$) steam, $T_{\text{rxn}}=300^\circ\text{C}$

The application of the shrinking core model (SCM) as developed by Blamey¹⁴⁵ is shown in Fig. 5-4. It is observed that in the early stages of reaction ($t < 30$ s) the model produces a very close fit regardless of steam concentration or calcination temperature. During this phase of the reaction it is expected that the reaction rate was driven by the kinetics hence this suggests that the SCM predicts the kinetics-controlled phase well. Subsequently the predictions in the latter stages of reaction ($t > 30$ s) consistently overestimate the conversions; the magnitude of overestimation is noted to be larger at lower steam concentrations. It is likely that this overestimation is caused by the SCM over-accounting for intra-molecular diffusion. This would be as the model assumes a constant particle size – while the particles are in fact known to expand during hydration and become more tortuous. The SCM does however show good responsiveness to varying steam concentrations and the effects of particle sintering; further development of the model was thus considered.

5.2.2 Random Pore Model

In Fig. 5-5, two models have been applied to illustrate the effects of two different reaction control regimes within the random pore model. The first model is the kinetics-controlled model developed by Bhatia & Perlmutter¹⁴⁷; and the second model is an adaptation by Morales et al¹⁵⁰ of a diffusion-controlled model also developed by Bhatia & Perlmutter, which focuses on mass transfer limitations.

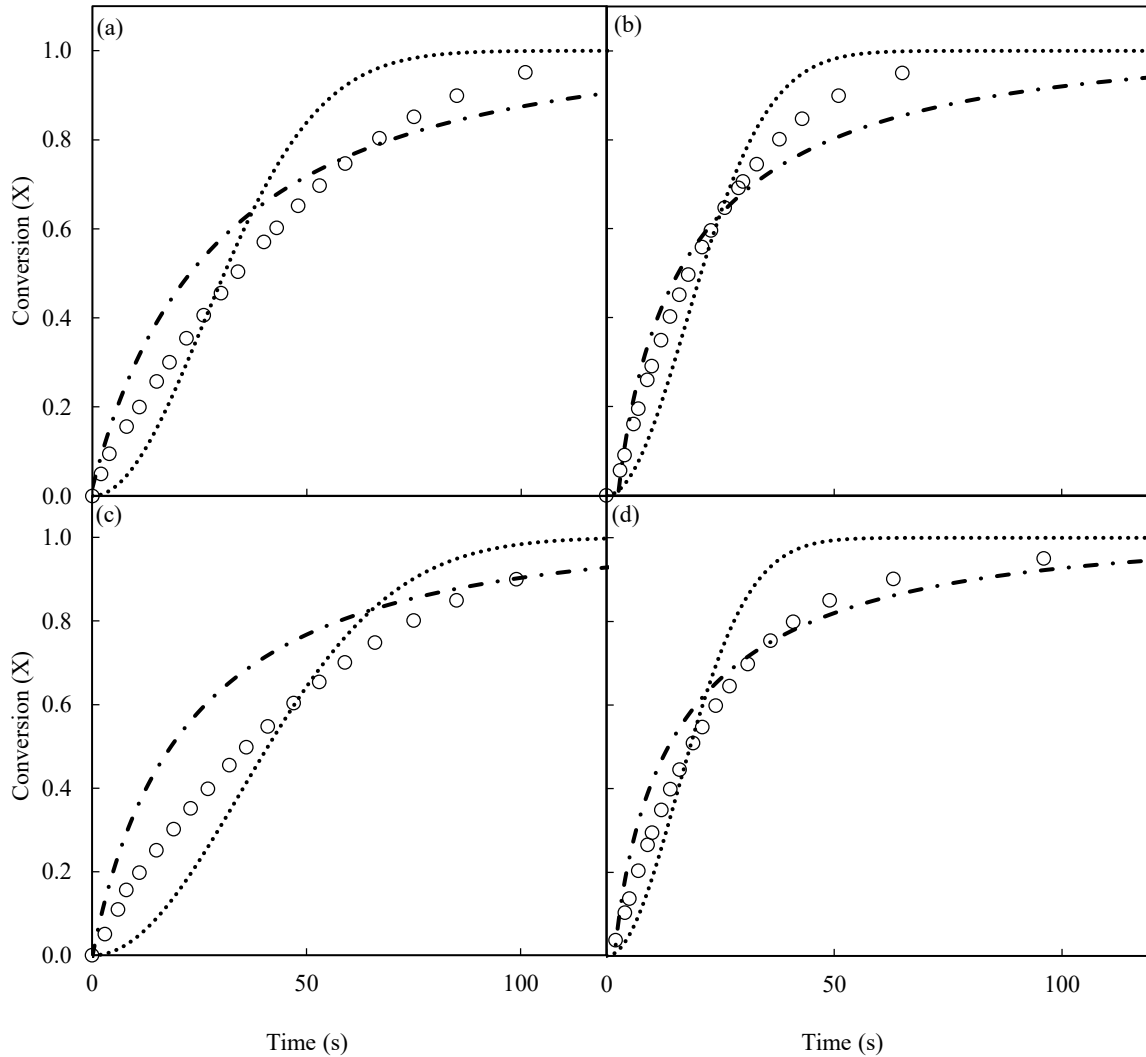


Fig. 5-5: Application of the kinetic-controlled ($\cdots$) and diffusion-controlled ($- \cdot -$) random pore models (RPM) to hydration data using 500-710 μm LC particles ($\circ$) with $T_{\text{rxn}}=300^\circ\text{C}$ and subject to: (a) 10% steam, $T_{\text{calc}}=850^\circ\text{C}$ (b) 20% steam, $T_{\text{calc}}=850^\circ\text{C}$, (c) 10% steam, $T_{\text{calc}}=950^\circ\text{C}$, and (d) 20% steam, $T_{\text{calc}}=950^\circ\text{C}$.

The data illustrates that the kinetic and diffusional regimes of the reactions are within the range predicted by either model. The kinetic RPM presents a sigmoidal profile, initially undershooting the data at low

conversions and over-predicting it at high conversions. In contrast, the mass-transfer RPM over-predicts the data at low conversions and under predicts at high conversions. By overlaying both models it was more clearly observed that the hydration of CaO with steam could be qualitatively described by a balance between the two models in most cases. There is kinetic-control at lower conversions as the reaction surface area is readily available to the reactant, while at higher conversions the controlling mechanism shifts toward intra-particle mass-transfer resistance as the products form deeper within the particle.

However, obtaining a good fit from the RPM is dependent on the steam concentration. As the steam concentration increases, rapid initial rates of reaction cause premature pore blockages at the exterior of the particles leading to lower final conversions. This gives rise to a reaction system that is more diffusion controlled which follows the simplified model by Morales et al, while a lower steam concentration would follow the kinetic model described by Bhatia & Perlmutter. However, the limitation of both models is that they are not able to account for a change in controlling mechanism over the course of the reaction.

Across the experimental data sets, for Bhatia's RPM the average k_a value was $(9.6 \pm 2.0) \times 10^{-5} \text{ s}^{-1}$ and for Morales' RPM the average fitting parameter values were $\omega = (0.27 \pm 0.12) \text{ h}^{-1}$ and $\theta = (2.0 \pm 0.67) \text{ h}^{0.5}$. The large range of error associated with these parameters suggests that the individual RPMs do not manage to describe the kinetics of the reaction consistently across the reaction conditions and particle specifications tested. This indicates that the models are unsuitable for quantitatively describing the CaO hydration reaction.

5.2.3 Grain Catalyst Model

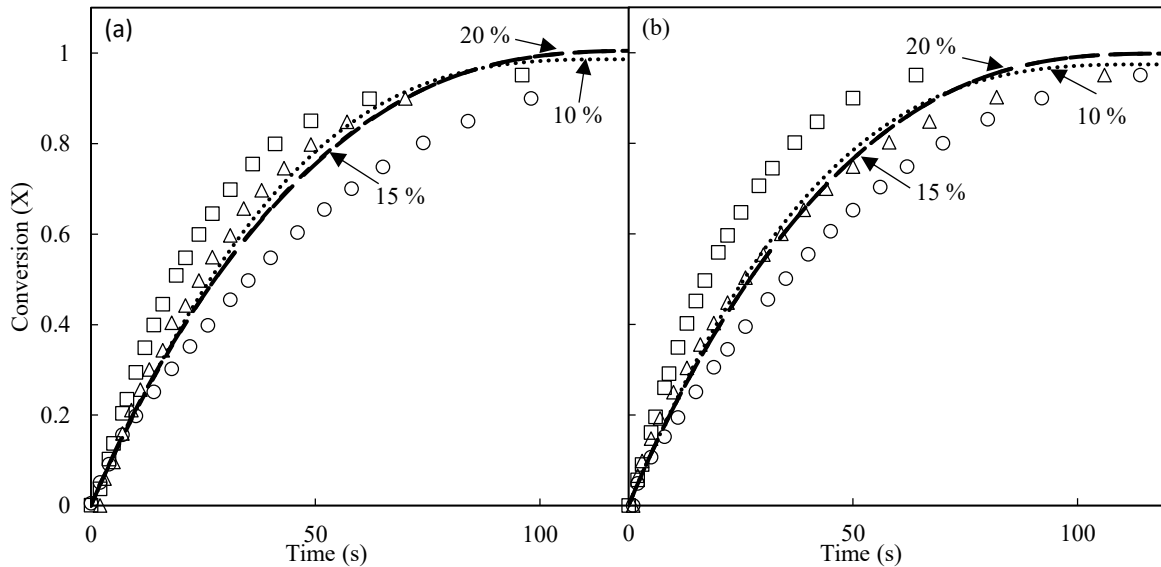


Fig. 5-6: Application of the grain catalyst model (GCM) to data using 500-710 μm LC particles calcined at (a) 850°C and (b) 950°C, hydrated under 10% (O), 15% (Δ), and 20% ($\square$) steam, $T_{\text{rxn}}=300^\circ\text{C}$

Although the original application of the GCM was for a chemical heat pump system, here it was initially applied without any modification. The closeness of the fit of the GCM to the data during the initial kinetic regime was better for larger particles – a result also noted by Zhang and Ogura¹⁵¹. This was attributed to the larger particles undergoing a greater extent of particle expansion which contributes to a decreased reaction rate by increasing the intra-particle diffusional resistance. The GCM was however unresponsive to changes in steam concentration (Fig. 5-6). This was as the model does not consider changes in steam concentration as an input as per Eq. 12 and the effect this has on the transition between a kinetic-control and mass transfer-driven regime. It was noted that there was scope for further development of the model in this regard.

5.3 Developing the SCM and GCM

Based on the qualitative observations made in Section 5.2 the SCM and the GCM were found to have potential for development to overcome their major limitations in an AFBR setup; the SCM lacked consideration of particle size changes while the GCM could not adjust for varying steam concentrations. In this section, each of these considerations are tackled by adding additional quantitative considerations into the two models and applying their developed version to the data afresh.

The two versions of the RPM however were found to be unsuitable to describe the hydration reaction. This was not expected based on their previous application in the literature for the carbonation reaction; something that had also been done using the SCM. This result emphasized the usefulness of considering a range of potential models as, by assessing which ones continued to produce accurate modelling results, the most influential phenomena for modelling the reaction under fluidized conditions could be identified.

5.3.1 Theoretical Development for the SCM (D-SCM)

Several modifications were made to the model used by Blamey et al.¹⁴⁵ for this application. Most notably, the particle size was no longer assumed as constant over the course of reaction, but was instead modelled to expand based on prior work by Blamey et al¹⁴⁶.

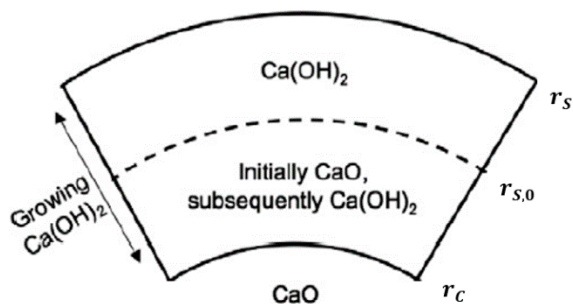


Fig. 5-7: Particle expansion modelled in the D-SCM, adapted from Blamey et al¹⁴⁶

$$\alpha = \frac{\rho_{CaO}(1-\varepsilon_{CaO})M_{Ca(OH)_2}}{\rho_{Ca(OH)_2}(1-\varepsilon_{Ca(OH)_2})M_{CaO}} \quad (5-21)$$

$$\frac{r_S - r_{S,0}}{r_{S,0}} = \frac{\Delta r}{r} = \left(\alpha X_{Ca(OH)_2} + (1 - X_{Ca(OH)_2}) \right)^{1/3} - 1 \quad (5-22)$$

Eq. 5-21 – 5-22 model the change in particle radius with respect to conversion and were obtained by performing a mole balance through the particle for the conversion of CaO while assuming the radius to the particle surface r_S increases over the course of reaction as the volume of Ca(OH)₂ is greater than that of CaO; a full derivation is available in the source text. As the particle size was no longer assumed as constant, the average porosities and densities of the particle were also re-calculated at each step, resulting in a more complex model than the initial version discussed in the introduction to models.

Fig. 5-7 illustrates the modelled growth of the product layer over the course of the reaction. The estimated increases in particle diameter (Table 5-1) are consistent with prior measurements by Wu et al. showing an expected increase of up to ~22% for particles subject to similar calcination conditions¹⁵². The incorporation of particle expansion effects has not been seen in other models in the literature for this system and it makes the D-SCM more physically representative of the reaction.

Table 5-1: Particle expansion ratios across particle sizes subject to various calcination conditions

Initial average particle diameter (PSD), μm	Particle expansion ratio, $r_{S,0}/r_{S,final}$	
	$T_c = 850^\circ\text{C}$	$T_c = 950^\circ\text{C}$
142 (212-355)	1.059	1.094
195 (355-425)	1.073	1.106
303 (500-710)	1.107	1.213

However, the simple model here utilised here does not account fully for inter-phase mass transfer within the fluidized bed. Yao et al.¹⁴⁹ compared kinetics parameters calculated through employing a two-phase fluidized bed model versus a simpler continuous stirred-tank reactor (CSTR) model for a similar fluidized bed setup (with a similarly rapid reaction) and noted that the determined rate constants differed by <20% and the activation energy was practically identical. This suggests that using the two-phase model does not offer any significant improvement in the accuracy of kinetics calculations in such a setup.

Hence, the AFBR was treated as a CSTR, and so X_B was no longer assumed to be the inlet mole fraction of steam (a constant) but instead was assumed to be the measured reactor outlet steam concentration due to

treating the system as well-mixed. Following a method presented by Zhang et al¹⁵³ to verify the extent of mixing in the AFBR, a cross flow factor of 16.31 was obtained, which indicates that the system in the AFBR undergoes a high degree of mixing, allowing this assumption for X_B to be made. The calculation was computed using MATLAB; the code is included in Appendix A.3.

5.3.2 D-SCM Modelling Results

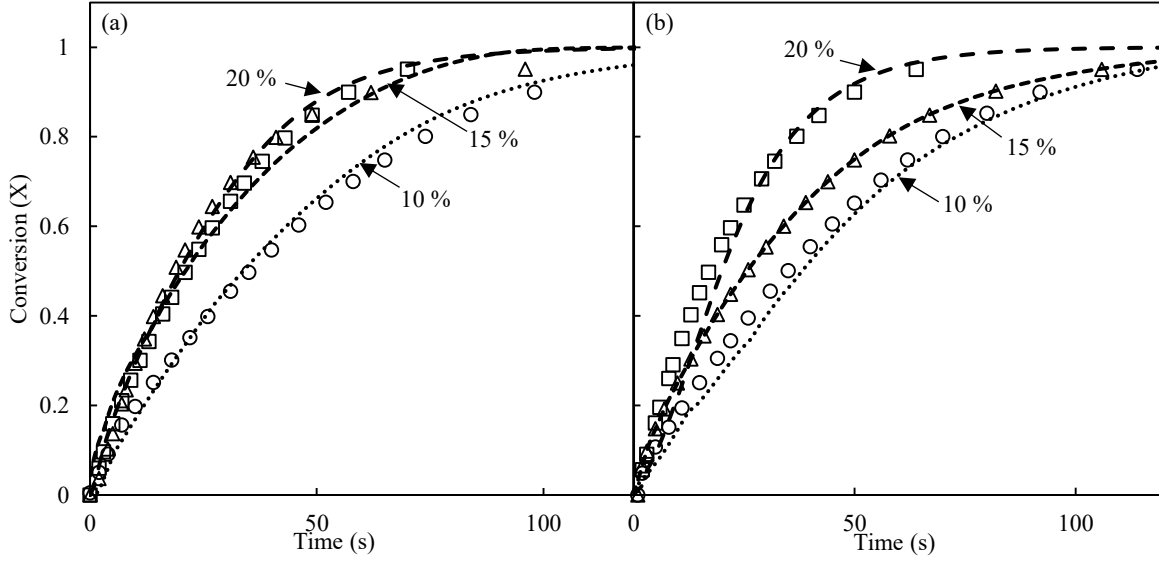


Fig. 5-8: Application of the developed shrinking core model (D-SCM) to data using 500-710 μm LC particles calcined at (a) 850°C and (b) 950°C, hydrated under 10% (O), 15% (Δ), and 20% ($\square$) steam, $T_{rxn}=300^\circ\text{C}$

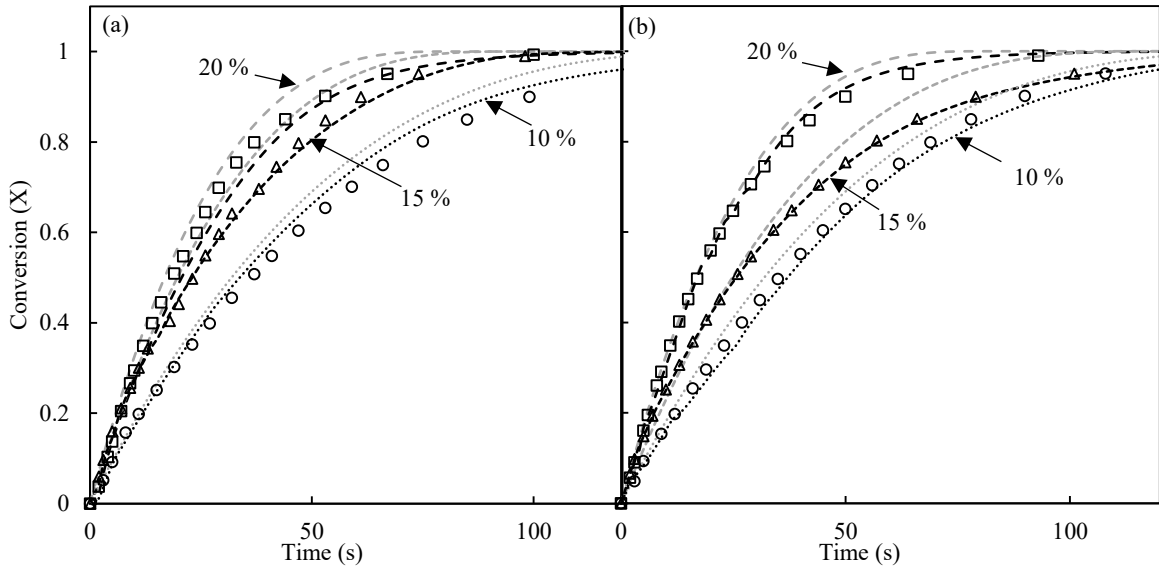


Fig. 5-9: Comparison of SCM (in grey) and D-SCM (in black) applied to data using 500-710 μm LC particles calcined at (a) 850°C and (b) 950°C, hydrated under 10% (O), 15% (Δ), and 20% ($\square$) steam, $T_{rxn}=300^\circ\text{C}$

Fig. 5-8 demonstrates the application of the D-SCM as considered in this work. It is observed that the data is predicted very well across all steam concentrations and particle sizes tested in this study. The consideration of particle expansion as well as a changing X_B term appear to significantly improve the responsiveness of the D-SCM to differences in reaction conditions and particle specifications. It was noted that the k_a values predicted by these calculations were consistently within 10^{-7} to 10^{-8} in magnitude, comparable to results obtained by Blamey et al. under similar reaction conditions¹⁴⁵.

Fig. 5-9 shows the improved prediction accuracy of the D-SCM compared to basic SCM predictions. While the basic SCM performs well at lower conversions, it over-predicts the rate at higher conversions and at higher steam concentrations. This suggests that the additional considerations present in the D-SCM produce improved rate predictions across a range of concentrations, particle specifications, and phases of reaction.

5.3.3 Theoretical Development for the GCM (D-GCM)

A developed version of the GCM (henceforth referred to as the D-GCM) was produced in which Eq. 5-18 was replaced by Eq. 5-23 for calculating ΔP_h . Eq. 5-23 accounts for the changing (measured) partial pressure of steam as the reaction progresses (variable, P_p) compared with the assumption of a fixed steam partial pressure, P_θ used by Eq. 5-18. This approach was based on a similar modification used by Lee et al. and Ogura et al who used a modified GCM for modeling the hydration of CaSO_4 ^{154, 155}.

$$\Delta P_h = (P_p - P_E)/(P_{sat} - (P_p - P_E)) \quad (5-23)$$

This modification was employed to allow for comparison with literature modelling efforts involving adaptations of the GCM and to produce a more appropriate and physically accurate version of the GCM for a fluidized bed setup. As a result of incorporating this development into the GCM to produce the D-GCM, a fairer comparison could be made between the D-SCM and D-GCM as both models now accounted for particle expansion in the course of reaction and were able to adjust to a changing steam concentration – serving to address each major drawback of the forms in which they were initially considered in Section 5.2.

5.3.4 D-GCM Modelling Results

The D-GCM (Fig. 5-10) was more responsive to changes in reactant concentration compared to the GCM. It better accounted for the effects of particle sintering – something that was not apparent in the GCM. The reaction rate was still over-predicted at higher conversions and at higher steam concentrations. Nonetheless, the predicted rate for the kinetic-controlled regime of the reaction was reasonably accurate across particle sizes and calcination conditions, suggesting that the D-GCM is a more versatile model suitable for use in studying kinetics of CaO hydration in a fluidized bed under atmospheres of up to 20% steam.

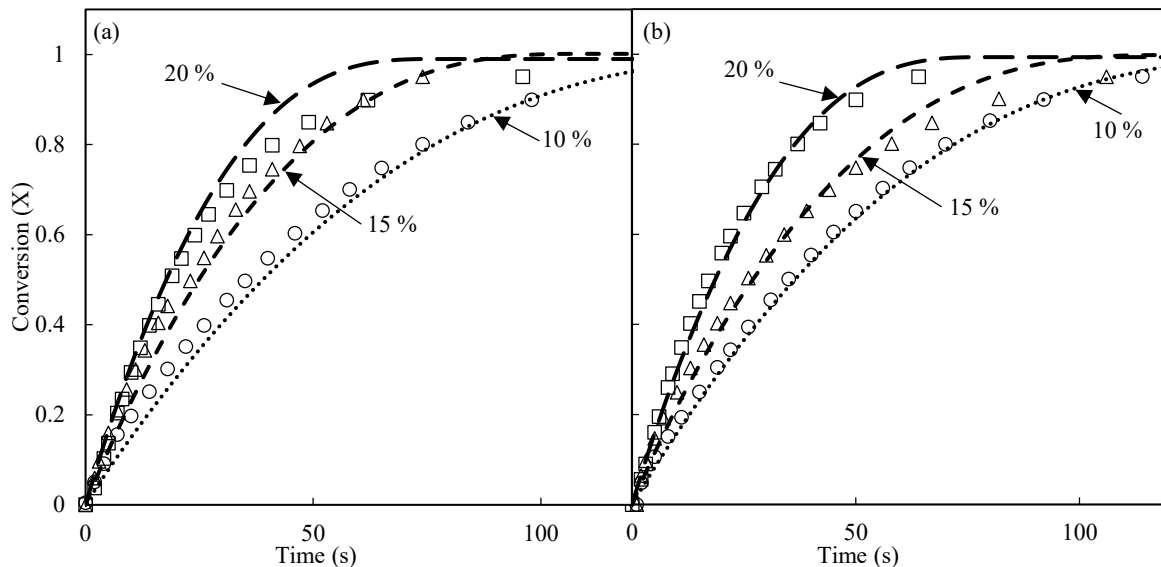


Fig. 5-10: Application of the developed grain catalyst model (D-GCM) to data using 500-710 μm LC particles calcined at (a) 850°C and (b) 950°C, hydrated under 10% (O), 15% (Δ), and 20% ($\square$) steam, $T_{\text{rxn}}=300^\circ\text{C}$

5.4 Additional Testing of the Developed Models

The results from Section 5.3 indicated that the D-SCM and the D-GCM, by way of accounting for additional reaction phenomena, were much more accurate at modelling the reaction kinetics than their initial forms. No obvious distinction in effectiveness was perceived at this level after having considered their adaptability to varying steam concentrations, calcination temperatures, and particle sizes. To this end, a fourth variable – hydration reaction temperature – was considered here for the two developed models to further assess their capabilities. Their performance was then also compared to previous literature results to explore whether they also offered flexibility in being applied to setups elsewhere.

5.4.1 Modelling Results at 400°C

Several experiments were performed at 400°C under 10% and 15% steam concentrations to further test the adaptability of the D-SCM (Fig. 5-11) and the D-GCM (Fig. 5-12) to changing reaction conditions. At these temperatures, the measured reaction rate during the initial kinetically-controlled stage of the reaction (up to ~40% conversion) was not significantly affected by differences in steam concentration. It must be noted that due to the faster kinetics, the time axes in these figures are zoomed in compared to those in Section 5.2.

Fig. 5-11 shows that the D-SCM consistently predicts the reaction rate across steam concentrations and calcination conditions at both lower and higher conversions. In comparison, D-GCM significantly over-

predicts the rate at higher conversions leading to more inaccurate conversion estimates as the reaction progresses (Fig. 5-12). This suggests that the D-GCM does not fully account for the effects of particle sintering on the diffusional resistances faced under higher steam concentrations or reaction temperatures. There could be scope for further development in this regard for the D-GCM.

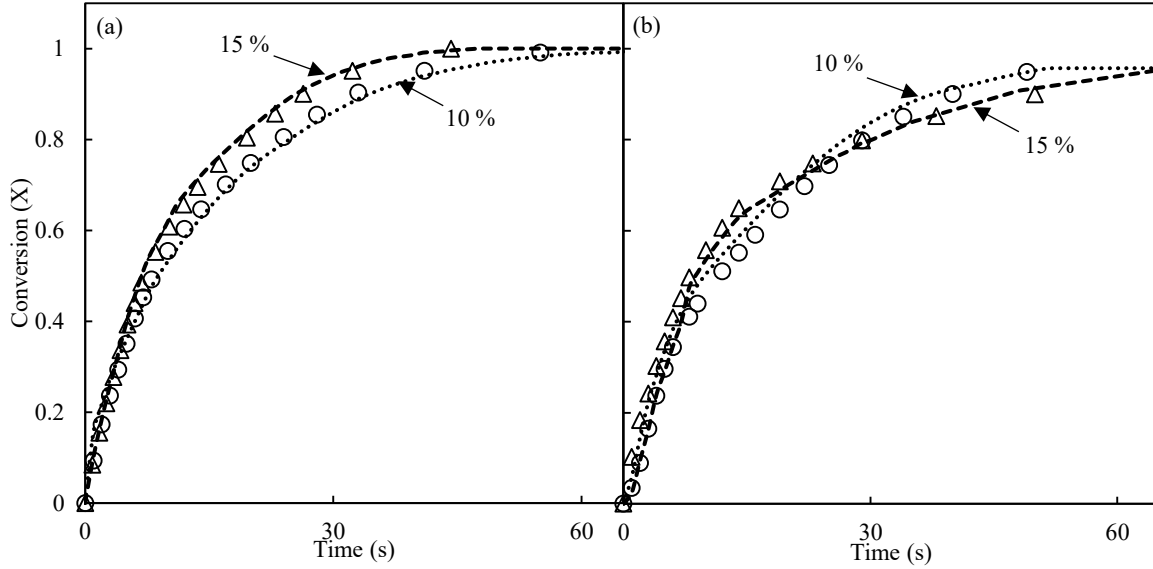


Fig. 5-11: Application of the developed shrinking core model (D-SCM) to data using 500-710 μm LC particles calcined at (a) 850°C and (b) 950°C, hydrated under 10% (O) and 15% (Δ) steam, with $T_{rxn}=400^\circ\text{C}$

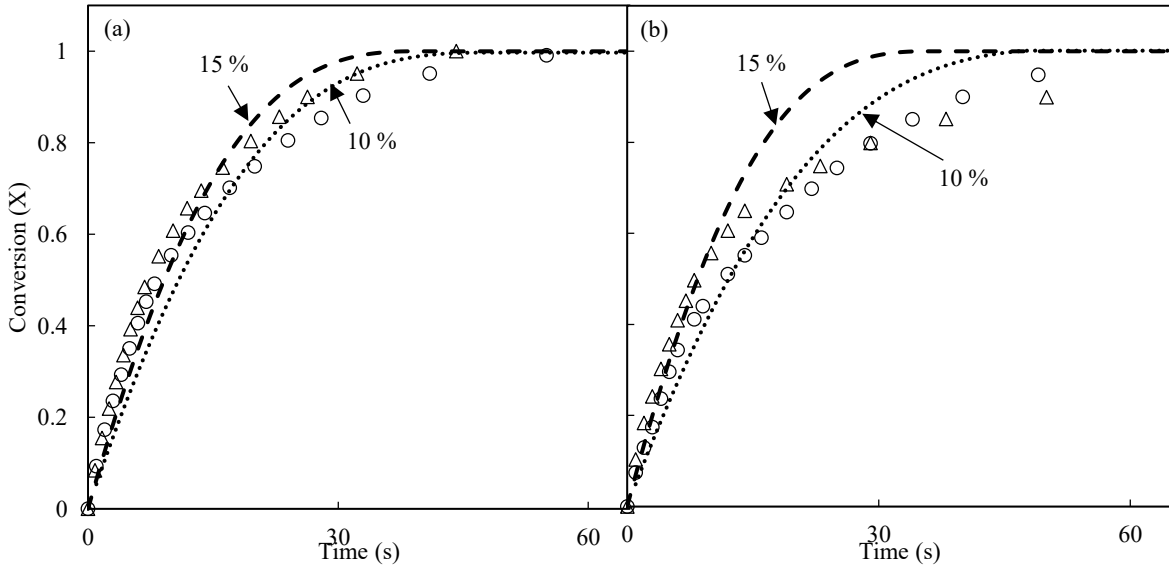


Fig. 5-12: Application of the developed grain catalyst model (D-GCM) to data using 500-710 μm LC particles calcined at (a) 850°C and (b) 950°C, hydrated under 10% (O) and 15% (Δ) steam, with $T_{rxn}=400^\circ\text{C}$

5.4.2 Modelling of Literature Data

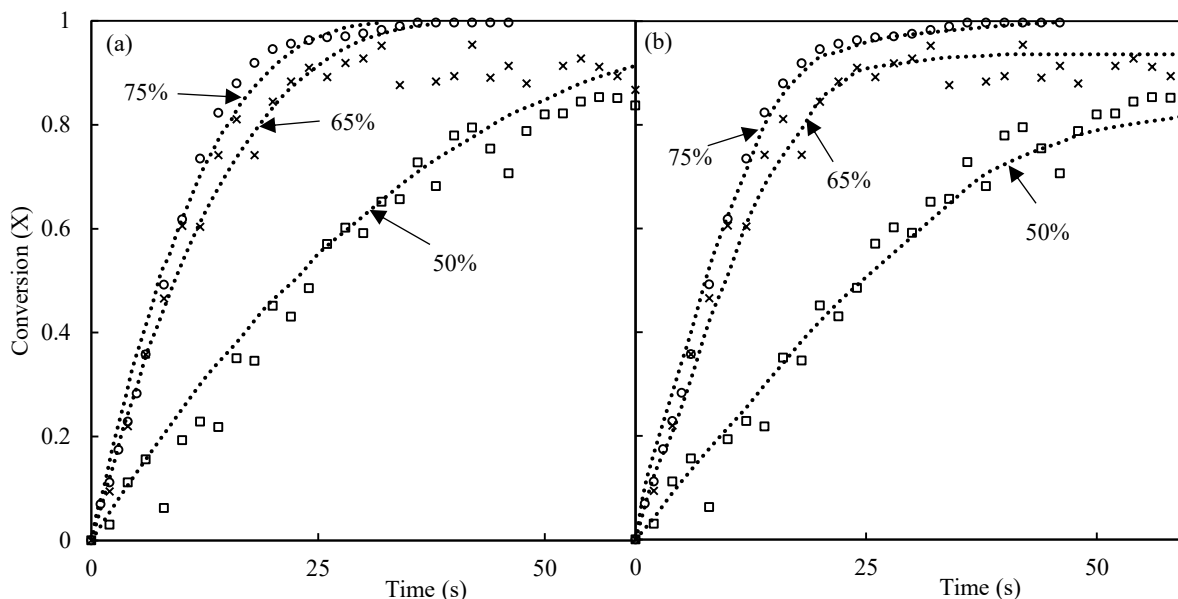


Fig. 5-13: Application of the (a) SCM and (b) D-SCM to literature data¹¹¹ using 3 mg samples of 100-200 μm Compostilla limestone particles calcined at 800°C for 10 min and hydrated under 50% ($\square$), 65% ($\times$), and 75% ($\circ$) steam in a TGA, $T_{\text{rxn}}=450^\circ\text{C}$

In order to more thoroughly test the flexibility of the D-SCM, data for higher reaction temperatures and steam concentrations was needed. However in the AFBR, going to a higher temperature or steam concentration would result in too fast a reaction to obtain accurate kinetics measurements. Moreover, testing the model with data obtained from other setups would help cement its practical usefulness.

To this end, the SCM and D-SCM were applied to literature data in Fig. 5-13. In this application, X_B was treated to be constant due to the change in setup from an AFBR to a TGA. It is observed that even at these conditions with a different specification of reactant and reaction setup, the D-SCM still produces a more accurate fit than the SCM across the course of each reaction. This demonstrates that the D-SCM has the potential for practical application to measurements from other independent experimental setups.

5.5 Comparison of Modelling Results

In Section 5.2 and Section 5.4 the modelling predictions of the SCM, RPM, GCM, D-SCM, and D-GCM were qualitatively analysed according to phases of reaction and their flexibility in adapting to the four controlled variables of material calcination temperature, hydration reaction temperature, particle size, and steam concentration.

However, for thoroughness and a numerically-oriented objective comparison between the models – for in certain applications, the performance of a model is a greater priority than ascertaining whether all theoretical considerations are being addressed – a statistical analysis was conducted based on all data sets modelled by each model. It is to be noted that the data from the RPM was excluded from this analysis as the poorness of its fitting results meant that quantification of them would yield no useful information.

5.5.1 χ^2 Goodness of Fit Test

A quantitative comparison of the models was made by performing the χ^2 -GOF test¹⁵⁶ on the predicted rates of reaction at equal conversion intervals for the D-SCM and the D-GCM (Fig. 5-14). Comparisons with predictions from the basic forms of the models (qualitatively discussed in the preceding section) to have also been made. The RPM predictions were not included as part of the χ^2 -GOF comparisons due to the visibly poor fit provided as discussed in the modelling section (Fig. 5-5), while the results of modelling experimental data were excluded as too few measurements were available to make a fair comparison. The test returns the probability that the differences between observed data and modelled data are due to sampling error; values close to 1 indicate ideal fitting. The objective of this is to quantitatively understand and compare how accurate the kinetic models were in predicting the experimental data.

5.5.2 Statistical Testing Results

Table 5-2: Goodness of Fit test results for various kinetic models

Particle Size (μm)	T_{rxn} ($^{\circ}\text{C}$)	D-SCM	SCM	D-GCM	GCM
212-355	300	0.977	0.871	0.898	0.584
355-425	300	0.987	0.875	0.880	0.441
500-710	300	0.980	0.898	0.930	0.347
Mean		0.981	0.881	0.903	0.457
S.D.		0.005	0.015	0.025	0.119
500-710	400	0.884	0.707	0.751	0.254
Mean		0.884	0.707	0.751	0.254
S.D.		0.041	0.068	0.069	0.133

The statistical results in Table 5-2 show that the predictions made by the basic forms of the SCM and GCM are consistently less representative of the experimental data compared to predictions made by the developed

versions. This means that the developed forms of the SCM and GCM discussed in this work appear to produce the most accurate predictions among the six models discussed in this work altogether, suggesting that the assumptions and parameters accounted for in these two models are more representative of the physical reaction system of the hydration of CaO.

The D-SCM returned the most accurate predictions overall with the greatest consistency evidenced by its data producing the lowest standard deviation. This is corroborated by Fig. 5-14 where it is observed that the D-SCM consistently produced a very close fit to the data at all stages of the reaction, while the fit produced by the SCM deviated more during later stages of reaction.

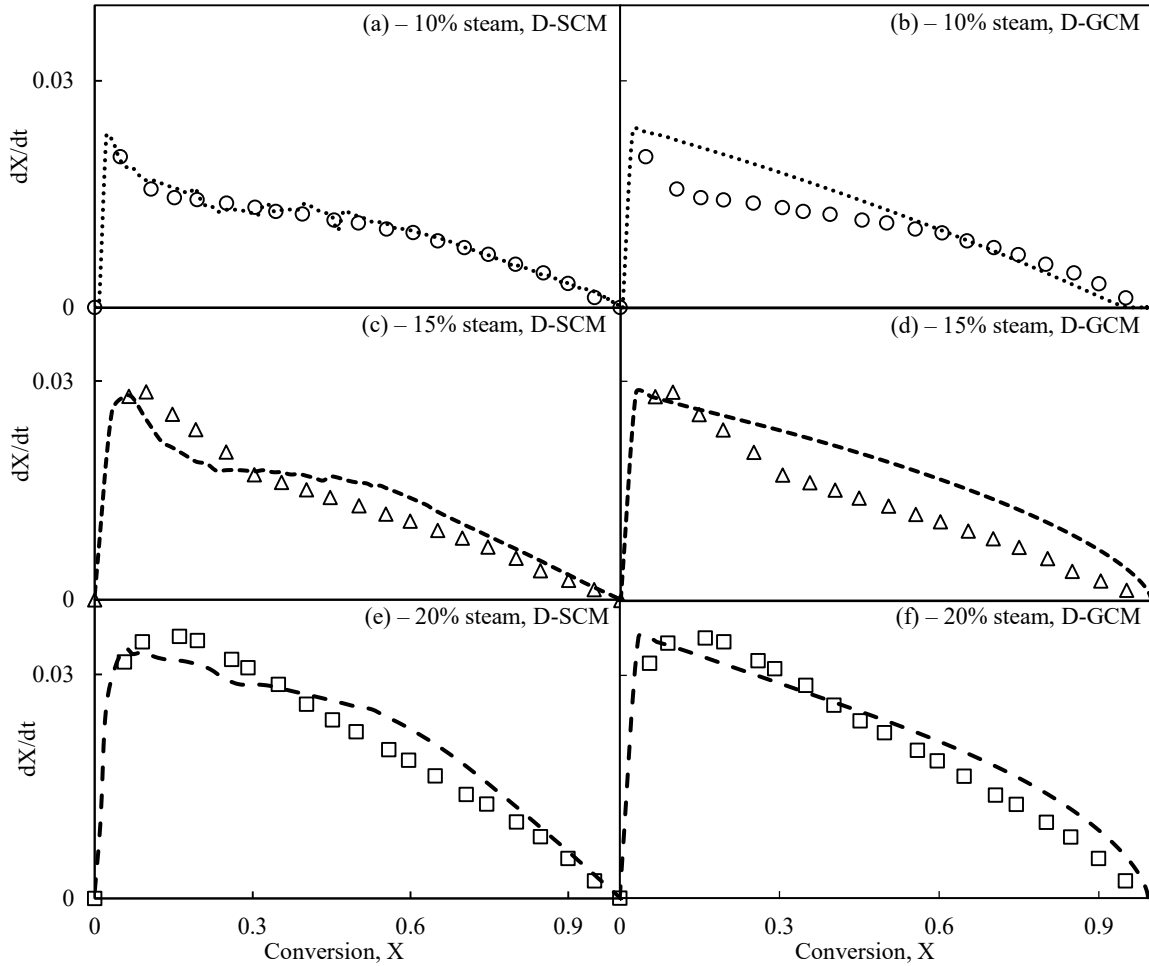


Fig. 5-14: Comparison of reaction rate predictions from the D-SCM [(a), (c), (e)] and the D-GCM [(b), (d), (f)] versus conversion of 500-710 μm LC particles calcined at 850°C, hydrated under 10% (O), 15% (Δ), and 20% ($\square$) steam, $T_{\text{rxn}}=300^\circ\text{C}$

Comparing the means of the modelling results at 300°C and 400°C, the D-SCM produced in this work yielded improvements of 11% and 25% in modelling accuracies compared to the previously most accurate available model in the literature (the SCM). These margins of improvement as well as the quantitative goodness-of-fit results produced by the D-SCM are a significant advancement in the kinetic modelling space and the model developed here can be henceforth used for more accurate and reliable solid-gas kinetic modelling conducted under fluidized conditions such as for process scale-up studies.

5.6 Chapter Summary and Concluding Remarks

This chapter introduced and examined the suitability of various analytical kinetic models to describe the hydration reaction between calcium oxide and steam under fluidized conditions. In addition, it developed two kinetic models to a level not seen before in the literature for studies in this area.

On the basis of the research objectives in Chapter 1, the following was concluded about the initially considered reaction models:

- (i) The non-equimolar counter-diffusion SCM developed by Blamey et al.¹⁴⁵ modified for a CST model showed very good consistency with data across a range of concentrations and particle sizes; however it over-predicts the rate at higher conversions to a larger extent with smaller particle sizes. It showed good potential for being improved upon.
- (ii) The diffusion-controlled RPM developed by Morales-Florez et al.¹⁵⁰ showed good consistency with data across a range of concentrations and particle sizes; however deviations were noted at initial stages due to kinetic control which the model did not consider. The kinetics-controlled RPM meanwhile provided a very poor fit overall but improved at higher conversions.
- (iii) The GCM developed by Ogura & Zhang¹⁵¹ consistently under-predicted the data but was able to predict the general shape of the conversion curves in terms of phases of kinetics-control and diffusion-control. The poorness of fit at smaller particle sizes noted by the original authors was verified, and the model was unable to adjust for changes in steam concentration in an AFBR and thus could not adjust to varying steam concentrations.

Through statistical testing, the D-SCM was found to be most accurate for studying the hydration of calcium oxide, producing 11-25% more accurate model fitting than possible before. The analytical assumptions involved in the D-SCM are applicable in the study of doped sorbents, synthetic analogues, or derivative materials on the bench scale as well as more importantly for scale-up studies. This is as in the latter application, larger particle sizes and more sintered particles are often used – both conditions where the D-SCM has performed better in this study compared to other models considered. The improved accuracy and

flexibility of the D-SCM allows future analytical and optimisation studies of the overall processes to be more reliable and will allow for better understanding of the effect of varying process conditions as well as sorbent characteristics on the overall course of the reaction.

There were a few areas identified for further work. Firstly, the AFBF setup could be upgraded to allow for higher steam concentrations to be tested – potentially achievable by setting up multiple steam generators in parallel. Pursuing a higher steam concentration could result in very rapid initial conversion rates but only partial hydration at equilibrium, which could be suitable for batch hydration runs on larger time scales.

Despite showing good responsiveness and closeness of fitting after the updating of X_B and the incorporation of particle expansion considerations, the D-SCM could be still further developed to take into account any sintering that occurs over the course of reaction. This would be especially helpful for cycled experiments and could lead to more accurate predictions over longer periods of cycled reactions, such as in thermochemical energy storage applications.

The diffusion and kinetics controlled versions of the RPM could be adapted and merged, by means of a prediction weighting factor or otherwise, in order to account for transitions between the two regimes that occur over the course of a reaction. The two versions showed very responsive fits to the data across varying conditions and could point toward a better model.

The D-GCM's theoretical development could be revisited to assess the author's definition for ΔP_h in order to improve the model's responsiveness to different steam concentrations as although efforts have been made here, the results at higher reaction temperatures indicated significant room for improvement in this regard. This would supplement the fact that it already accounts for particle expansion and heat and mass transfer resistances in the fluidised bed which had not been treated by the other models initially considered.

On the scope of the experimental study, a wider range of reaction temperatures could be assessed to further examine the versatility of the three models in predicting the conversion profiles. As economic considerations and the influence of other connected processes would cause the actual temperatures used in an industrial setup to vary, determining the ability of each model to give good predictions would be crucial. Further study could also be done through optical microscopy to supplement the model predictions by observing the reaction pathways on the surface of the particles. By examining partially and fully hydrated samples, more well-supported conclusions could be drawn through scanning electron microscopy (SEM) pictures as this would allow visual investigation of the particle surfaces at a higher magnification.

Chapter 6

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CSP-TCES Plant Modelling – CaO/Ca(OH)₂ System

Chapter Contents

Sections	Subsections
1. Aspen Plus Fluidized Bed Simulation	1. Physical Design Considerations 2. Solid Material Specification
2. Design of CaO Hydration and Dehydration Reactors at Steady-State	1. Reaction Specifications, Controlled Variables, and Boundary Conditions 2. Hydration Reactor Design and Optimization 3. Dehydration Reactor Design and Optimization 4. Comparison with Analytical Results from Literature
3. CSP-TCES Plant Flowsheet Design for the CaO/Ca(OH) ₂ System	1. Designed Flowsheets and Process Outcomes 2. Initial Integration of CSP Resource 3. Integration of Steam Rankine Cycle
4. Chapter Summary and Concluding Remarks	

6.1 Aspen Plus Fluidized Bed Simulation

Over the past decades, analytical models have been used to simulate FBRs running the calcium hydroxide system¹⁵⁷ at steady state. Previous work (described in Appendix A.10) has approximated FBRs through combinations of stirred tank reactors in parallel, with detailed kinetic and mass transfer specifications being required. This made it challenging to simulate the behavior of the plant, with few studies simulating FBR-based TCES plants integrated with CSP and discharging infrastructure.

However, Aspen Plus can now characterize FBRs in a single process unit. The first objective of this study was to utilize this software to produce a steady-state simulation of the FBR hydroxide system and compare the results with those from analytical models. In the 2012 update to the Aspen Plus software (Aspen Plus V8, further improved in 2016 with the release of V9), a new processing block, *Fluidbed* allowed customizable modelling of fluidized beds. Fig. 6-1 shows a schematic for the block which is a single unit with several inputs and outputs.

The *Fluidbed* process unit simulates the reaction by considering multiple *RCSTR* blocks in series with specifications varying according the height within the bed.¹⁵⁸ It uses the K-L-models.¹⁵⁹⁻¹⁶¹ In these models, the reactor is considered to comprise of two phases: a dense phase (emulsion) and a lean phase (bubbles), and heat and mass transfer take place within either phase and across both phases. The K-L-model is well-suited for handling reactions where the gas phase composition varies across the emulsion and bubble phases, such as in the $\text{CaO}/\text{Ca}(\text{OH})_2$ system under certain conditions. Some background on how these models have been used before in simulation studies is in Appendices A.10-A.12.

Fluidbed also incorporates additional models and design parameters for other aspects of reactor design, including:

- Pressure drop calculations,
- Transport disengagement height models,
- Elutriation models,
- Vessel dimensions and aspect ratio,
- Gas distributor designs,
- Bed heat exchanger specification, and
- Variable particle size distribution models.

In the software, these attributes have a range of commonly-used calculation models and correlations from literature and pilot trials as options to accommodate the modelling of materials with diverse and complex properties and behaviors. The *Fluidbed* block feature has thus far been tested¹⁵⁸ only for modelling systems

with one solid material species, while most commercial applications as well as the planned TCES applications here involve multiple solid species. This means that performing this study using the CaO/Ca(OH)₂ system (and subsequently the CMO redox system) can help to assess the accuracy and reliability of this modelling tool through comparison with literature modelling results.

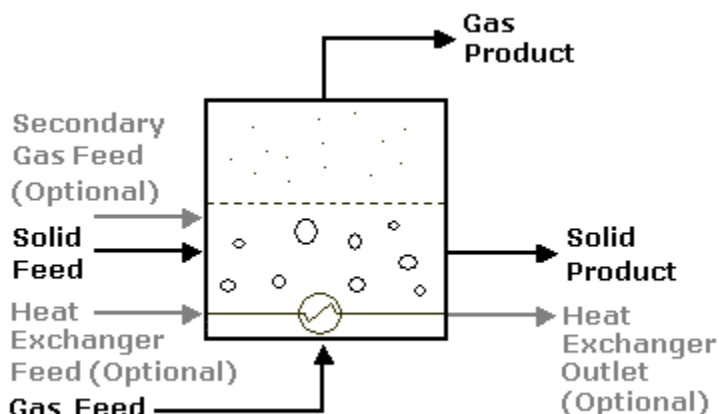


Fig. 6-1: Aspen Plus V9 Fluidbed process unit schematic¹⁵⁸

6.1.1 Physical Design Considerations

Not all *Fluidbed* input parameters are of consequence for this work. Some are mainly relevant to the physical construction of the reactors, e.g. gas distributor design and so are not considered here. More details on these parameters are in Appendix A.14. Several physical considerations were made based on particle characteristics and material flowrates. These included the Geldart classification, transport disengagement height (TDH), and the particle elutriation behavior. They are explored here in more detail.

Geldart classification

The Geldart classification¹⁶² (Fig. 6-2) distinguishes how solid particles behave under fluidized conditions based on their mass density and particle diameter. For the particle sizes in the CaO/Ca(OH)₂ system under consideration (discussed in Section 6.2.1), the two compounds fall in different classifications, as Ca(OH)₂ (2200 kg/m³) has a significantly lower density than CaO (3320 kg/m³) and falls into the ‘B’ category (sand-like bed behavior) while CaO is in the ‘D’ category (spoutable bed behavior). Thus it is necessary to consider the design and operating conditions of the FBR separately for the hydration and dehydration reactions and in fact design them as entirely separate processes within the CSP-TCES plant. This is because of their differing fluidization behavior which necessitates separate design and optimization of FBRs for each reaction in terms of physical considerations such as reactor dimensions, bed mass, and freeboard height.

A major assumption made in this study is that the CaO and Ca(OH)₂ materials can retain their mechanical stabilities (and thus, their Geldart classifications) even after cycling. As noted in previous chapters, the pure form of these materials physically deteriorate through cycling. This produces powder-like materials that would be in the ‘C’ category and be more challenging to fluidize, due to strong inter-particle forces¹⁶³ thereby obstructing gas flow through the bed.^{164, 165} Having a ‘cohesive’ bed is undesirable for operating an FBR and poses further challenges for downstream solids separation. Separately, supported and/or composite forms of CaO and Ca(OH)₂ are being developed (as noted in Chapters 4 & 5) to offer improved mechanical stability and preserve their ‘B’ and ‘D’ category attributes. The need for such a mechanically stable material to be developed is critical, in order for such a TCES technology to be practicable for CSP. It was assumed that this would be a surmountable experimental problem.

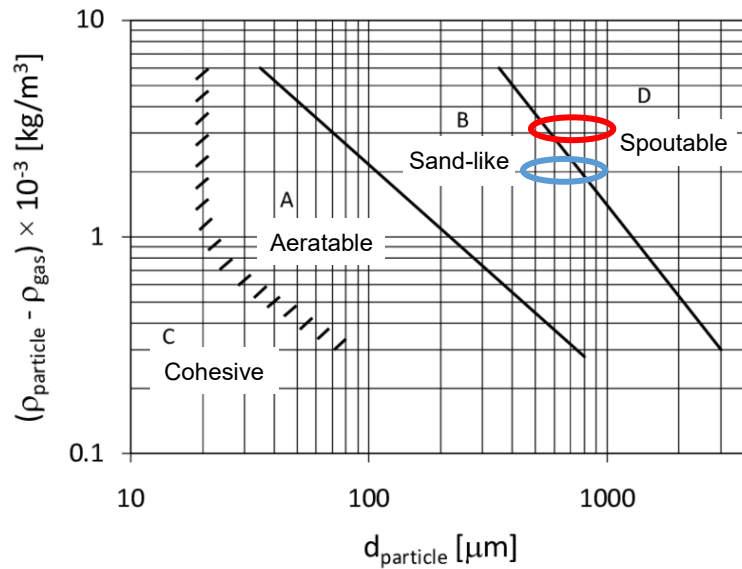


Fig. 6-2: The Geldart classification chart for fluidized materials (red is for CaO; blue is for Ca(OH)₂)

Transport disengagement height

The transport disengagement height (TDH) (Fig. 6-3) is the additional height required above the bed for rising fluidized particles to lose their momentum and settle back towards the bulk bed, thus reducing bed mass losses and improving overall conversion. Determining the TDH is important for establishing a minimum height requirement for the designed FBRs as the reactors would need to be taller than the sum of the dense bed and TDH to prevent excessive particle loss.

A range of potential correlations summarized in Table 6-1 were explored – all for solid-gas systems but some providing unrealistic results potentially due to being tested under conditions dissimilar to those being considered in this study – and Chan and Knowlton’s expression¹⁶⁶ was identified as being the most suitable

based on the particle sizes tested and the behavior of the tested bed; their correlation to calculate the TDH of the bed is described in Eq. 6-1 where u is the linear velocity of the fluidizing gas.

Table 6-1: Experimental conditions of literature studies for TDH correlations

Source	Nature of system
Chan and Knowlton ¹⁶⁶	Solid-gas, spoutable bed, $u < 3.3$ m/s, $d_p < 0.8$ mm
George and Grace ¹⁶⁷	Solid-gas, sand-like bed, $u < 1.3$ m/s, $d_p < 0.1$ mm
Fournol et al. ¹⁶⁸	Solid-gas, spoutable bed, catalytic cracking, $d_p < 50$ mm
Fung and Hamdullahpur ¹⁶⁹	Solid-gas, aeratable bed

$$TDH = 0.85u^2 \cdot (7.33 - 1.2 \cdot \log(u)) \quad (6-1)$$

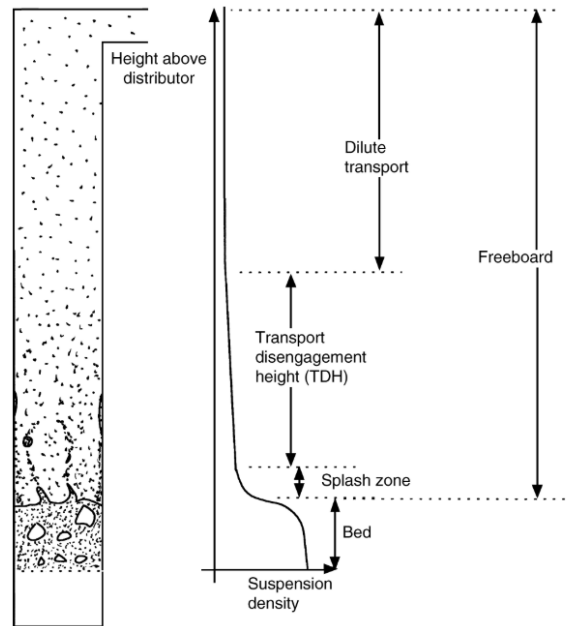


Fig. 6-3: An illustration of a solids concentration profile in a fluidized bed depicting the transport disengagement height in relation to the freeboard height¹⁷⁰

Elutriation behavior

Elutriation is the loss of particles, typically as fines, from the bed through excessive fluidization and being buoyed out of the reactor by the fluidizing gas through bubbles exploding at the surface of the bed. Quantifying this phenomenon required determining the elutriation coefficient $k_{\infty,i}$. Estimating the velocity of the fluidization gas (steam) and specifying the average diameter of the $\text{CaO}/\text{Ca}(\text{OH})_2$ particles were necessary for identifying the most suitable correlations from the literature. Table 6-2 summarizes the main experimental studies in the literature and their experimental conditions. In this study, particles in the 500-

1000 μm range were simulated and according to initial results a fluidizing steam velocity of ~ 5 m/s was set. Based on Table 6-2, the correlation by Colakyan & Levenspiel¹⁷¹ for $k_{\infty,i}$ (Eq. 6-2) was deemed to be the most suitable for this study and so was used for the calculating elutriated mass flow $\dot{m}_{e,i}$ (Eq. 6-3).

Table 6-2: Experimental conditions for literature studies to determine elutriation coefficient correlations

Source	u [m/s]	D [m]	$d_{p,bed}$ [mm]
Tasirin & Geldart ¹⁷²	0.1-0.6	0.15	0.03-0.2
Colakyan & Levenspiel ¹⁷¹	0.9-3.7	0.92	0.3-1.0
Zenz & Weil ¹⁷³	0.3-0.7	0.05	0.04-0.2
Geldart et al. ¹⁷⁴	0.3-0.7	0.05	0.04-0.2

$$k_{\infty,i} = A_E \cdot \rho_{s,t} \cdot \left(1 - \left(\frac{u_{t,i}}{u}\right)\right)^{B_E} \quad (6-2)$$

$$\dot{m}_{e,i} = k_{\infty,i} \cdot A_t(H_B) \cdot \Delta Q_{3,b,i} \quad (6-3)$$

Here A and B are adjustable fitting parameters, $\rho_{s,t}$ is the density of the entire bed of solids at any point in time, $u_{t,i}$ is the terminal velocity of the particles in question, $\Delta Q_{3,b,i}$ is the mass fraction of particles with terminal velocity and $A_t(H_B)$ is the cross-sectional bed area.

6.1.2 Solid Material Specification

While the properties of the product particles can only be estimated, the fresh feed material streams were specified to match the physical design factors discussed in Section 6.1.1. It was assumed that the feed materials had negligible impurities; the material characterization results in Chapter 4 show this to be valid. The main property specified was the particle size distribution (PSD). The kinetic data obtained in Chapters 4 and 5 pertain to CaO particles in the 200-710 μm range so it was preferred to consider a PSD within this range. The correlations discussed in Section 6.1.1 were derived for particles within the 800-1000 μm range and so this size range was considered as an upper boundary.

It was further considered that smaller particles would experience excessive attrition and their buoyancy would vary more drastically over the course of reaction making reactor design optimization more complex. In addition, variance within the PSD was considered. A PSD with a narrow range allows for more consistent fluidization and reaction conversions. It was assumed that particles would be produced within the approximate size range considered. A further consideration was that since CaO particles grow and Ca(OH)_2 particles shrink during reaction, it was necessary to choose PSDs that would result in product PSDs at least partially overlapping with the feed PSDs of the same material. The estimated particle growth ratio for 500-

710 μm CaO particles during hydration is 1.213 (on a radius basis; Table 4-1) and so this multiplier was used to estimate the mean of the Ca(OH)_2 PSD from that of the CaO PSD, though it should be remembered that conversion would not be 100 %, limiting particle diameter changes; this is discussed in Section 6.2.1.

Table 6-3 provides more information on the normal distributions used for the two PSDs which are illustrated in Fig. 6-4. Within Aspen Plus, a number distribution equivalent growth model was selected for modelling changes in the PSDs through reaction as it would conserve the total number of particles.

Table 6-3: Specification of the CaO and Ca(OH)_2 PSDs for fresh feeds, based on particle diameters, following normal distributions

Normal distribution parameters	Feed CaO	Feed Ca(OH)_2
Lower limit (μm)	400	500
Upper limit (μm)	700	800
Discretization intervals	8	8
Mean (μm)	550	650
Standard Deviation (μm)	20	30

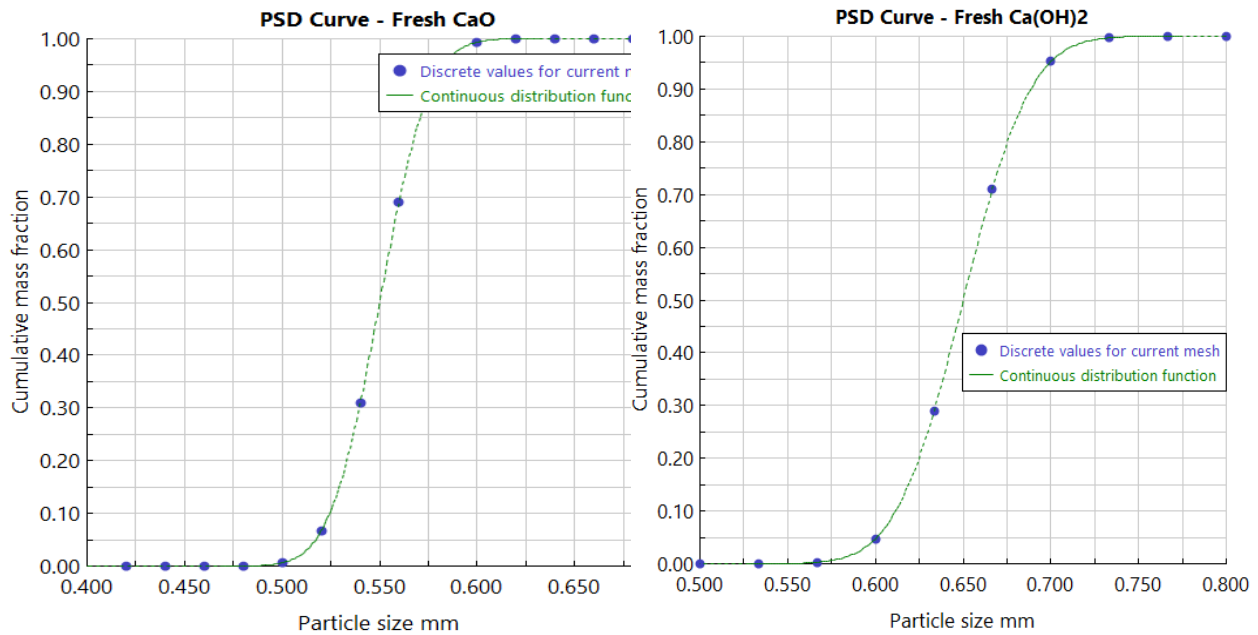


Fig. 6-4: PSD curves for fresh CaO and fresh Ca(OH)_2 streams used in Aspen Plus study

6.2 Design of CaO Hydration and Dehydration Reactors at Steady-State

The first step was the design and optimization of FBRs for each process. As noted before, this modelling capability was a recent addition to the software and no literature was found that attempted to study its reliability compared to traditional analytical models.

When operating a TCES process a wide range of incoming energy sources can be used which have characteristic time-based fluctuations or scheduled variations, e.g. wind power based on weather conditions, or solar power based on day/night cycles. For CSP, a time-varied simulation is the most appropriate due to hourly, daily, and seasonal variations in solar availability affecting the operation of any TCES process connected to it. However, a basis of comparison was required to assess the credibility of the simulated FBRs. Typically, literature modelling studies (Appendices A.10-A.12) have only involved steady-state designs. The work by Criado et al.¹⁵⁷ is the closest study that involves FBR design and examines the same TCES process at steady-state. This was deemed to be the most suitable basis for comparison in the literature.

The FBRs were first designed at steady-state. This entailed adding considerations that analytical models have not included in the literature such as variations in reactor geometry, hydrodynamic behavior of bed particles, and the effect of changing particle size on the performance of the reactors.

6.2.1 Reaction Specifications, Controlled Variables, and Boundary Conditions

Among the specifications in Tables 6-4 and 6-5, the residence time, target conversion and reaction rate constants were informed by Chapters 4 and 5, previous work studying the reaction kinetics^{142, 175}, and longer term conversion trends of the system. For instance, the final hydration conversion was constrained to 0.6 as that is the average residual maximum conversion achievable by cycled unsupported CaO sorbents¹¹⁷ and thus suffices as a conservative conversion target that can be realistically achieved after cycling (the dehydration conversion was limited to 0.8 based on this). Another point is that although in a continuously operated FBR there will be fresh feed that is uncycled and thus more fully reactive, it is observed in Chapter 4 that reaction rates decrease sharply after 50% of final conversions are achieved; there is a trade-off between higher conversions and the additional operating time and energy required.

The selection of kinetic parameters presented in Table 6-4 warrants discussion. To specify the reaction within Aspen Plus, the reaction rate constant expressions need to be identified. In Chapter 4 the first-order behavior of the hydration system was observed and this corroborated literature results; hence the estimated pre-exponential factor and activation energies found earlier were used here. Although the experiments conducted here were at lower temperatures and steam concentrations, the reported rate constants in the literature were very similar and so the experimental values obtained here were presumed to be suitable. For the dehydration reaction, while no studies were done in this work, the reported kinetic parameters from the literature study¹⁵⁷ were used as it was presumed that since the hydration reaction parameters were consistent, the reported dehydration reaction parameters would also be accurate. Additionally, doing this also allowed for greater consistency with the literature and for a fairer comparison of the subsequent modelling results.

Table 6-4: Kinetic rate parameters used for CaO hydration and dehydration reactions

Kinetic Parameters	Hydration	Dehydration
Activation energy, E_a (kJ/mol)	51.0	60.8
Pre-exponential factor, A (s^{-1})	3.5×10^{-6}	5.2×10^2
Reaction temperature ($^{\circ}C$)	470	540
Calculated $k_{(hyd/dehyd)}$ (s^{-1})	0.0145	0.018

While testing the reactor designs in Aspen Plus, it was found that the large bed masses (>12000 kg) and reactor sizes (>20 m height and >8m diameter) required by the processes necessitated complex calculations that the software struggled to compute within a reasonable time. A simple solution was to reduce the bed masses and reactor sizes by reducing the specified residence times. Specifically, halving the residence time to 60 s allowed the complexity of the system to come within the current software capabilities and achieved convergence within minutes. Implementing this solution did not compromise the validity of the defined setup as 60 s was sufficient for either reaction to go to completion. This will be kept in consideration later in Section 6.2.4 when comparing the modelling results to that of the literature study.

The FBR feed specification in Table 6-6 was informed by optimized results from literature¹⁵⁷ and from discussions presented in Section 6.1.2. For instance, the choice of using pure steam as the fluidizing gas was influenced by recent studies using pure steam to allow for higher thermodynamic efficiencies in the system compared to dilution with N_2 .^{176, 177} The kinetic parameters were also produced from experiments conducted under pure steam. In a cycled process with incomplete reactions, the stored products are always a mixture of the oxide and hydroxide materials. These are then withdrawn to run the reverse reactions and so mixed with external fresh feeds as they return to the FBRs. To account for this, the feed streams used here are weighted mixtures; the proportions and flowrates are informed by the reference study.¹⁵⁷ Simulations were conducted separately for the hydration and dehydration processes.

Table 6-5: Boundary conditions and pre-determined constants for hydration and dehydration reactions

Variables	Hydration	Dehydration
Estimated residence time (s)	60	60
Minimum bed mass (kg)	4000	5000
Reaction temperature ($^{\circ}C$)	470	540
Reaction pressure (bar)	1.0	1.0
Target reaction conversion, X	0.6	0.8
Target $Q_{out/in}$ (MW)	100	140

Table 6-6: Specification of inlet streams into Fluidbed for hydration and dehydration reactions

FBR initial feed specifications	
Particle Size Range (mm)	0.4-0.7 (hydration); 0.5-0.8 (dehydration)
Fluidizing gas	Pure steam
Initial gas mass flowrates (kg/s)	20.0 (hydration); 16.1 (dehydration)
CaO/Ca(OH) ₂ feed (mass ratio)	9:1 (hydration)
Hydration solids feed flowrate (kg/s)	110.0
Ca(OH) ₂ /CaO feed (mass ratio)	3:1 (dehydration)
Dehydration solids feed flowrate (kg/s)	130.0

6.2.2 Hydration Reactor Design and Optimization

Here the FBR optimization results for the CaO hydration reactor are discussed. The trends in Fig. 6-5 suggest that manipulating the bed mass significantly impacts both reaction conversion and the overall heat released, and that there is a local optimum bed mass that achieves both the desired rate of discharge and the average particle conversion. The bed mass can be manipulated by varying either the residence time or the feed material flowrates. Within *Fluidbed*, the target bed mass can be specified along with the feed flowrates; hence when varying the bed mass it is effectively the residence time being varied. Based on the discussions in Section 6.2.1 care was taken to select a range of bed masses that resulted in residence times around the 60 s mark. It is observed that exceeding the target thermal discharge volume of 100 MW allows for reaching the highest conversion values of ~ 0.54 with a bed mass of ~ 7000 kg resulting in 130 MW of energy released (Q_{out}). Achieving high conversions is beneficial as the partially converted material will be dehydrated again and so a more hydrated material stream will have greater availability of Ca(OH)₂ thereafter.

The effect of varying bed mass on the conversion was as expected. With a larger bed mass, the extent of fluidization within the bed will reduce if steam flowrates are kept constant, as the increased uptake of steam reduces the gas flowrate through the bed progressively with height, resulting in less fluidization. This would make it less well-mixed with the possibility of temperature and concentration gradients, thus causing lower conversion for a given residence time. The effect of varying reactor diameter on conversion is also as expected; with a larger diameter, the bed is thinned out vertically and spread horizontally. As a result there may be reduced lateral mixing taking place which explains the lower conversions achieved with the fixed residence time. This is more likely as with a fixed mass flowrate of gas, having a larger cross-sectional area for the reactor means that the initial volumetric gas flowrate and linear gas velocity will be reduced, which would reduce the extent of fluidization and the average conversion in the bed.

The observed relationship between the extent of elutriation predicted and the height of the reactor is significant as due to vigorous fluidization a large proportion of particles are vertically transported up the reactor. This can lead to large scale elutriation and even ejection of the bed mass for reactors shorter than 9 m; beyond this height it is expected that mostly fines and ~10% of particles still retain elutriation velocities due to being buoyed by the exiting gas stream. As the elutriated mass fraction levels off after this height, there is little advantage to having taller reactors and so 10 m was identified to be a suitable reactor height.

In each scenario the marked data-point indicates the optimized parameter value that satisfies the specifications in Table 6-5. This allows for designing an effective flowsheet for comparison with literature studies. Having the optimization data also illustrates the sensitivity of the FBR to design and operating specifications, which is important when planning and developing pilot scale studies of such a system.

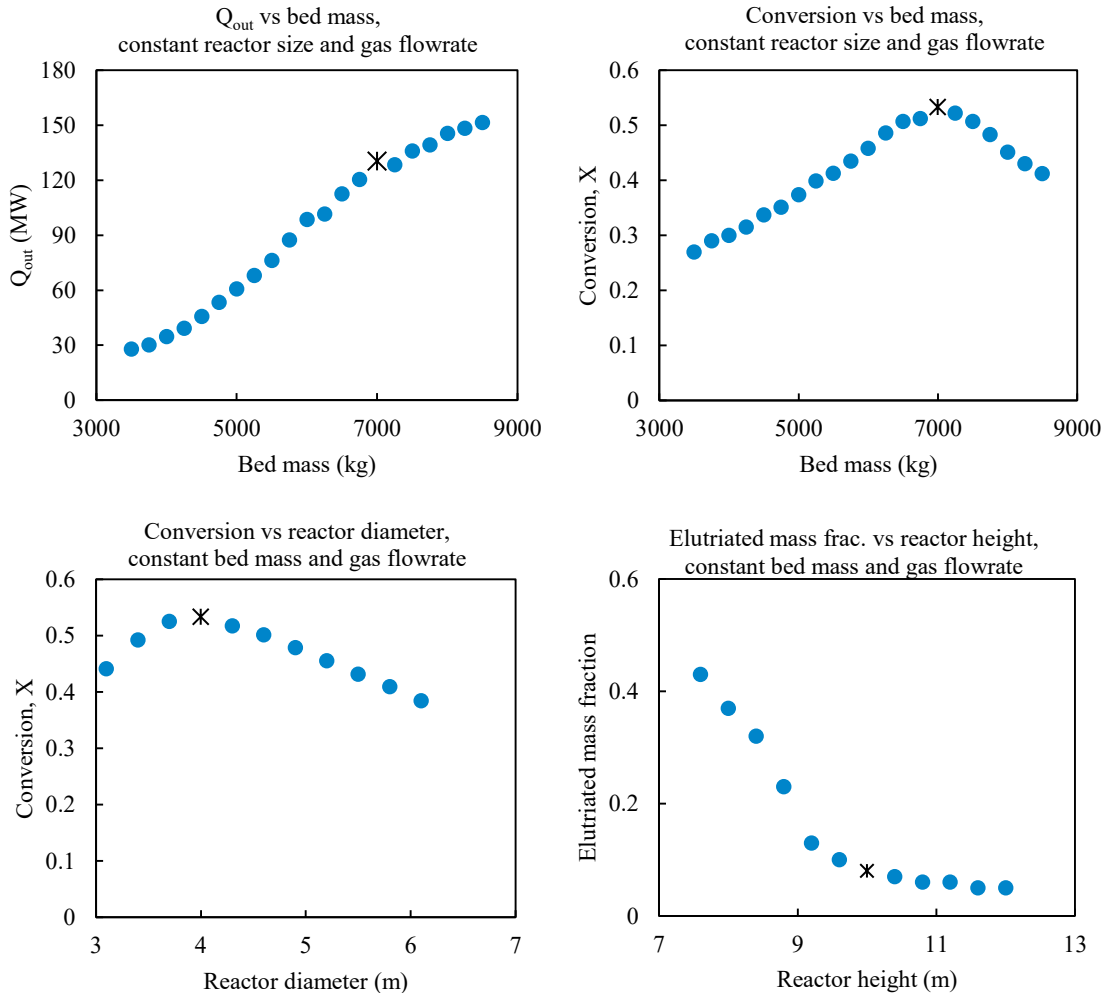


Fig. 6-5: Simulated trends in reaction system behavior within FBR for the CaO hydration TCES discharging process, varying bed mass and reactor dimensions

6.2.3 Dehydration Reactor Design and Optimization

The optimization results for the dehydration FBR showed some similar qualitative trends in Fig. 6-6 as compared to the discharging process. Quantitatively, the optimal bed mass range was lower, as would be expected due to the dehydration reaction releasing additional steam into the gas phase and influencing the phase composition and exit gas flowrates. The preferred reactor size to minimize elutriation is also taller as a result of the increased downstream gas velocity and thus a larger estimated TDH. As this is an endothermic reaction, while the discharging FBR uses an exothermic one, the observed relationship between Q_{in} and the bed mass is expectedly different; the thermal energy collected by the bed increases with an increasing bed mass until a bed mass of ~6300 kg after which the relationship plateaus.

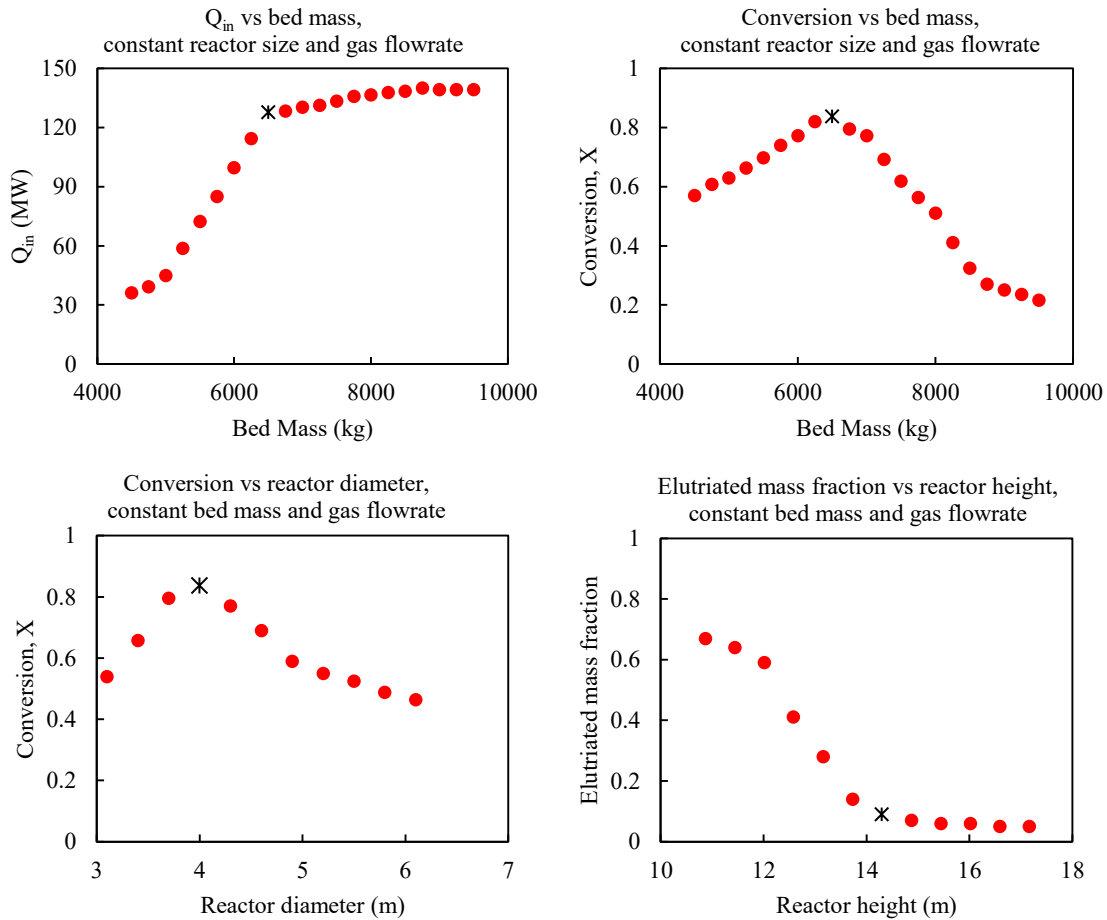


Fig. 6-6: Simulated trends in reaction system behavior within FBR for the CaO hydration TCES charging process, varying bed mass and reactor dimensions

Both these considerations can also explain the observed relationship between conversion and bed mass, as the average bed conversion increases with bed mass up to a bed mass of ~6600 kg and then drops off sharply. Hence a bed mass of ~6500 kg was determined as a local optimum that would maximize both the

dehydration conversion and the thermal energy stored by the bed. Similarly to the discussion in Section 6.2.2, prioritizing a higher conversion is important for process considerations where the materials in the product stream will eventually be used for the reverse reaction.

In observing the relationship between conversion and reactor diameter, the same behavior was observed here as was noted for the hydration reactor, with the conversion peaking at a certain diameter (in this case ~4 m) and dropping off thereafter. Here the drop is considerably more pronounced. The explanation for this can be deduced from observing the relationship between reactor height and the extent of elutriation: due to the increased steam flowrate through reaction, there are far larger extents of elutriation observed. This is as the TDH is increased by both the higher gas flowrate and the generation of CaO particles which are more susceptible to elutriation than the denser Ca(OH)₂ particles. Hence the sharp drop in conversion may also be due to the more converted particles being elutriated leaving the less converted particles in the bed. It was observed that a minimum reactor length of ~14 m kept the total elutriated mass to <10% of the bed mass.

6.2.4 Comparison with Analytical Results from Literature

When comparing the thermal energy volumes in and out of the system (Fig. 6-7), it is noted that the discharging process has good agreement with the optimal values in the reference study; however the required thermal energy supplied during the charging process is lower (130 MW) compared to the reference value of 159 MW which is a result that requires some discussion. This is due to the reporting methodology used in the reference study where the quoted Q_{in} value also incorporates the energy required to heat the feed streams from standard conditions (37 MW). This consideration was not included in the simulated study as this energy duty is accounted for in the flowsheet design and techno-economic analysis.

The calculation for thermal efficiency (η_P) (Eq. 6-4) was affected by this as the thermal efficiency for the reference study was 63% owing largely due to the pre-heat considerations taken into account. The authors of the reference study note that their figure is a worst-case scenario without energy integration. Correcting for this, the reference case thermal efficiency was adjusted to exclude the pre-heat duty and so yielded a more consistent value of 87% (vs 90 % here). The scaled residence times were found to be ~8-18% longer for both processes; this was likely influenced by more conservative and realistic kinetics employed in this study accounting for both sintering and particle size changes¹⁴². The energy storage density from the simulation was marginally lower than in the literature and this is likely due to the slightly lower conversions achieved here compared to in the reference study. This work considered the density of support materials to yield an overall storage material density of 1000 kg/m³; it remains to be seen what the densities of advanced materials designed for this are. The simulation results approximate the literature data reasonably closely, allowing the design of a complete TCES process flowsheet based around the two FBRs.

$$\eta_P = \left[\frac{Q_{out} \cdot \text{residence time (hyd)}}{Q_{in} \cdot \text{residence time (dehyd)}} \right] \cdot 100 \quad (6-4)$$

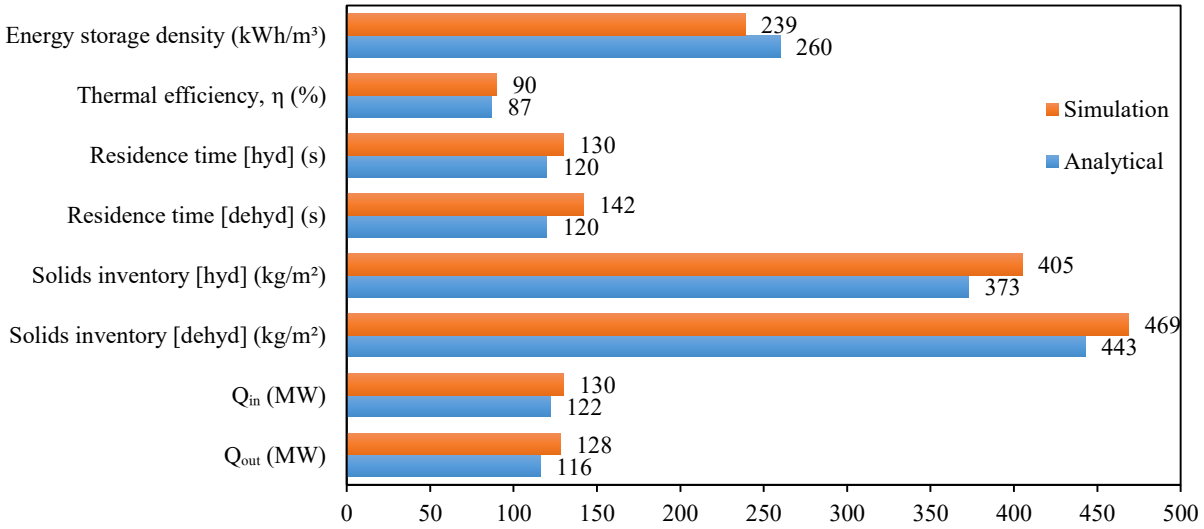


Fig. 6-7: Comparison of key FBR operating and performance parameters from literature¹⁵⁷ vs this study

6.3 CSP-TCES Plant Flowsheet Design for the CaO/Ca(OH)₂ System

In this section, a fully specified process approximating an actual CSP-TCES plant is designed. This allows for assessing the impacts of changing particle size on the characterization of the solid process streams, understanding what process design considerations are needed, and characterizing the CSP plant and the power generation blocks connected to the flowsheets. The flowsheet designs were simulated at steady-state to facilitate the initial thermodynamic analyses of the main TCES processes and for designing the power generation cycle. These flowsheets were later used for TVP simulations in Chapter 8. To this end, this section analyzes the designed flowsheets, presents additional results from the overall designed flowsheets, and designs the upstream CSP plant and downstream power block connected to the TCES process.

6.3.1 Designed Flowsheets and Process Outcomes

The designed CSP-TCES plant has four sub-systems, three of which were simulated here: the Ca(OH)₂ dehydration storage system, the CaO hydration discharging system, and the steam cycle power generation system. The flowsheets shown in Fig. 6-8 were constructed in Aspen Plus V9. While the heliostat field sub-system was not simulated, the incoming thermal energy had to be specified as an input to the FBR and so superheated steam was used as the process fluid for this although molten salts could also be used; there are differences in performance between the two materials which may require future consideration.

A simplified flowsheet is presented here to focus on key unit processes. The storage tanks were assumed to be insulated to store materials at a minimum of 150°C; this is a conservative estimate, as in a dynamic

operating scenario they would only be stored for a day before reuse. The surplus latent heat of the solid streams exiting the FBRs were thus used to partially preheat the fresh feeds. The recovered ‘tops’ streams were meanwhile used in the power generation block as discussed later in Section 6.3.3. Process steam was looped between the processes at steady-state; surplus steam produced through dehydration is separated and sent to the discharging process, to be mixed with recycled fluidizing steam from hydration, which needs to be topped up continuously. This would allow both processes to run continuously, reducing fresh steam requirements. However if either process is not running (as discussed in Chapter 8), then the greater thermal inefficiencies associated with condensing surplus steam/producing fresh steam must be considered.

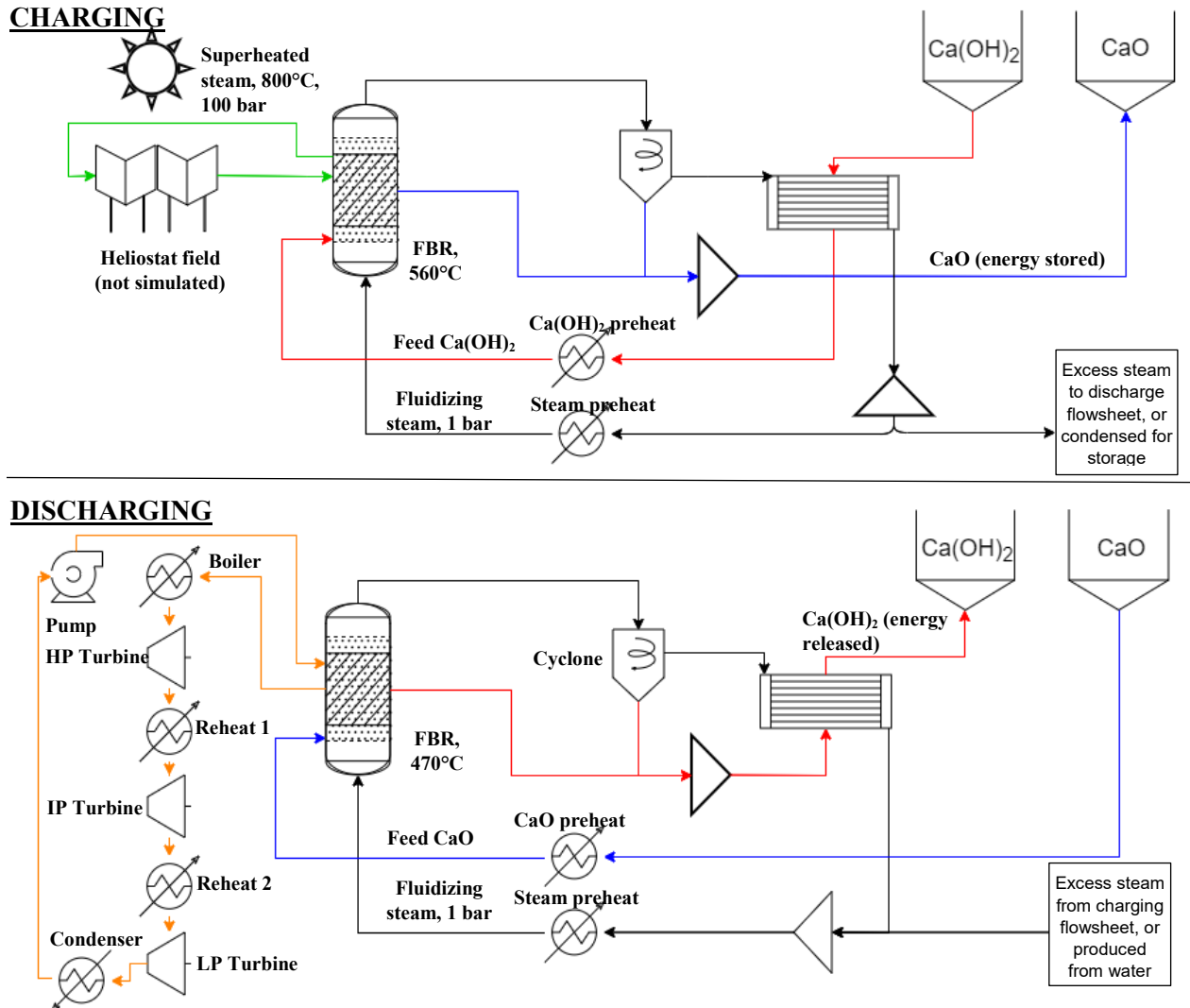


Fig. 6-8: Flowsheet of the combined CSP-TCES plant based on the $\text{CaO}/\text{Ca(OH)}_2$ system, separated as: charging (top) and discharging (bottom). The colored streams are process steam (black), solar heat transfer steam (green), solid CaO (blue), solid Ca(OH)_2 (red), and the steam-based power cycle (orange).

Table 6-7 presents relevant information from the stream table for key streams in the hydration (discharging) flowsheet. As noted previously, the top exit stream from the discharging FBR does contain a significant amount of elutriated material nonetheless (25.4 wt% of this stream consists of solids) and so a cyclone was necessary addition to recover solids for storage and steam for recycling.

Table 6-7: Stream table for key streams for the CaO hydration TCES flowsheet at steady-state

Stream	FBR Fresh Feed	FBR Gas Feed	FBR Bottoms	FBR Top	Storage Feed	Recycled Gas
Mass flow (kg/s)	106.9	40.0	113.5	33.4	125.9	23.4
P (bar)	1.0	1.0	0.96	0.96	1.0	1.0
T (K)	743	743	743	743	423	775
Composition (wt%)						
CaO	90.0		30.5	13.7	30.5	
Ca(OH) ₂	10.0		69.5	11.7	69.5	
H ₂ O		100.0		74.6		100.0

Table 6-8 presents the relevant data for key streams in the dehydration (charging) flowsheet. It is again observed that the top exit stream from the charging FBR has a significant amount of solids present (13.7 wt% of the stream) and a cyclone is necessary. The steam stream after cyclonic separation is split between fluidization steam and a second stream which is condensed for storage or immediately reutilized as fresh feed steam for the hydration flowsheet. This is illustrated in Fig. 6-8. It was discussed in Section 6.1.2 that changes in PSDs as a result of reaction had to be considered as part of the simulation study and the feed stream PSDs were produced. Here in Fig. 6-9 the final product stream PSDs are shown alongside for comparison and the effects of particle size changes in the course of reaction are prominent.

Table 6-8: Stream table for key streams for the Ca(OH)₂ dehydration TCES flowsheet at steady-state

Stream	FBR Fresh Feed	FBR Gas Feed	FBR Bottoms	FBR Top	Storage Feed	Recycled + Stored Gas
Mass flow (kg/s)	130.0	10.0	103.6	36.4	108.6	31.4
P (bar)	1.0	1.0	0.93	0.93	1.0	1.0
T (K)	813	813	813	813	423	573
Composition (wt%)						
CaO	30.5		90.0	11.7	90.0	
Ca(OH) ₂	69.5		10.0	2.0	10.0	
H ₂ O		100.0		86.3		100.0

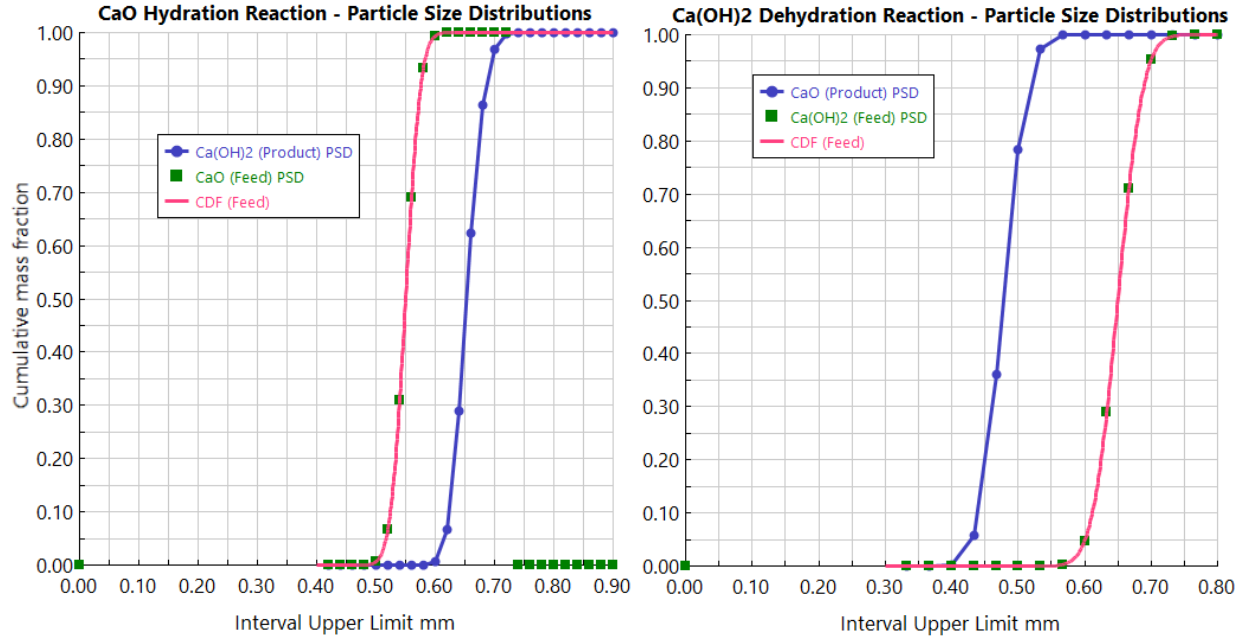


Fig. 6-9: PSD curves for feed and product streams for CaO hydration (left) and Ca(OH)_2 dehydration (right) flowsheets generated in Aspen Plus

The PSDs here were estimated only for the final solids streams headed for storage instead of comparing the PSD data for the bottoms exit streams from the FBRs which contain the vast majority of the solids. Doing this allowed accounting for additional reaction undergone by elutriated particles in the top exit streams as a result of their increased residence time in contact with steam (for hydration) or at suitably high temperatures (dehydration) and/or due to attrition in the cyclones and consequent exposure of additional available surface areas for reaction. This would be less of a concern when using synthetic supported materials with good mechanical stability but this is an ongoing area of research and not considered here.

The PSDs of the product streams have good agreement with those of the corresponding feed streams, with a minor discrepancy for the CaO streams where the feed material is mostly within 0.5-0.6 mm while the product material has a wider distribution of 0.4-0.6 mm. This is likely due to the fact that none of the streams are homogeneous; they contain mixes of CaO and Ca(OH)_2 causing the streams to have overall wider PSDs than would be the case for streams purely composed of one material. Further refinement is clearly possible.

6.4.2 Initial Integration of CSP Resource

For the charging process, the thermal energy collected had to be supplied by the heat exchanger integrated within the FBR. As this plant was designed as a TCES process integrated with a CSP plant, the thermal energy has to be sourced from a CSP setup. As discussed in Chapter 2, the particular configuration of CSP

being considered in this study is a solar tower design which involves a heliostat field and solar receiver, with intermittent heat input—a factor given due consideration for TVP process simulation in Chapter 8.

For this initial steady-state simulation, a simplified approach was taken. The upstream portions of the CSP plant were not simulated; instead the plant was treated as a black box operating at a steady-state solar collection capacity. The downstream section i.e. the HTF carrying the thermal energy was specified so that sufficient thermal energy was available to meet the design specification for the charging process.

For process design simplicity, pressurized steam was chosen for this. Suitable pressures, temperatures, and flowrates were chosen as reported in Table 6-9 to maintain temperature differences as a driving force for heat transfer into the FBRs. It was noted that the choice of HTF would have significant influence on the design of FBR heat exchangers but this was not considered further in this study. This is as the FBR heat exchangers are outside the established scope of this work and this aspect of CSP-TCES process design already faces extensive research efforts elsewhere. It is acknowledged as a limitation of this work that no HTF has yet been demonstrated to achieve these temperatures at large scales in a CSP setup. However as noted in earlier discussions, recent developments have demonstrated solar tower CSP technologies delivering heat to storage processes at up to 1000°C (such as via direct solar irradiation of the reactor). Hence this work provides an early high-level assessment of FBR-based TCES at these temperatures and should be revisited as more developments are made in HTF material research and TCES reactor design.

Table 6-9: Specification of HTF stream representing CSP thermal energy supply for the $\text{Ca}(\text{OH})_2$ dehydration reaction

Heat transfer fluid	Pressure	Temperature	Flowrate	Heating provided
Steam	100 bar	800°C (FBR inlet) 625°C (FBR outlet)	200 kg/s	130 MW _{th}

6.4.3 Integration of Steam Rankine Cycle

For the discharging process, the thermal energy released through reaction to the heat exchanger built into the FBR was converted to electricity. As discussed in Chapter 2, for the operating temperature range of a CaO hydration TCES process, a steam Rankine cycle is most suitable based on thermodynamic considerations and so this was implemented as seen in Fig. 6-8. The steam cycle was designed in accordance with the thermal output of the discharging FBR; it was found that up to 95% of the 128 MW_{th} discharged could be recovered for conversion. The design specification is given in Table 6-10 where the parameters are informed by traditional industrial choices for similar designs.

To improve the overall thermodynamic efficiency of the cycle, a system of three turbines were used to expand the high pressure steam to produce electrical energy – operating at high pressure (HP), intermediate pressure (IP), and low pressure (LP) in that order. In between each turbine operation, the steam is re-heated in part via the filtered (post-cyclone) gaseous steam exit stream of the FBR; this stream is able to account for 70% of the re-heat duty needed across the three stages of the steam cycle.

The Rankine thermal efficiency (Eq. 6-5) of the 3-stage steam cycle is 39%, as 49.8 MW_e is generated from the steam cycle as calculated from Table 6-11; this is not far from the maximum theoretical efficiency of 44%. This efficiency cannot be improved significantly as the main limiting factor is the boiler outlet temperature (411°C), which is low compared to the steam Rankine cycle temperature (> 560°C) in a power station, which allows for greater power generation via the HP turbine.¹⁷⁸

$$\eta_{Rankine} = \frac{W_{thermal} - W_{pumps}}{\dot{Q}_{in}(from\ FBR)} \quad (6-5)$$

Table 6-10: Design specification for the steam Rankine cycle for the CaO hydration (discharging) flowsheet

Steam Cycle Specification	Value
Isentropic efficiency (turbines: HP, IP)	0.72
Isentropic efficiency (turbine: LP)	0.85
Specified vapor fraction (turbine: LP)	0.95
Boiler outlet temperature	411°C
HP inlet pressure	100 bar
IP inlet pressure	30 bar
LP inlet pressure	0.1 bar
Pump efficiency	0.85
Condenser temperature	30°C

Traditional CSP plants utilise pressurized steam at ~540°C and typically have a 42% Rankine efficiency.¹⁷⁹

However given the greater flexibility in power generation obtained through implementing the CaO hydration TCES system in this case, the slight loss in efficiency is most likely outweighed by the gains in economic viability through increased power production. In Table 6-12 the peak round trip efficiency (RTE) of the designed plant with a CaO hydration/dehydration TCES is evaluated in comparison to a base case CSP plant operating with molten salt TES. For CSP energy storage technologies, this is commonly¹⁸⁰⁻¹⁸² based on thermal energy supplied during charging versus thermal energy released during discharging. It is observed that implementing CaO hydration/dehydration TCES does not reduce the RTE for a CSP setup

(up to 92% instead of 86%), while enabling much longer storage durations. However this RTE of 92% depends heavily on the longer-term cycling stability of the reactants. Significant advancements in stable CaO-based materials need to be made to achieve RTEs close to this in practice. In addition an important caveat to consider is that the RTE of this setup will likely be lower in practice as it will also be influenced by the thermal inefficiencies associated with the choice of steam storage/regeneration approaches used. It is estimated that the RTE could fall to 70% if minimal steam storage is achieved as up to 40 MW_{th} of input thermal energy is carried by the stream of produced steam during charging. The technical exploration of those approaches is discussed further in Chapter 8. It is an important area for study beyond the scope of this work and it is recommended that the RTE evaluation be updated in the course of such study.

Table 6-11: Results for the steam Rankine cycle for the CaO hydration (discharging) flowsheet

Steam Cycle Parameter	Value	Input (-ve)/Output (+ve)
HP turbine power output	23.5 MW	+
HP-IP reheat duty (Reheat 1)	11.4 MW _{th}	-
IP turbine power output	33.4 MW	+
IP-LP reheat duty (Reheat 2)	6.2 MW _{th}	-
LP turbine power output	3.1 MW	+
Condenser duty	6.0 MW	-
Pump power required	0.7 MW	-
Heat recovered from FBR top stream	14.1 MW _{th}	+
Net power produced	49.8 MW	+

Table 6-12: Round trip efficiency calculations for the CaO hydration/dehydration TCES-CSP flowsheet

Steam Cycle Parameter	Value
Energy output with TCES	128 MW _{th}
Energy output without storage	140 MW _{th}
CaO CSP-TCES round trip efficiency	70-92%
CSP-TES round trip efficiency ¹⁸⁰	86%

6.5 Chapter Summary and Concluding Remarks

The design and optimization of the CaO hydration and dehydration FBRs were carried out using Aspen Plus. Due to the differing physical properties of the solid materials as well as planning ahead for studying the dynamic operation of the plant, it was determined that separate reactors had to be designed for each reaction. To assess the validity and reliability of the modelled reactor designs, an analytical modelling study on a 100 MW storage basis for the same process by Criado et al.¹⁵⁷ was chosen as a reference case for subsequent comparison.

The FBR for the exothermic hydration reaction was then designed and optimized. It was determined that a minimum reactor height of 10 m with a diameter of 3.5-5 m would yield the most effective reaction performance while minimizing particle losses through elutriation, while a bed mass of ~7000 kg provided the best trade-off between maximizing reaction conversion and heat released.

Similarly the dehydration FBR was then designed and studied. In this case the optimal reactor dimensions and bed mass were expected to be different due to the endothermic nature of the reaction and the fact that the gas stream flowrate would significantly increase within the reactor due to the released water vapor through reaction. The results matched the expectations with an optimal reactor diameter of 4 m but taller reactor height of 14 m to counter the additional expected elutriation effects in the bed, while a bed mass of ~6500 kg was enough to store the required amount of heat while maintaining reaction conversion performance. For both reactors the importance of reactor dimensions in influencing the fluidization behavior of their systems was observed serving to vindicate the added focus on this in this study.

Based on these results, key process parameters and results from the two designed FBRs were compared with those from the reference case. After controlling for certain differing assumptions made in calculations, it was observed that Aspen Plus FBRs using *Fluidbed* was in good agreement with analytical models. The specification of the processes external to the main TCES flowsheet were then carried out. For modelling the input from the CSP plant, the main consideration was the selection of HTF to use as part of the simulation; while molten salts and thermal oils were industry standards, specifying them would be significantly more complex than the use of simple gases such as pressurized steam. As the design of the CSP plant was not a focus of the study and the heat exchangers in the FBRs were previously stated to be excluded from detailed study, design simplicity was prioritized and pressurized steam at 100 bar was chosen as the HTF for this part of the flowsheet.

Lastly, the power generation block was modelled using a pressurized steam Rankine cycle. A 3-stage cycle was designed and specified, achieving a $\eta_{Rankine}$ value of 39%; this was identified as close to the maximum possible due to the below-average boiler temperature of 411°C. This resulted in a net electrical

power output at steady-state of 49.8 MW from the CSP-TCES plant. The thermal round trip efficiency of the flowsheet was estimated to be 70-92%, potentially offering a comparable performance to the 86% achievable through molten salt TES technologies while facilitating longer storage durations; this estimate can be refined through future work investigating potential thermal inefficiencies in handling steam storage in more detailed flowsheet designs.

With this the steady-state design of the $\text{CaO}/\text{Ca}(\text{OH})_2$ -based CSP-TCES plant flowsheet was completed, simulated, and analyzed. The process simulation tool was compared with literature and found to produce similar results, resulting in a potential contribution to the literature in this area; the design of the subsequent flowsheets were greatly aided by being directly compatible with the designed FBRs. The energy input and power production mechanisms were also designed and specified, producing a fully operable plant design.

Chapter 7

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CSP-TCES Plant Modelling – CMO Redox System

Chapter Contents

Sections	Subsections
1. Technical Considerations for CMO Redox Plant	1. Choice of Reaction Scheme and Thermodynamic Requirements 2. Physical Design Considerations 3. Solid Material Specification
2. Design of CMO Reducer and Oxidizer at Steady-State	1. Reaction Specifications, Controlled Variables, and Boundary Conditions 2. Reducer Design and Optimization 3. Oxidizer Design and Optimization
3. CSP-TCES Plant Flowsheet Design for the CMO Redox System	1. Designed Flowsheets and Process Outcomes 2. Initial Integration of CSP Resource 3. Integration of Brayton Cycle
4. Chapter Summary and Concluding Remarks	

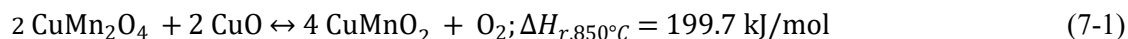
7.1 Technical Considerations for CMO Redox Plant

Based on the literature review and planned investigation discussed in Chapter 5, this phase of work involved the design and simulation of TCES processes for the two chosen reaction systems. As Chapter 6 presented the results of this work for the $\text{CaO}/\text{Ca}(\text{OH})_2$ TCES system and developed a design methodology and analysis framework, this work was now continued in Chapter 7 for the CMO redox system which is a more complex system and has not been studied previously in the literature in this manner. This work is especially novel as an original modelling and simulation approach is developed and implemented to describe these new materials accurately.

The CMOs identified from literature are synthesized materials and as they involve transition metal oxide mixtures they exhibit more complex reaction mechanisms and stoichiometry, which were considered in this study. Furthermore, the identification of suitable material and reaction specifications for the reduction and oxidation systems was carried out based on a combination of literature data and thermodynamic calculations presented here. Subsequently, key design considerations are reintroduced and the specification of the solid CMO materials is discussed in detail in preparation for the subsequent design of FBRs using Aspen Plus.

7.1.1 Choice of Reaction Scheme and Thermodynamic Requirements

The stoichiometry of the CMO redox system being considered was proposed by Patzschke²⁷ as stated in Eq. 7-1, based on phase identification through XRD analysis:



The equilibrium temperature of the redox system is significantly influenced by the composition of the reacting gas mix. Based on the kinetic data available, T_{red} of 925°C and T_{ox} of 850°C were chosen for reactions. While it was possible to operate at temperatures higher by $\sim 50^\circ\text{C}$, the temperature constraint of the HTF from the CSP block had to be considered and a sufficient ΔT maintained for operating the reduction process for energy storage; the oxidation temperature was accordingly specified to be close to the reducer temperature to reduce thermal inefficiencies. It was noted that the kinetics were fast across the whole temperature range considered. There is some discussion required for the selection of gas mixes for the reduction and oxidation reactions. For the reduction reaction O_2 is to be produced and so a carrying gas doubling as the fluidizing agent needs to be selected. Based on kinetic studies, gas mixes involving CO_2 , N_2 , and H_2O do not result in significantly different kinetic behaviors of the reaction.²⁷

However, a feed gas mix of 10 vol% $\text{O}_2 + \text{CO}_2$ is preferred in the reducer instead of using $\text{O}_2 + \text{N}_2$ or $\text{O}_2 + \text{H}_2\text{O}$ as the exit gas is expected to be O_2 -rich as a result of reaction and so a gas mix that can be conveniently

separated is preferred. O₂ and CO₂ are relatively easy to separate from each other through reversible chemisorption which has low energy costs, while O₂ and N₂ require cryogenic separation which is highly energy intensive, and O₂ and H₂O require condensation of water which is also significantly energy intensive.

For the oxidizer, a feed gas mix of 10 vol% O₂ + N₂ is preferred as this gas stream is expected to be recycled within the process by replenishing the O₂ concentration during looping. Hence there are no gas separation considerations to account for. Such a gas mix is also relatively cheap to obtain and use as N₂ is inert and poses nearly no process hazards, and a mixture of such proportions is easily obtainable from commercial sources through air scrubbing and N₂ dilution.

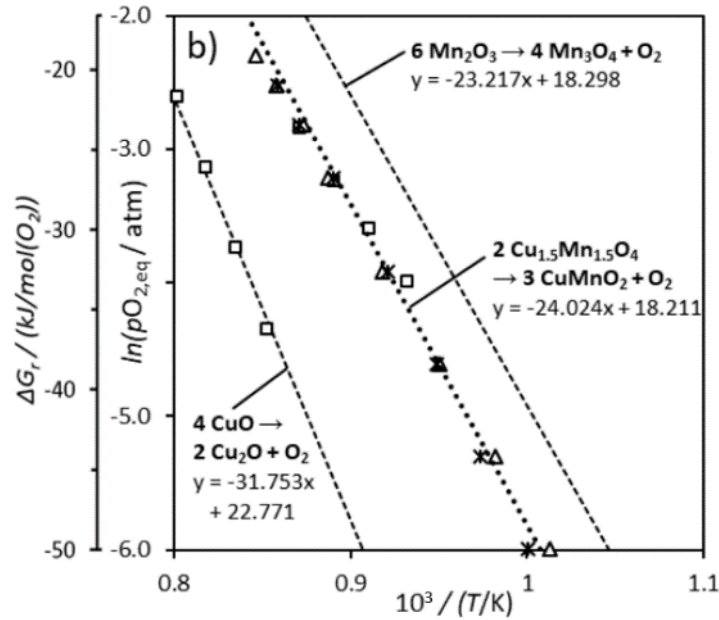


Fig. 7-1: Equilibrium O₂ partial pressure ($p_{O_2,eq}$) - temperature and – Gibbs free energy relationships for pure Cu and Mn oxides and the synthesized CMO, adapted¹⁰⁷

An additional thermodynamic constraint for the design of the FBRs was that the equilibrium partial pressure of O₂ ($p_{O_2,eq}$) had to be considered: at a specified reaction temperature if the O₂ concentration in the gas mix within the reactor reaches this value, the oxidation or reduction reaction will stop as there would be no driving force to maintain it. Based on calculations by Patzschke²⁷, at the chosen oxidation and reduction temperatures of 850°C and 925°C the values of $p_{O_2,eq}$ are 0.041 atm and 0.164 atm respectively for the CMO material as shown in Fig. 7-1. As a result, this was an additional boundary condition imposed on the simulation which had to be met by balancing the excess flowrate of inlet gas mix (to ensure the supply of enough moles of O₂ for reaction such that $p_{O_2,outlet} \geq 0.041$ atm) with the corresponding greater extents of fluidization and elutriation in the case of the oxidizer feed gas. This also had to be met by specifying the reducer feed gas mix with a sufficiently high flowrate such that $p_{O_2,outlet} \leq 0.164$ atm

7.1.2 Physical Design Considerations

In using the *Fluidbed* block in Aspen Plus, the same physical design considerations had to be assessed and specified as discussed in Section 6.2.2 for the CaO/Ca(OH)₂ TCES plant design. These involved the Geldart classification for particle behavior, estimations of the TDH of the bed, and correlations to describe the elutriation of particles from the bed. For consistency, the same parameters excluded from study in Chapter 6 as discussed in Section 6.1.1 were also excluded here (such as detailed design of the FBR heat exchangers and the FBR gas distributors).

Geldart classification

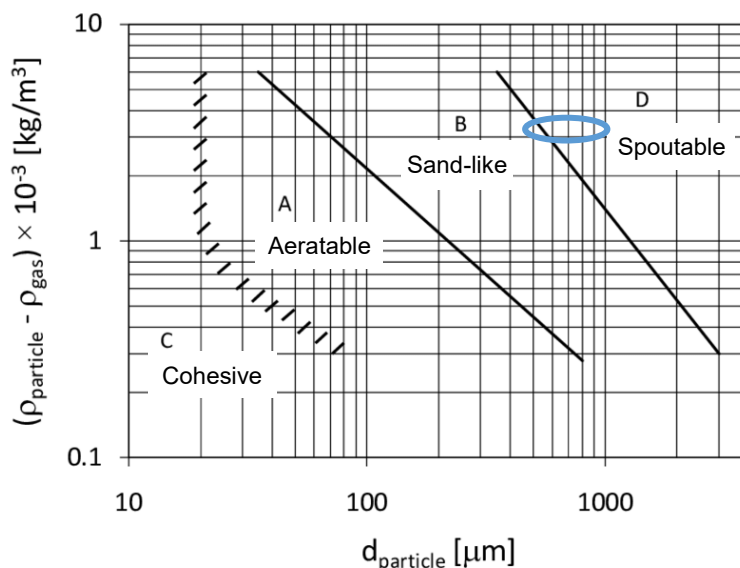


Fig. 7-2: The Geldart classification chart for fluidized materials (blue is for both CuMnO₂ and CuMn₂O₄)

As the design approach from Chapter 6 was also used here, the main physical design considerations for the reducer and oxidizer here were similar. Some physical properties of the general materials first had to be established in order to proceed. Based on the data available²⁷, the mass density of the CuMnO₂ material was estimated to be ~2880 kg/m³ if supported, varying based on the synthesis route, while that of the CuMn₂O₄ material is estimated to be ~2970 kg/m³ with the same pre-conditions. The particle size range expected to be used is in the 500-1000 μm range due to the availability of kinetic data for materials of this size.

Based on these properties, the Geldart classification of the reducer and oxidizer beds would both fall under category D according to Fig. 7-2. It is noted that there is a significant possibility for this to change in reality depending on the exact composition of material that results from development efforts elsewhere, including the addition of supports; ultimately only the mass density is likely to vary due to this which may bring the system more towards category B (sand-like behavior) or more comprehensively into category D. However for now choosing a category D classification is a conservative first approximation.

Transport disengagement height

Similarly for the TDH, the correlations available in Table 6-1 were considered and tested. It was observed that correlations by Chan and Knowlton¹⁶⁶ as well as Fournol et al.¹⁶⁸ were obtained through experiments performed under conditions similar to those expected in the reducer and oxidizer here in terms of particle diameters, Geldart classification, and gas velocities.

Upon testing of the two correlations in simulations separately, it was found that the expression by Chan and Knowlton yielded unrealistically small TDH estimates of <2 m while that by Fournol et al. estimated a TDH in the range of 18-24 m which appeared more likely to be representative of the required designs based on the results of Chapter 6; hence the correlation produced by Fournol et al. was selected for this study, shown in Eq. 7-2 where u is the linear velocity of the fluidizing gas and g is the acceleration due to gravity.

$$TDH = 1000 \cdot \frac{u^2}{g} \quad (7-2)$$

Elutriation behavior

For describing elutriation behavior, by examining Table 6-2 it was identified that the correlation of Colakyan & Levenspiel¹⁷¹ as used in Chapter 6 for the CaO hydration system was also the most suitable one for this system due to the similarities in gas velocities and particle diameters of solid reactants involved. This was based on the 500-1000 μm particle size range dictated by the kinetic data and fluidizing gas mix flowrates of 4-6 m/s expected based on similarities in particle mass densities and sizes. Hence, Eq. 6.2 and Eq. 6.3 were used to calculate the elutriation coefficient and elutriated mass flows respectively.

7.1.3 Solid Material Specification

As highlighted previously in Section 7.1.1, the proposed treatment of the CMO redox systems involves three main solid materials in two feeds – $\text{CuMn}_2\text{O}_4 + \text{CuO}$ for the reducer, and CuMnO_2 for the oxidizer. With the current capabilities of Aspen Plus, specifying complex materials such as CuMnO_2 and CuMn_2O_4 could not be done without extensive data pertaining to their physical properties as these materials do not currently exist in the databanks of the software. Due to this, they needed to be entered as user-defined components with all properties specified as the software currently is able to estimate parameters for user-defined components based on a limited range of chemical species which does not include Cu or Mn.

While fundamentally it may be possible to obtain estimates for most if not all of the required properties through various fundamental calculations, doing so is beyond the scope of this work. The next best approach was taken which was to select existing compounds from the databanks that are the most similar in terms of chemistry and physical properties to the materials involved in the CMO system. Due to the fact that Cu and

Mn are transition metals with multivalent configurations, there exist a range of MMO compounds in the literature that would potentially serve as suitable substitutes. Within the databanks, the best available compounds found were Cu-Fe oxides due to their uses as industrial catalysts. In particular, data for CuFeO_2 and CuFe_2O_4 (henceforth CFOs) were found to be available and so their relevant properties were compared with those of CuMnO_2 and CuMn_2O_4 in Table 7-1. While melting point data for the materials could not be obtained, the CMOs were used for reaction at temperatures up to 950°C by Patzschke²⁷ and the CFOs have been reported to be used in the solid state at temperatures up to 1100°C ^{183, 184} and so it was assumed that all materials considered would remain stable in the solid state at the temperatures of interest.

One key uncertainty that remained was whether the specific heat capacities of the materials were also sufficiently similar. However, no data at these temperatures was available for the CMOs for comparison with the correlations for the CFOs and so an estimation of the heat capacity functions was performed based on work by Leitner et al.¹⁸⁵; further details are included in Appendix A.5. Fig. 7-3 shows the estimated molar heat capacities of each material across an extensive temperature range and it is noted that for the temperatures being considered in the redox process here ($850\text{--}925^\circ\text{C}$) the $C_{p,m}$ values differ by $<2\%$. The suitability of CFOs as simulation substitutes was further assessed by checking the PSDs of the specified feeds and the product streams. Patzschke²⁷ reported that the PSD of the CMOs were found to be unchanged after 100 redox cycles under fluidized conditions and so any variations in the product PSD in Aspen Plus would allow for further indirect comparisons of the structures of the CFOs and CMOs as used in this study.

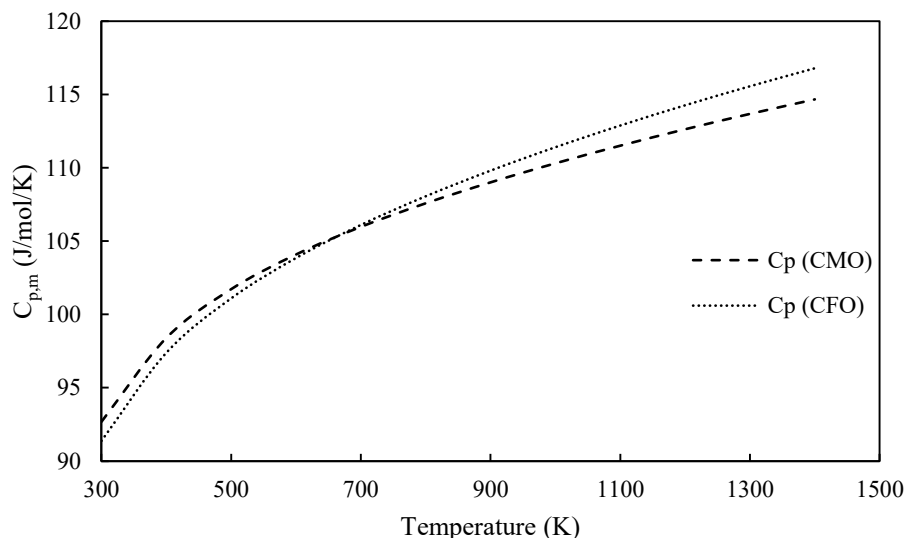


Fig. 7-3: Estimated molar heat capacities of CMO and CFO materials in reduced form with varying temperature based on the modified Neumann-Kopp rule

From Fig. 7-4 by inspecting the $p_{O_2,eq}$ curves for the CFO and CMO redox systems it is observed that their equilibrium characteristics do differ significantly at the temperatures of interest in this study. For the CFO material, at the chosen oxidation and reduction temperatures of 850°C and 925°C the values of $p_{O_2,eq}$ were calculated to be 0.145 atm and 0.280 atm respectively – both of which are much larger than the values for the CMOs noted earlier in Section 7.1.1. For the CFO system to have $p_{O_2,eq}$ matching those of the CMO redox system at the reaction temperatures specified, the CFOs would have to be oxidized at 725°C and reduced at 860°C. The higher $p_{O_2,eq}$ value at 925°C is not a concern for reducer design and simulation as the lower partial pressure constraint is the only one that will be accounted for in the optimization of the design case and the reaction rate is specified and thus the extent of reaction is controlled via kinetic data. However the higher $p_{O_2,eq}$ value at 850°C presents difficulties for simulating the oxidizer as the equilibrium O_2 partial pressure would be higher than that in the gas feed causing reduction to take place instead.

Table 7-1: Comparison of Cu-Fe oxides and Cu-Mn oxides for purposes of substitution in Aspen Plus study

	CuFeO₂	CuMnO₂	CuFe₂O₄	CuMn₂O₄
Mass density (kg/m ³)	5520	5490 (supported)	5400	5390 (supported)
Molar mass (g/mol)	151.39	150.48	239.23	237.42
Species charges	Cu (+); Fe (3+)	Cu (+); Mn (3+)	Cu (2+); Fe (3+)	Cu (2+); Mn (3+)

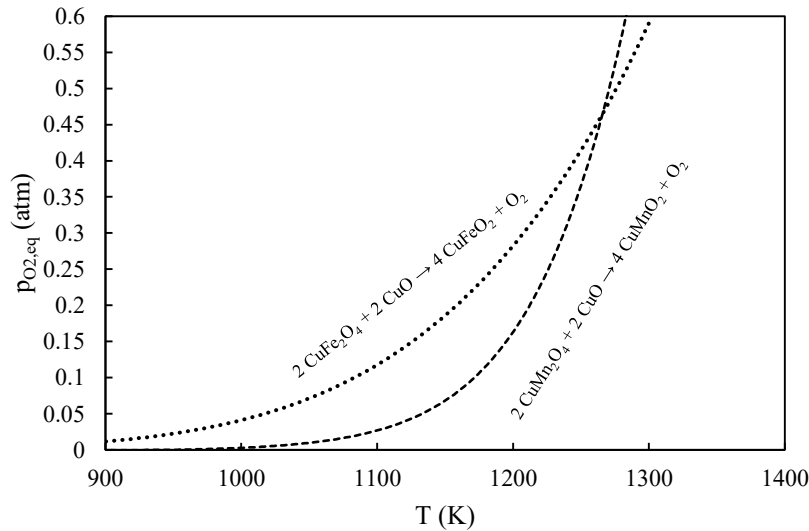


Fig. 7-4: Equilibrium $p_{O_2,eq}$ (atm) – temperature curves for the CFO (···)¹⁸⁶ and CMO (---)²⁷ redox systems

The workaround implemented for this within Aspen Plus was to operate the oxidizer FBR at 725°C so that the $p_{O_2,eq}$ of the system would match that of the CMO material at 850°C; to account for the omitted enthalpy, the exit solid and gas streams were then separately heated to 850°C. This would not affect the conversions achieved as based on the kinetics the reaction is still sufficiently fast at these temperatures compared to the

residence times involved. It was noted however that this lower temperature would have minor effects on the gas velocities within the FBR and fluidization behavior of the reacting bed hence a conservative specification was to be selected from the optimization to compensate for this. Calculations were also performed to quantify the impact of the lower operating temperature on properties of the gas mix. The expected gas velocities would be influenced by the gas densities and viscosities at the two temperatures in question and so in Table 7-2 the calculated values for these properties are reported; the calculation details are presented in Appendix A.6. It was noted that at 725°C the gas mix density is only 6% higher and the viscosity is 8% lower compared to their values at the reaction temperature of 850°C. These were considered to be negligible differences and it was noted the u/u_{mf} resulting from the gas flowrates employed (as discussed later) were still sufficiently high to allow for thorough fluidization.

Table 7-2: Calculated densities and viscosities of the 10 vol% $O_2 + N_2$ gas mixture for the CMO oxidation reaction at temperatures relevant to the Aspen Plus simulation

<i>Gas mix: 10 vol% $O_2 + N_2$</i>		
T (°C)	ρ_g (kg/m ³)	μ_g (m/s)
725	0.334	$1.328 \cdot 10^{-4}$
800	0.323	$1.375 \cdot 10^{-4}$
850	0.316	$1.463 \cdot 10^{-4}$

Table 7-3: Measured and calculated compositions of supported/unsupported oxidized and reduced forms of CMO material used for the study of the CMO redox TCES system in Aspen Plus

Property	Value
Composition of oxidized CMO (mass frac.)	CuMn ₂ O ₄ (0.740); CuO (0.260)
Composition of oxidized CMO (mol frac.)	CuMn ₂ O ₄ (0.488); CuO (0.512)
Molar mass of oxidized CMO (g/mol)	156.61
Composition of oxidized supported CMO (mass frac.)	CuMn ₂ O ₄ (0.296); CuO (0.104); ZrO ₂ (0.60)
Composition of oxidized supported CMO (mol frac.)	CuMn ₂ O ₄ (0.168); CuO (0.176); ZrO ₂ (0.656)
Molar mass of oxidized supported CMO (g/mol)	134.71
Composition of reduced CMO (mass frac.)	CuMnO ₂ (1.00)
Composition of reduced CMO (mol frac.)	CuMnO ₂ (1.00)
Molar mass of reduced CMO (g/mol)	150.48
Composition of reduced supported CMO (mass frac.)	CuMnO ₂ (0.400); ZrO ₂ (0.600)
Composition of reduced supported CMO (mol frac.)	CuMnO ₂ (0.349); ZrO ₂ (0.651)
Molar mass of reduced supported CMO (g/mol)	132.74

In the source study²⁷ a ZrO₂-supported CMO demonstrated the best cycling results under fluidized conditions and hence this was chosen for consideration. As it is a complex mixture, physical data is presented in Table 7-3 for its reduced and oxidized forms. The expansion and shrinkage behavior observed in Chapter 6 for the CaO/Ca(OH)₂ system was not of concern here, as the PSD of the supported CMO was reported to be virtually unchanged after 100 redox cycles in a FBR as measured via laser diffraction.²⁷ Hence, the PSDs for the feed streams of the reducer and the oxidizer were specified to be identical.

The kinetic data used was obtained for particles with a wide PSD of 300-1000 μm . Using such a large PSD range would lead to a more widely dispersed bed due to greater buoyancy of the smaller particles and so a smaller PSD range of 650-950 μm was selected for the simulations. The final specifications of the PSDs are presented in Table 7-4 and illustrated in Fig. 7-5. As in Chapter 6, a number distribution equivalent growth model was specified in Aspen Plus to account for any changes to the PSDs in the course of reaction.

Table 7-4: Specification of the ZrO₂, CuMnO₂, CuMn₂O₄ and CuO PSDs for fresh feeds, based on particle diameters, following normal distributions

Normal distribution parameters	Feed CuMnO ₂ + ZrO ₂	Feed CuMn ₂ O ₄ + CuO + ZrO ₂
Lower limit (μm)	650	650
Upper limit (μm)	950	950
Discretization intervals	12	12
Mean (μm)	800	800
Standard Deviation (μm)	50	50

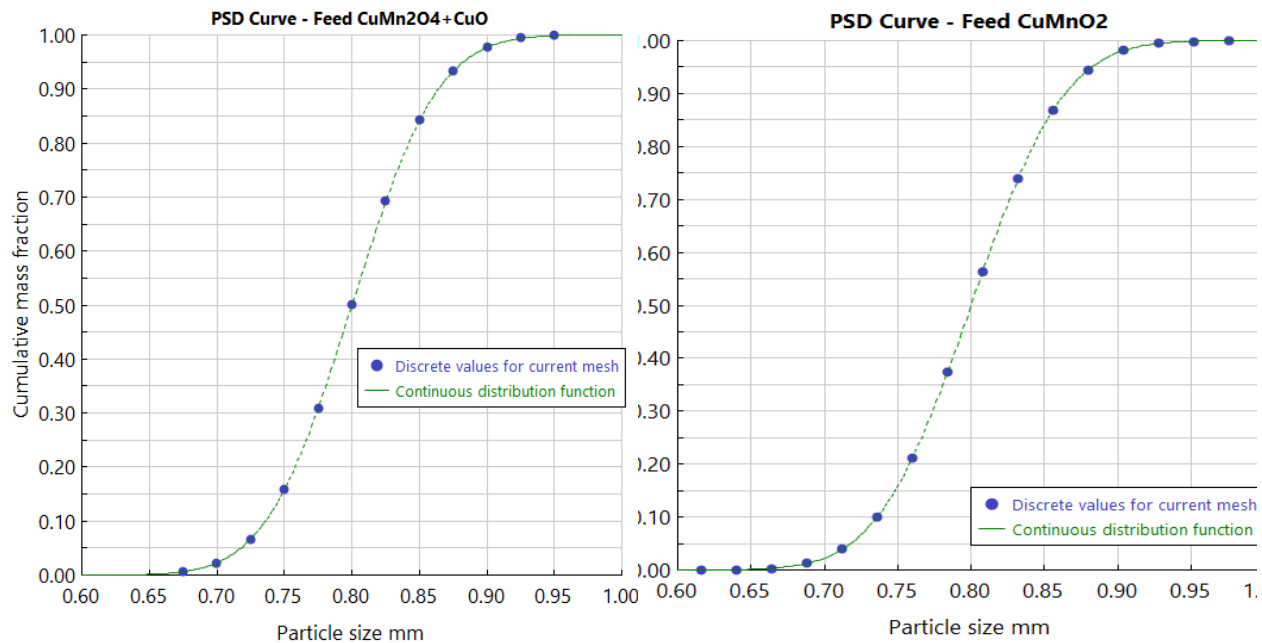


Fig. 7-5: PSD curves for feed CuMn₂O₄+CuO and feed CuMnO₂ streams used in Aspen Plus study

7.2 Design of CMO Reducer and Oxidizer at Steady-State

In the design methodology employed in Chapter 6, the initial designs and optimizations were performed for processes at steady-state. No literature pertained to the modelling of FBRs for such a TCES system for comparison and hence this study aimed to further establish FBR simulations for TCES applications.

7.2.1 Reaction Specifications, Controlled Variables, and Boundary Conditions

In Table 7-5 the kinetic parameters for the redox system are presented as reported by Patzschke²⁷ for the unsupported CMOs; however as the ZrO₂ support material used is inert during the redox reactions they were considered to be suitable for describing the reaction of the supported CMO as well. It was noted in the same study that the Arrhenius expression of the kinetics of the system was more accurate for the oxidation reaction than for the reduction reaction as for the latter an additional factor accounting for the equilibrium O₂ concentration as a driving force was needed. However as the temperature used for the reducer in this work fell within the studied temperature range used to derive the Arrhenius parameters, it was deemed to be sufficiently accurate for the purposes of this study.

In Table 7-6 the reaction specifications used for the redox system are listed amongst which the estimated residence times and target conversions were specified based on data reported by Patzschke²⁷; these were based on measurements made for the supported CMOs. The conversion limit of 0.6 used here was a conservative figure as the supported CMOs were found to have a residual and stable conversion limit of 0.7 after 50 redox cycles.²⁷ This corresponds to a carrying capacity of 0.93 mol (O₂)/kg (CMO). The reaction temperatures, pressures, and p_{O_2} requirements were established in Section 7.1.1 and the target charging/discharging capacity was chosen to be consistent with Chapter 6.

Table 7-5: Kinetic rate parameters used for CMO reduction and oxidation reactions²⁷

Kinetic Parameters	Reduction	Oxidation
Activation energy, E_a (kJ/mol)	277.2	30.06
Pre-exponential factor, A (s ⁻¹)	8.46×10^{-10}	2.87×10^{-6}
Reaction temperature (°C)	925	850
Calculated $k_{(hyd/dehyd)}$ (s ⁻¹)	113.35	407.74

The inlet feed specifications for the two FBRs are reported in Table 7-7 and were informed by specifications used in the literature^{27, 78} and discussions presented in Section 7.1.3. The choice of having a product/feed mix in the solid streams was based on the expected incomplete conversions in either reaction and to subsequently account for complementary utilization of product and feed streams in the TVP simulation through cycling; the same consideration was made for the CaO/Ca(OH)₂ system in Chapter 6.

Table 7-6: Boundary conditions and pre-determined constants for CMO redox reactions

Variables	Reduction	Oxidation
Estimated residence time (s)	60	60
Minimum bed mass (kg)	20000	18000
Reaction temperature (°C)	925	850
Reaction pressure (bar)	1.0	1.0
Target conversion, X	0.6	0.6
Target $Q_{out/in}$ (MW)	100	120
$p_{O_2,outlet}$ (atm)	≤ 0.164	≥ 0.041

Table 7-7: Specification of inlet streams into Fluidbed for CMO reduction and oxidation reactions

FBR initial feed specifications	
Particle Size Range (mm)	0.65-0.95 (red); 0.65-0.95 (ox)
Fluidizing gas	10 vol% O ₂ + CO ₂ (red); 10 vol% O ₂ + N ₂ (ox)
Initial gas mass flowrates (kg/s)	17.5 (red); 60.0 (ox)
CMO _{ox} /CMO _{red} feed (mol ratio)	3:1 (red)
Reduction solids feed flowrate (kg/s)	700.0
CMO _{red} /CMO _{ox} feed (mol ratio)	4:1 (ox)
Oxidation solids feed flowrate (kg/s)	690.0

7.2.2 Reducer Design and Optimization

The trends observed in Fig. 7-6 are qualitatively similar to those observed Section 6.3.3 for the design of the Ca(OH)₂ dehydration reactor as both are endothermic processes that involve the release of additional gas into the reaction mix. It is first noted that the significantly larger reactor dimensions and bed masses required are a result of the higher molar masses of the CMO materials compared to the CaO/Ca(OH)₂ materials. This is further compounded by the presence of the ZrO₂ support material which accounts for 60% of the material mass. In addition, with larger bed masses the larger volumes of O₂ released into the gas mix would mean that $p_{O_2,eq}$ would be reached prior to complete conversion of the bed.

The observed relationship between Q_{in} and bed mass is as expected with Q_{in} increasing proportionally to the bed mass until a bed mass of ~21500 kg where the Q_{in} is ~125 MW; after which only very gradual increases in Q_{in} occur. As before, these factors likely contribute to the relationship observed between conversion and bed mass as the average conversion steadily rises up till a bed mass of ~22000 kg where it reaches a value of 0.61 after which it drops sharply. This mass was therefore selected.

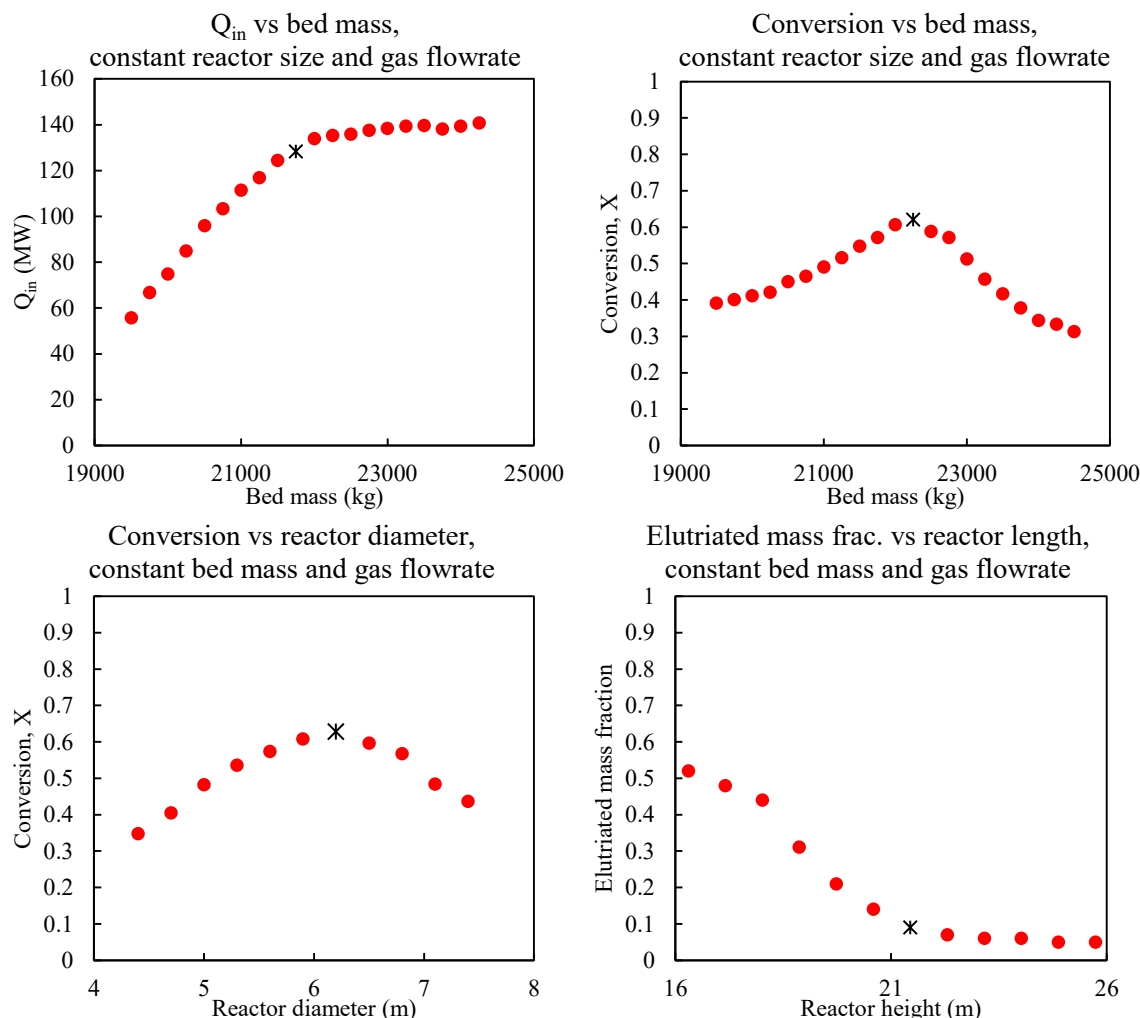


Fig. 7-6: Simulated trends in reaction system behavior within FBR for the CMO redox TCES charging process, varying bed mass and reactor dimensions

An optimal diameter of ~6.2 m was identified resulting in a conversion of 0.63. Diameters wider than this resulted in drops in conversion likely due to slower linear gas velocities limiting fluidization which may negatively impact heat distribution (and thus reaction conversion) in areas of the bed. The increased gas flowrates and velocities due to O_2 evolution are expected to be the main factors behind the relationship observed between the reactor height and the elutriated mass fraction as large portions of the bed are ejected for reactor heights <20 m. Based on the TDH calculations the elutriated mass fraction is then observed to drop significantly and a reactor length of >21 m resulted in <10% of the bed mass being elutriated.

7.2.3 Oxidizer Design and Optimization

The trends presented in Fig. 7-7 are also for the most part qualitatively similar to those observed for the CaO hydration reactor design in Section 6.3.2 as both are exothermic reactions that remove a gas species

from the fluidized mix. As before, the much larger bed masses and reactor dimensions required are due to the higher molar masses of CMOs coupled with the presence of significant quantities of inert support material. A noticeably different trend is however observed for the relationship between bed mass and Q_{out} . Although Q_{out} steadily increases as the bed mass increases, after a bed mass of ~ 17800 kg very little further heat is released from the system. This is in line with expected behavior as due to the constant gas flowrate maintained for this study, as after a certain bed mass, p_{O_2} within the FBR would be expected to fall to $p_{O_2,eq}$ prior to complete conversion of the bed mass and hence no further reaction will occur, leading to a reduction in conversion as more bed material is added. Hence, 18000 kg was chosen as the optimal bed inventory.

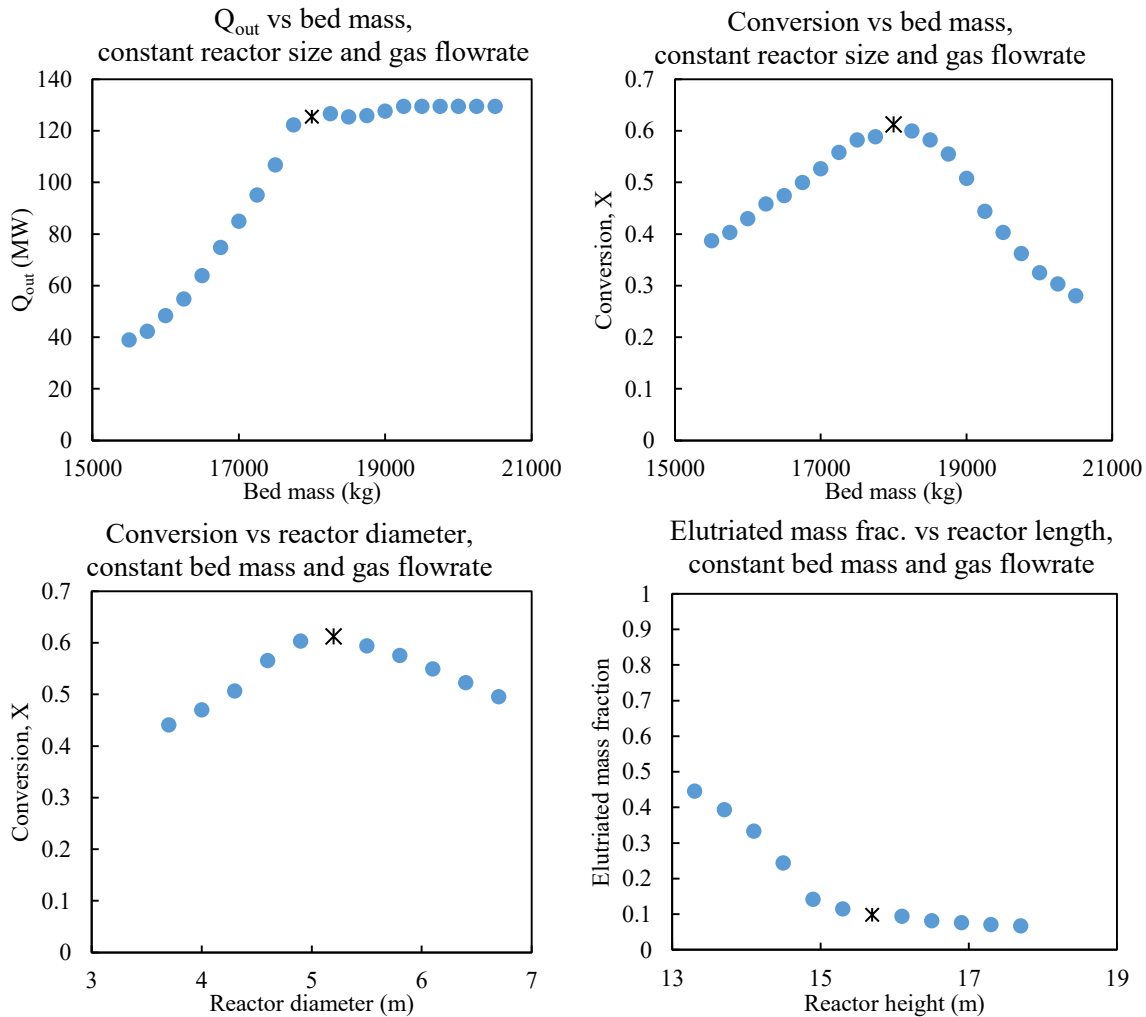


Fig. 7-7: Simulated trends in reaction system behavior within FBR for the CMO redox TCES discharging process, varying bed mass and reactor dimensions

Although the oxidation reaction results in the uptake of O_2 from the gas stream, much higher overall gas flowrates were used in the oxidizer to ensure the desired $p_{O_2,outlet}$ values could be met. Due to this the desired reactor diameter range remained relatively large with a diameter of ~ 5.3 m facilitating a peak

conversion of 0.64. For reactors wider than this the bed mass may experience reduced lateral circulation due to lower gas velocities, which would result in lower overall conversions. Due to the high gas velocities the overall reactor height required was also significant as significant elutriation occurred if the reactor was shorter than 14 m. A reactor height of 16 m was chosen as heights above 15 m resulted in <10% of the bed mass being elutriated and so significantly taller reactors would not offer any advantages.

7.3 CSP-TCES Plant Flowsheet Design for the CMO Redox System

The next step in the design study as was conducted in Chapter 6 was to produce complete flowsheets for the overall CSP-TCES plant that would incorporate the designed CMO reducer and oxidizer FBR units. This was done in order to facilitate the investigation of the overall thermodynamic performance of the proposed plant at steady-state and to specify the requirements for the design of the upstream CSP facility and downstream power generation block connecting to the TCES processes. As was the case for Chapter 6, the flowsheets constructed here were directly used for the TVP simulation studies for the CMO redox CSP-TCES plant conducted next in Chapter 8.

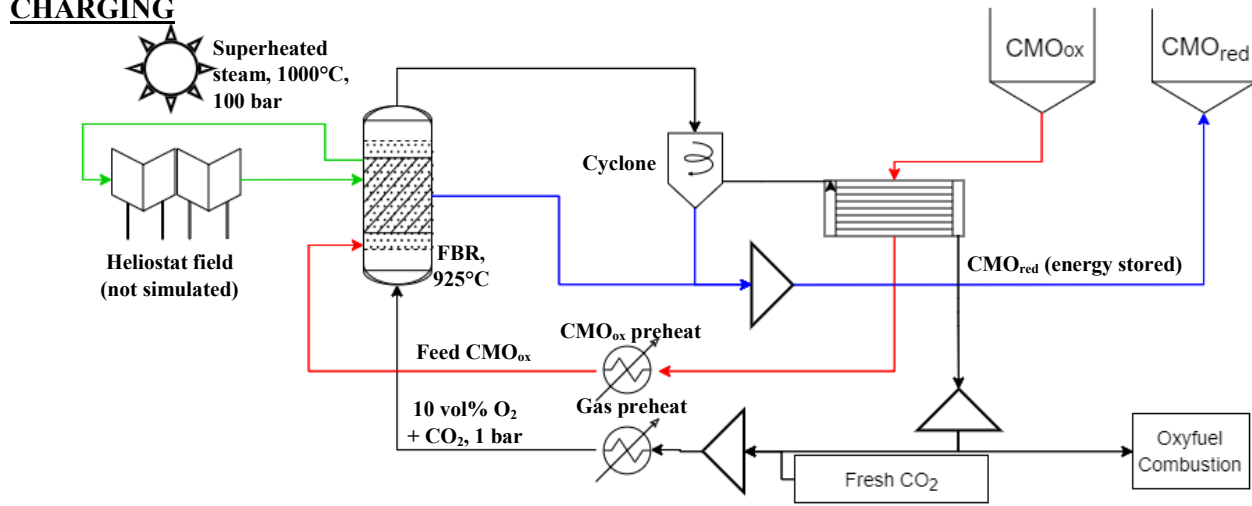
7.3.1 Designed Flowsheets and Process Outcomes

The flowsheet for the CMO redox process consists of four sub-systems, of which three were simulated in this study: the CMO reduction heat storage system, the CMO oxidation heat discharging system, and the supercritical CO₂ (sCO₂) cycle for power generation. These flowsheets were constructed and simulated in Aspen Plus V9 at steady-state. The specification of the heliostat field, which was not simulated, was done in the same way as in Section 6.4.1 where it was simply treated as a HTF carrying the desired heat flows in and out of the flowsheets. As before only a simplified flowsheet is presented here for clarity of reading and so minor unit processes such as most heat exchangers are not included in the flowsheet shown in Fig. 7-8. The reducer and oxidizer FBRs were the focus of the studies carried out in Section 7.2. Due to the different gas feed mixtures and solid feed streams for either reaction each reactor was designed separately and will have different material fabrication considerations to account for such as the reducer requiring higher quality corrosion-resistant material due to the large volumes of CO₂ used in the reduction process. The optimal dimensions for the two FBRs also differed significantly validating the need for independent design.

For both processes, the storage tanks for the solids (reduced and oxidized forms of the CMO) were assumed to be sufficiently thermally insulated to keep the solids at temperatures of at least 500°C. The duration of storage is not expected to be more than several days as the material is meant to be regularly cycled. As this temperature is still significantly below the solid exit stream temperatures, the surplus latent heat available

from these streams were reused for heat integration to preheat the feed streams into the FBRs. The gas exit stream was separately used to provide heating to the sCO₂ power cycle as discussed later in Section 7.3.3.

CHARGING



DISCHARGING

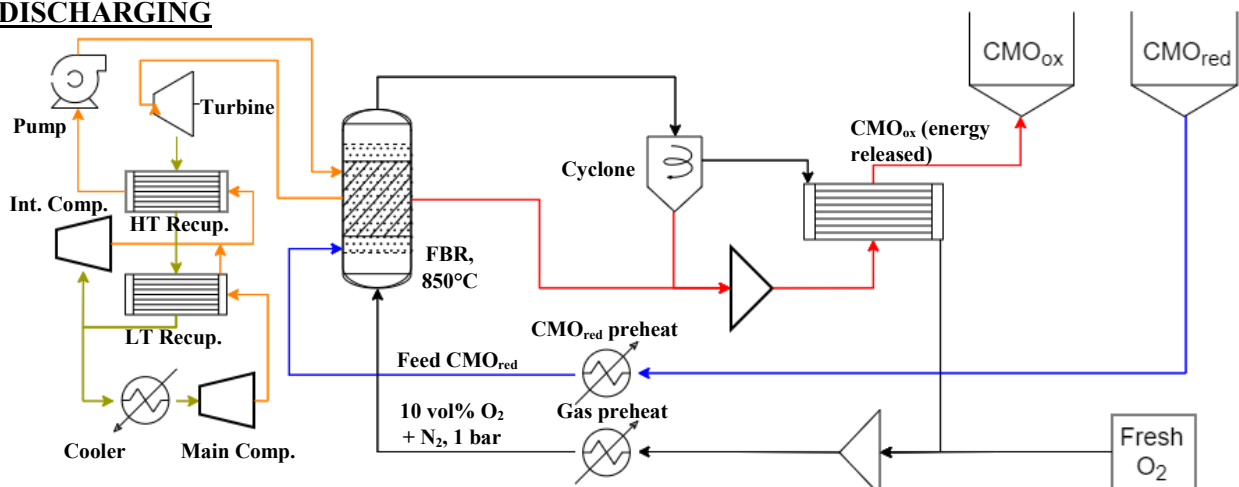


Fig. 7-8: Flowsheet of the combined CSP-TCES plant based on the CMO redox system, focused on the TCES section and separated into the charging (top) and discharging (bottom) processes. The colored streams are process gases (black), solar heat transfer steam (green), solid CMO_{red} (blue), solid CMO_{ox} (red), and the sCO₂ power cycle (orange for high pressure, gold for low pressure)

For the product gas stream from the reduction flowsheet, a fractional split is first done to recover the desired O₂ for the fluidizing gas feed stream, which is mixed with pure CO₂ to regenerate the desired molar compositions and total flowrates. For the residual bulk gas stream, there are several options for reutilization. It can be sent to a stripping process (such as the Benfield process) to obtain a high-purity CO₂ stream for compression, storage or selling. The stream can also be O₂-enriched by partially stripping the CO₂ to produce a stream with 25-35 vol% O₂ usable in oxyfuel combustion furnaces.¹⁸⁷ Relevant information pertaining to the key streams in the CMO reduction (charging) flowsheet is presented in Table 7-8. The

very large mass flowrates of solids are noted here in contrast to the CaO/Ca(OH)₂ system; for more detailed design it could be considered whether two parallel processes with half the flowrate each could be operated instead. The presence of significant amounts of elutriated solids in the exit gas stream from the reducer as noted in Section 7.2.2 necessitates a cyclone is used. The O₂ concentration of 16.2% in the recycled stream was noted to meet the design threshold based on the $p_{O_2,eq}$ at T_{red} .

Table 7-8: Stream table for key streams for the CMO reduction TCES flowsheet at steady-state

Stream	FBR Fresh Feed	FBR Gas Feed	FBR Bottoms	FBR Top	Storage Feed	Gas for Re-util.
Mass flow (kg/s)	700.0	17.5	695.4	21.7	697.1	20.4
P (bar)	1.0	1.0	0.94	0.94	1.0	1.0
T (K)	1198	1198	1198	1198	923	1260
Composition (mol%)						
CuMn ₂ O ₄	12.7		5.2	0.2	5.2	
CuO	12.7		5.2	0.2	5.2	
CuMnO ₂	8.9		19.3	0.8	19.3	
ZrO ₂	65.7		70.3		70.3	
O ₂		10.0		16.1		16.2
CO ₂		90.0		82.9		83.7

Table 7-9: Stream table for key streams for the CMO oxidation TCES flowsheet at steady-state

Stream	FBR Fresh Feed	FBR Gas Feed	FBR Bottoms	FBR Top	Storage Feed	Recycled Gas
Mass flow (kg/s)	690	60.0	703.4	56.6	705.4	54.6
P (bar)	1.0	1.0	0.93	0.93	1.0	1.0
T (K)	1123	1123	1123	1123	773	1186
Composition (mol%)						
CuMn ₂ O ₄	5.2		9.0	0.15	9.0	
CuO	5.2		12.5	0.15	12.5	
CuMnO ₂	19.3		12.5	0.5	12.5	
ZrO ₂	70.3		66.0		66.0	
O ₂		10.0		4.0		4.1
N ₂		90.0		95.2		95.9

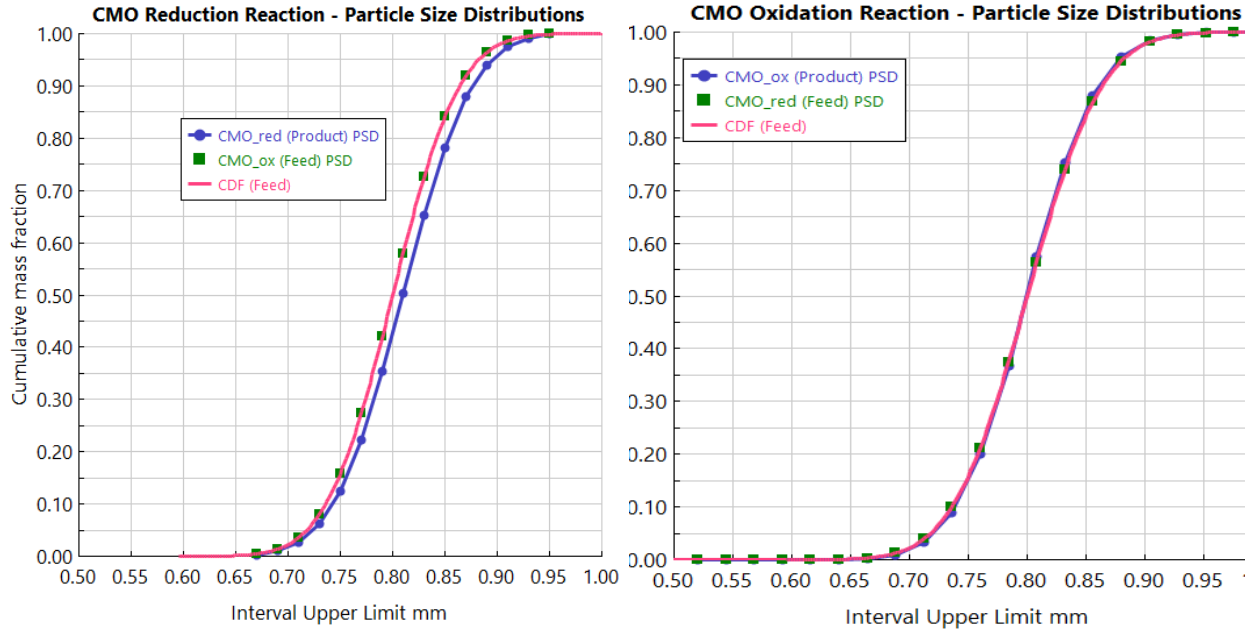


Fig. 7-9: PSD curves for feed and product streams for CMO reduction (left) and CMO oxidation (right) flowsheets generated in Aspen Plus

Relevant information for key streams in the CMO oxidation (discharging) flowsheet is presented in Table 7-9. A cyclone was required to produce the filtered gas stream suitable for recycling (after re-enrichment). The O_2 concentration of 4.0% in the recycled stream was noted to meet the design threshold based on the $p_{O_2,eq}$ at T_{ox} . Negligible PSD changes were estimated with the PSD shifting slightly towards producing larger particles during reduction. Overall the calculated PSDs corroborate experimental observations.

7.3.2 Initial Integration of CSP Resource

Consistent with the design approach used in Section 6.3.2, the CSP resource here was modelled as a HTF supplying heat to the reduction flowsheet. Pressurized steam was chosen as the HTF for process simplicity considerations although it is acknowledged that bespoke thermal oils or molten salts would offer a superior performance. The specification of the HTF stream used is presented in Table 7-10. Several important assumptions were made in implementing this HTF stream. Firstly it was assumed that a CSP solar tower is able to heat a HTF stream to 1000°C. This would mean that the solar receiver operates at even higher temperatures (>1300°C), which is not possible with commercial technologies which only produce HTFs at up to 700°C. However, Heliogen²⁹ has recently demonstrated a receiver design with output temperatures approaching 1500°C and work by DLR⁵¹ is also underway to cross the 1000°C threshold. Operating a receiver at such high temperatures would also reduce the thermal efficiency of the heliostat as radiative heat losses would pose a significant design challenge – and so it is acknowledged that major developments are needed to establish the feasibility of this component of the envisaged combined CSP-TCES plant.

It was also assumed that FBR heat exchangers can tolerate a hot stream of 1000°C steam. Currently advanced alloys used for heat exchangers have only been demonstrated at up to 700°C.¹⁸⁸ While heat exchanger design is outside the scope of this work, this is nonetheless acknowledged as a significant engineering limitation for the proposed TCES process. The proposed heating and reaction configuration for the charging step and the choice of HTF material should be revisited as advancements in high temperature CSP arise. The receiver design used at a pilot conducted by DLR⁵¹, for instance, does away for the need for HTFs and heat exchangers by employing ceramic spheres as the heat absorption and release medium.

Table 7-10: Specification of HTF stream representing CSP energy supply for the CMO reduction reaction

Heat transfer fluid	Pressure	Temperature	Flowrate	Heating provided
Steam	100 bar	1000°C (FBR inlet)	240 kg/s	130 MW _{th}
		952°C (FBR outlet)		

It is clear that while advancements continue to be made, there remain significant challenges to overcome for CSP plants to become compatible with TCES systems at such temperatures. Hence it is accepted that the technical viability of a CMO redox TCES system for CSP, as described here, is additionally contingent on commercial demonstration of compatible solar receiver and heat exchanger designs.

7.3.3 Integration of Brayton Cycle

It was noted in Chapter 5 that a key difference in the expected flowsheets for the CaO/Ca(OH)₂ and the CMO redox TCES systems would be the type of power cycle used. While the moderate discharge temperatures of the CaO hydration system meant that only steam Rankine cycles were thermodynamically suitable for integration, the higher discharge temperatures in the CMO redox system allow for the possibility of a Brayton cycle using sCO₂ as the HTF. Such a cycle manipulates the irregularities (non-ideal behavior) in the physical properties displayed by CO₂ close to its critical point and offers higher theoretical efficiencies than a steam Rankine cycle. While many configurations exist in the literature, the optimization of the power generation cycle is not within the scope of this work and so a basic recompression cycle design was implemented for the sCO₂ Brayton cycle as seen in the flowsheet in Fig. 7-8.

The configuration of the recompression Brayton cycle and the parameters in Table 7-11 were informed by existing literature designs¹⁸⁹ including studies where such cycles were modelled to be integrated directly with CSP plants at these temperatures.^{190, 191} Based on a 125 MW_{th} discharging process, the thermal efficiency of the recompression sCO₂ Brayton cycle is 47.5% as 59.3 MW (net) of electricity is generated by the plant as calculated from Table 7-12. At the operating temperatures involved the maximum theoretical

efficiency is 57%^{190, 191} and so there is room for further optimization of the design as is possible with advanced designs involving inter-stage cooling and partial cooling stages.¹⁹⁰⁻¹⁹² These results suggest that a high-temperature CSP-TCES plant would offer a greater thermal-to-electricity energy efficiency than current CSP plants can offer and this could be further improved by optimizing the power cycle.

Table 7-11: Design specification for the sCO₂ Brayton cycle for the CMO oxidation (discharging) flowsheet

sCO₂ Cycle Specification	Value
Turbine inlet pressure	250 bar
Turbine outlet pressure	75.5 bar
Turbine inlet temperature	825°C
Pressure ratio	3.3
Isentropic efficiency (Turbine)	0.90
Isentropic efficiency (Compressors)	0.89
Isentropic efficiency (Recompressor)	0.89
Main Compressor inlet temperature	32°C
Compressors outlet pressure	250 bar
Pressure drop (Recuperators)	0.25 bar
Splitting fraction	0.705
Pressure drop (Heater and cooler)	0.8 bar
CO ₂ flowrate (kg/s)	73.8

Table 7-12: Results for the sCO₂ Brayton cycle for the CMO oxidation (discharging) flowsheet

sCO₂ Cycle Parameter	Value	Input (-ve)/Output (+ve)
Turbine power output	72.4 MW	+
Heater duty	5.5 MW _{th}	-
Cooler duty	4.1 MW	-
Main compressor duty	6.2 MW	-
Intermediate compressor duty	2.8 MW	-
Heat reused from FBR top stream	5.5 MW _{th}	+
Net power produced	59.3 MW _e	+

In Table 7-13 the thermal round trip efficiency (RTE) of the designed plant is evaluated in comparison to a base case CSP plant with molten salt TES. It is observed that implementing CMO redox TCES improves the RTE for a CSP setup from 86% to 89%, while enabling much longer storage durations. As before, this RTE of 89% depends heavily on the longer-term cycling stability of the reactants. Hence the durability of supported-CMO materials needs to be assessed in pilot studies to validate this RTE projection.

Table 7-13: Round trip efficiency calculations for the CMO redox TCES-CSP flowsheet

Steam Cycle Parameter	Value
Energy output with TCES	125 MW _{th}
Energy output without storage	140 MW _{th}
CMO CSP-TCES round trip efficiency	89%
CSP-TES round trip efficiency ¹⁸⁰	86%

7.4 Chapter Summary and Concluding Remarks

In Chapter 7, the second area of study in this thesis was continued from the work done in Chapter 6 where FBRs for the CaO/Ca(OH)₂ TCES process were designed and optimized using the *Fluidbed* functionality in Aspen Plus and subsequently flowsheets for the overall process were designed and analyzed based on thermodynamic considerations. The work in this chapter built on this by following the planned investigation set out in Chapter 5 in using the established design and optimization guidelines in Chapter 6 to perform a similar reactor and flowsheet design and optimization study for the CMO redox TCES process.

The stoichiometric and reversible reaction expression for the chosen CMO (with a 1:1 molar ratio of Cu to Mn) was identified from the literature as the first step towards designing the redox TCES process for it. Due to the limited literature availability of kinetic data, literature sources were used in conjunction with process design considerations to identify suitable reaction temperatures and gas mixes for both the reduction and oxidation reactions ($T_{red}=925^{\circ}\text{C}$, gas mix of 10 vol% O₂ + CO₂; $T_{ox}=850^{\circ}\text{C}$, gas mix of 10 vol% O₂ + N₂ respectively). A major design constraint pertaining to the equilibrium partial pressure of O₂ ($p_{O_2,eq}$) at either reaction temperature was identified and appropriate modification considerations required for operating the process were discussed.

The optimization results for the designed FBR for the endothermic (charging) CMO reduction reaction were then presented and discussed. The observed trends regarding the impact of varying reactor dimensions and reactor bed mass on the achieved conversions, volumes of heat stored, and the extents of elutriation were analyzed so as to determine local optima for each of the controlled variables based on the previously

established design specifications and requirements. It was identified that a minimum reactor height of 22 m with a diameter of 6 m and a bed mass of ~22000 kg would fulfil the design constraints and maximize the energy uptake and reaction conversions.

Similarly the designed FBR for the exothermic (discharging) CMO oxidation reaction was then considered and its optimization results discussed. Due to the exothermic nature of the reaction and the fact that the gas phase would be depleted during reaction it was expected that significantly different results would be observed. Based on evaluating the observed trends between the same factors on the same variables as in the design case for the reducer, the determined local optima were used to identify the most suitable oxidizer reactor specification. The resultant specification for the FBR that met the stipulated design constraints required a reactor height of 15 m with a diameter of 5.3 m and a bed mass of ~18000 kg.

The specification of the external upstream and downstream connections to the TCES flowsheet were then carried out. The modelling approach for the CSP plant was identical to that carried out for the CaO/Ca(OH)₂ TCES flowsheet in Chapter 6 where pressurized steam at 100 bar was selected as the representative HTF associated with the reduction (charging) flowsheet. In this case higher CSP-outlet temperatures of 1000°C were selected so as to be representative of upcoming improvements in solar tower CSP technologies that can produce HTF streams at such temperatures.

The power generation block was designed and modelled using a supercritical CO₂ Brayton cycle. A basic recompression Brayton cycle was design and implemented with specifications based recommendations from literature studies involving expansion of sCO₂ at 250 bar. The designed power cycle resulted in a net power output of 59.3 MW and a corresponding thermal efficiency of 47% which could potentially be further increased to approach 57% with optimized and more advanced designs for the Brayton cycle. The thermal round trip efficiency of the flowsheet was estimated to be 89%, offering an improvement over the 86% achievable through molten salt TES technologies in addition to facilitating longer storage durations.

Chapter 8

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Time-Variied Parametric Study of CSP- TCES Plants

Chapter Contents

Sections	Subsections
1. The Need for TVP Modelling	
2. TVP Modelling Approach	1. CSP Data Integration 2. Flowsheet Operation – Charging Process 3. Flowsheet Operation – Discharging Process 4. Steam Management for CaO Hydration Process
3. TVP Modelling Results – CaO Hydration System	
4. TVP Modelling Results – CMO Redox System	
5. Geographical Considerations for TVP Modelling	1. Specifications for Considered Geographical Locations 2. Impact of Geography on TVP Performance of TCES Systems
6. Chapter Summary and Concluding Remarks	

8.1 The Need for TVP Modelling

It is apparent that merely considering the steady-state performance of CSP-TCES plants does not paint an accurate picture of their performance due to external factors needing to be considered. Time-varied parametric (TVP) modelling studies were thus conducted to assess the flexibility of the systems in adjusting for sub-optimal and varying conditions experienced in the course of operation. This was a first step towards a more nuanced and realistic study with the eventual goal of informing a true dynamic operation study in the future when FBR-based TCES processes are more thoroughly understood. Some background on previous modelling efforts is summarized in Appendix A.18. The merits of conducting a TVP modelling study are not just limited to the added rigor and more realistic nature of the underlying inputs, assumptions, and factors considered in evaluating the chosen processes. They also provide insights into the high-level behavior of the systems which cannot be studied through steady-state simulation alone.

Depending on which sections of the process are focused on, the standalone operating potential or synergistic connectivity of the CSP-TCES plants with other power sources on the grid or other storage facilities on the energy storage network can be investigated. For instance, by focusing on the CSP side of the plant, TVP modelling studies can be used to simulate and optimize ray-tracing trajectories and reflectance angles for individual reflectors in a heliostat field to maximize the performance of the solar tower design based on a variety of weather conditions, the angles of incident sunlight, etc. These insights would serve to identify the most flexible design configurations that offer the highest performance across a range of operating conditions and scenarios as opposed to a steady-state static study where a single conditional optimal configuration is designed based on a fixed scenario specification.

Likewise, when focusing on the TCES and power generation aspects of the plant, very different considerations can be accounted for. These include modelling and optimizing the variations in storage material flowrates needed for matching the inputs from a realistic (and thus varying) solar heat input from a CSP plant, evaluating the energy discharge performance resulting from varying levels of available stored energy as well as stipulated discharging schedules, and identifying the performance constraints for either process during periods of potentially unfavorable operating conditions. Doing so would allow for identification of suitable operating situations, geographies, and seasons for both the storage and discharge processes and facilitate an improved understanding of the extents to which integrated TCES would address intermittency issues of traditional CSP installations while supplying power to the grid when demanded. Based on the work done in Chapters 6 and 7, the focus of the TVP simulation studies conducted here was primarily on the TCES part of the CSP-TCES plant with a minor focus also cast on the power generation system.

8.2 TVP Modelling Approach

To account for the considerations highlighted and the factors of interest identified in Section 8.1, TVP simulations of the two CSP-TCES processes focusing on the TCES system and power generation blocks were performed. In this section the modifications that were made to the inputs of both the CaO hydration and the CMO redox systems are discussed. For specifying the CSP inputs, the hourly averaged solar irradiance data for January, April, July, and October for Seville, which was chosen as an initial case study location, was used as a means of achieving the effect of time-varying solar availability on the performance of the systems at two scales: hourly as well as seasonally.

The CSP inputs were directly used for TVP modelling of the charging process based on the resultant variations in incoming heat flow. The means to specify these variations using the available process variables were discussed and their practicality was evaluated. The impact of varying heat flows on the corresponding required solids inventories for the charging FBRs of either process was then evaluated for further investigation. The volumes of stored heat from this study were then used to inform the modeling of the possible hourly duties for the discharge process based on a 2-hour estimated dead-time for start-up and shut-down procedures for each process. While for the charging process, it is feasible to operate it batch-wise by only running it during the day, this is not as suitable for the discharge process as the regular temperature fluctuations involved could damage the turbines involved in the power cycle. Moreover it may be more economically attractive to have a continuous output to the grid similar to a baseload power plant.

However, it was noted that there could be circumstances in which a temporary batch-wise operation is better suited for the overall power production mix. Additionally, depending on weather conditions, a particular CSP-TCES site might not have enough stored energy to operate continuously, thus necessitating batch-wise operation. Hence, three scenarios were assessed for the operation schedule of the discharging flowsheet in particular – (S1) ‘batch’ operation every night, (S2) continuous operation at 50% of steady-state optimal thermal output, and (S3) continuous operation at 75% of steady-state optimal thermal output.

8.2.1 CSP Data Integration

For upstream solar energy collection, a basic CSP receiver setup was considered. A solar tower design was selected for this due to its suitability for the operating temperatures of both energy storage systems¹⁹³ and based on extended discussions presented in Chapter 2. For the steady-state simulations, the CSP plant was not modelled in detail for simplicity and instead treated as a constant thermal energy source via pressurized steam as a HTF being supplied to the TCES processes. However for TVP simulation, solar intermittency had to be translated into a process variable that fed into the TCES plant. The thermal energy content of the

HTF loops between the CSP and TCES plants was used for this. In a solar tower design (Fig. 8-1)¹⁹⁴, the sunlight incident on an array of planar mirrors in a heliostat field is reflected to focus on a central tower receiver unit through which the HTF flows and absorbs the energy in the form of heat. The resultant heat flow, $\dot{Q}_{CSP}$, was calculated by Eq. 8-1 to provide the heat flow by way of the chosen HTFs.

$$\dot{Q}_{CSP} = R_{BI} \cdot A_{HS} \cdot \eta_{HS+R} \quad (8-1)$$

Here R_{BI} denotes the average beam irradiance at a given location and time, A_{HS} is the cumulative surface area of the heliostat field, and η_{HS+R} is the estimated combined efficiency of the heliostat field and receiver unit which was assumed to have a value of 0.49 based on literature data¹⁹³. To realistically evaluate $\dot{Q}_{CSP}$ at various times of the day, solar irradiance data was required for which a geographical location had to be chosen. The CSP+TCES installation was in the first instance situated in Seville, Spain, as it is a location for which detailed solar irradiance data is available and where extensive CSP deployments already exist. Furthermore, designs for other combined energy storage and discharge plants have also been studied¹⁰⁷ using Seville as a case study location and thus doing this here would allow for future comparisons.

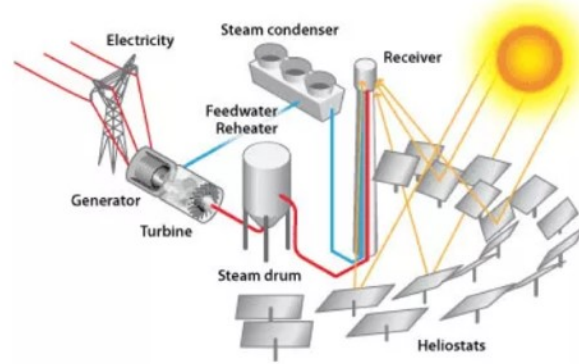


Fig. 8-1: Illustration of a solar tower design for CSP

The R_{BI} values for Seville were taken from the System Advisor Model (SAM)¹⁹⁴ – a calculation tool and database developed by the National Renewable Energy Laboratory (NREL) at the U.S. Department of Energy. Fig. 8-2 shows the historical averaged beam irradiance measurements at Seville throughout the day and at various times of the year, allowing for consideration of seasonal fluctuations. For the earlier steady-state studies, midday data for July was used to approximate steady-state operation of the charging processes.

The minimum value for A_{HS} was obtainable by rearranging Eq. 8-1 as the maximum charging capacity in the designed flowsheets had already been established to be 130 MW_{th}. Based on this the heliostat field size required was calculated to be 552,800 m² to achieve the specified peak charging capacity even during seasons of low availability – hence the peak R_{BI} data for April was used here according to Fig. 8-2.

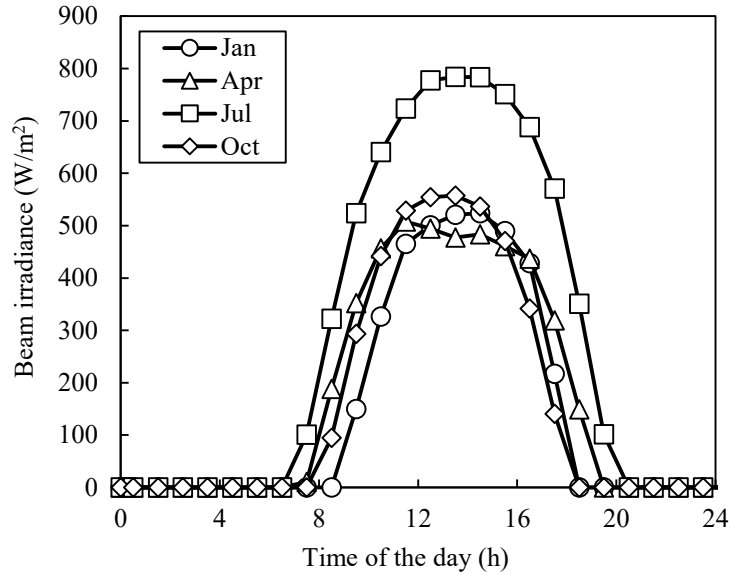


Fig. 8-2: Historical hourly solar irradiance data for Seville, Spain obtained from the SAM tool¹⁹⁴

For a sense of scale, specifications for an existing CSP facility in Seville were considered: the *Planta Solar 10* facility¹⁹⁵ has a heliostat field of 74,880 m² and has a power output capacity of 11 MW_e. When compared to the peak power outputs obtained in Chapters 6 and 7 of ~45-50 MW_e, it is noted that the designed CSP-TCES plants here require a heliostat field that is 7.4 times as big as the existing plant while offering a 4 times higher maximum power output. While this result is to be expected due to the addition of the TCES process resulting in additional thermal energy penalties in terms of solar energy to power conversion compared to the reference plant, the tradeoff is likely to be compensated for by the far greater power generation availability of the CSP-TCES plant. It is also possible to consider reducing the heliostat field size based on cost considerations such that the peak charging rates are only achieved during more favorable seasons. These economic considerations are considered further in Chapter 9.

8.2.2 Flowsheet Operation – Charging Process

To account for fluctuating solar irradiation levels, there were two options considered for translating the variations in heat flow into a process variable for manipulation: by keeping the mass flow of HTF constant and varying its temperature, or by keeping it at constant temperature and varying its mass flow. Typically for a CSP plant the flowrate of the HTF is kept constant as it directly feeds into a power generation block where a reboiler can compensate for temperature differences; however this is not a feasible scenario for TCES. The potential impact of either option on the behavior of the respective charging processes was considered and its feasibility from an operational perspective was also given attention. With a varying temperature but constant mass flow, the overall heat transfer coefficient across the heat exchangers in the FBR would be subject to regular changes due to changing log-mean temperature differences.

Given the high process temperatures required, it is recognized that during periods of low solar availability the HTF temperature may not be high enough to drive the charging reactions or even heat the beds to the required temperatures. This would be more likely for the CMO redox system than the CaO hydration system as the redox charging step operates at significantly higher temperatures. The impact of this would also be observed when sufficiently large temperature differences may be obtained, as the reacted material stored during very early parts of the operating schedule may have had significantly different conversions; hence the composition of the feed into the storage tanks would be varying regularly which in turn would make operation of the complementary discharging process much more difficult. However from a process control perspective, the constant flow rates required in this scenario would allow for easier operability of the CSP plant and little process manipulation would be required in that regard.

The alternative approach of keeping temperature constant but varying flow rate would preserve the overall heat transfer coefficient within the FBR heat exchanger. This would keep the thermal driving force for the reaction constant if the bed mass were varied appropriately - which is needed to preserve the post-reaction composition. Varying the bed mass would allow for even the lower HTF stream enthalpies around sunrise and sunset times to bring the bed up to temperature and operate the reaction. This would not be achievable in the first scenario where HTF temperature is allowed to vary. Implementing this would however require more complex process control to regularly adjust the HTF flowrate through the CSP receiver such that the outlet temperature will remain constant. Periods of low solar intensity may however result in flowrates required being too low from a process operation perspective to warrant plant operation. Hence it would be important to assess the extent to which low flowrates would impact the operability of the charging processes.

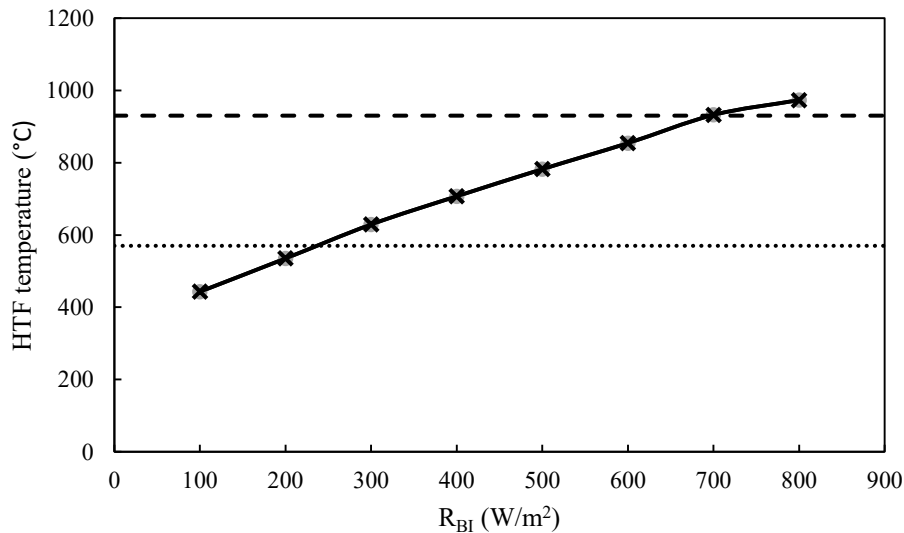


Fig. 8-3: Calculated HTF temperature (steam at 100 bar) with constant flowrate, for varying solar irradiation levels with minimum temperature for CaO dehydration (···) and for CMO reduction (---)

From Fig. 8-3 it is seen that with the first option of varying the temperature of the HTF, the resulting temperatures for $R_{BI} < 250 \text{ W/m}^2$ are too low for the CaO dehydration reaction and those for $R_{BI} < 700 \text{ W/m}^2$ are not high enough for the CMO reduction reaction. Based on the seasonal data in Fig. 8-2 this would mean that this approach would provide an insufficient temperature driving force for 30% of the time for a CaO process and 70% of the time for a CMO process. These would result in significantly shortened operating hours and failure to harness significant quantities of solar energy.

From Fig. 8-4 it is observed that the HTF flowrates required at low levels of solar irradiation vary greatly and drop to 8 kg/s at the lowest considered intensity. For a large scale process as the pipe diameters would be kept constant, the resulting steam velocities through the process may end up being slow enough to incur additional radiative heat losses in travelling between the receiver and the charging FBRs. It may thus not be sensible to operate the TCES process with such low flowrates; a cut-off of $R_{BI} < 200 \text{ W/m}^2$ was thus considered for implementing this scenario. Based on the data for Seville this would exclude 20% of potential operational hours for either TCES system which is a reasonable fraction.

It was thus decided that the HTF temperature would be kept constant and its flow rate be adjusted instead to accommodate variations in $\dot{Q}_{CSP}$. In conjunction, to account for the fluctuating (and most frequently lower than peak level) thermal heating power available, the bed masses within the charging FBRs were also varied to allow greater control over achieved conversions. This would maintain the compositions of the product streams that would be recycled in the discharging process. It was noted that due to the fast kinetics and short residence times of the reactions the conversions would be negligibly affected by doing this.

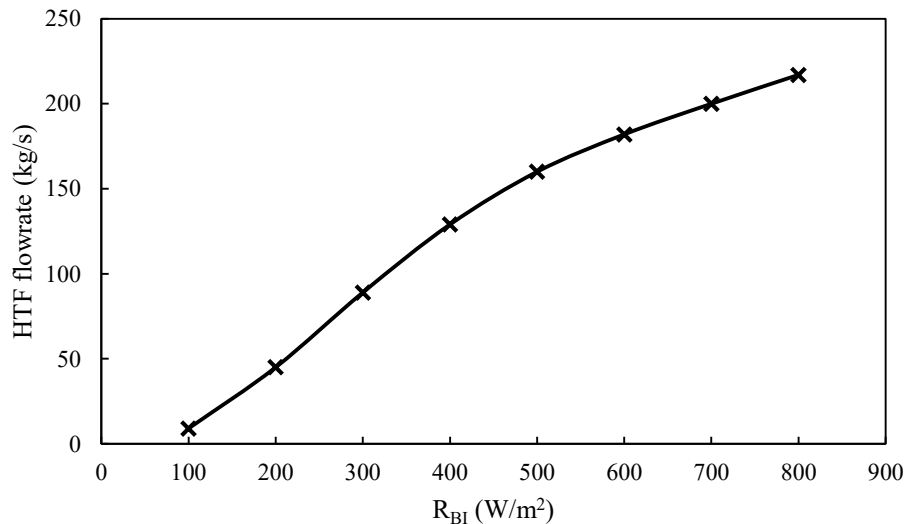


Fig. 8-4: Calculated HTF flowrates (steam at 100 bar) at 975°C for varying solar radiation levels

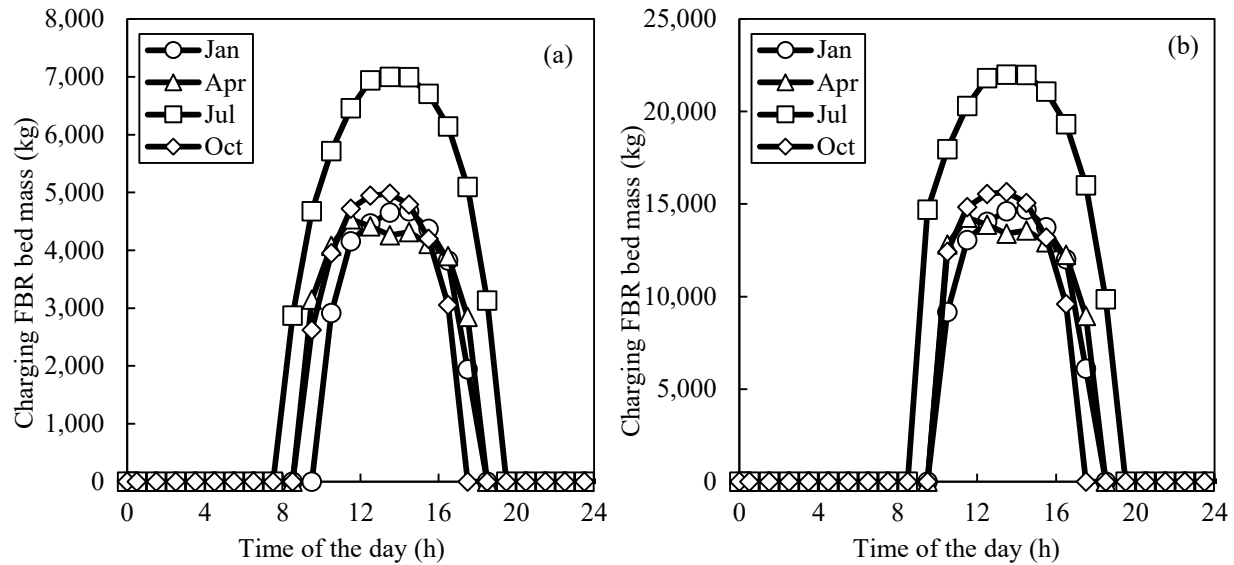


Fig. 8-5: Hourly bed masses required for the charging steps of the designed CSP-TCES plants based on solar irradiation levels for (a) CaO hydration system and (b) CMO redox system

A further consideration made was that for the sunrise and sunset periods, the solar irradiance levels are so low that operating the process with correspondingly small bed masses would not result in any significant volumes of stored energy but mainly only the heating of the bed masses to approach the desired reaction temperatures. Hence for the purposes of practicality, the TVP simulation of the charging process was conducted only for time intervals where $R_{BI} \geq 200 \text{ W/m}^2$ as decided based on the HTF flowrate discussion, which is observed to be achieved typically within 2 h after sunrise and prior to sundown.

The required hourly bed masses (based on the hourly data available as seen in Fig. 8-2) for the charging process in each CSP system are shown in Fig. 8-5. The direct relationship between the solar irradiation intensity and the corresponding required bed masses is identical for both processes. The bed masses corresponded to charging loads of 35-130 MW_{th} for CaO hydration and 39-130 MW_{th} for CMO redox. It is noted however that for each process there is a minimum bed mass specification that is required during winter in January ($\sim 1900 \text{ kg}$ for the CaO hydration system and $\sim 6100 \text{ kg}$ for the CMO redox system). This is important for operation planning as having a bed mass threshold reduces potential operating inefficiencies.

8.2.3 Flowsheet Operation – Discharging Process

For the discharging processes, three operating scenarios were to be examined as mentioned in Section 8.2; one involving batch-wise operation and two requiring continuous operation. The interpretation of night-time for scenario S1 is simply the hours of the day where there is no measured solar irradiation hence this period varies in length across the seasons based on the available data. For the continuous operation scenarios S2 and S3, significant changes to the operation of the discharging flowsheets were not required as they

essentially involved running the processes at steady-state. However to achieve the desired reduction in thermal output from the discharging FBR, a choice needed to be for which process variable to manipulate to fulfil this: the material residence time in the FBR, or the feed flowrate into the FBR.

Table 8-1: Steady-state flowrates and bed masses for discharging processes for each initial TVP operating scenario simulated

	CaO hydration system			CMO redox system		
Scenario	S1	S2	S3	S1	S2	S3
Gas feed flowrate (kg/s)	21	11	16	60	30	45
Solids feed flowrate (kg/s)	110	55	83	670	335	503
Bed mass (kg)	6500	3250	4875	18200	9100	13650

If the residence time were manipulated by varying the reacting bed masses and keeping other variables unchanged, it would have to be reduced such that the reactions do not achieve steady-state conversions. This would cause fewer moles of material to react per unit time despite the constant feed flowrates. A result of this would be that the FBR exit streams would have changed compositions. This would have complex consequences for the complementary charging processes due to their feed stream compositions also being changed due to this, and thus also for the combined TCES process as a whole.

On the other hand if the solids and gas feed flowrates were to be manipulated, to keep other factors constant the bed masses would also have to be varied to avoid changing the residence times and thus the reaction conversion extents. Doing so would cause fewer moles of material to react per unit time but would preserve the compositions of the exit solid streams and thus avoid any impacts on the charging process. Hence based on operational considerations it was decided that the feed flowrates and bed masses for the discharging FBRs would be appropriately varied to achieve the desired thermal outputs to the power generation systems for fulfilling the operating scenarios being considered; the calculated values are shown in Table 8-1.

Accordingly, in order to allow the results of each operating scenario to manifest, the circulating HTF within the power generation cycles also had its flowrates varied to keep the process temperatures involved constant while facilitating the corresponding changes in electrical power generated from the flowsheet. An additional consideration made here for the continuous processes was the fact that periodically, fresh feed material would have to be injected into circulation and deactivated material removed, potentially resulting in minor fluctuations in thermal output from the FBRs to the power cycles due to slight variations in reaction conversions achieved due to the greater availability of the fresh material.

It was thought to be potentially challenging from a process control perspective to counteract this and so in this initial study, $\pm 2.5\%$ fluctuations in electrical power output were incorporated into the results for the continuous operation scenarios S2 and S3 to account for this consideration. This was also done for scenario S1 as the regular and extended downtimes resulting from this scenario would require regular startup and shutdown periods where the system would be running at unsteady-state and so fluctuations in reaction temperatures and conversions would occur both in the reaction flowsheets and the power generation cycles.

8.2.4 Steam Management for CaO Hydration System

For the CaO hydration TCES plant, the question of closing the steam loop across the charging and discharging processes requires some further discussion for operating scenarios where only one of the processes is running. It is acknowledged that for standalone operation, a secure supply of high-temperature steam ($\sim 470^\circ\text{C}$) is needed during the night when only the discharging process is running.

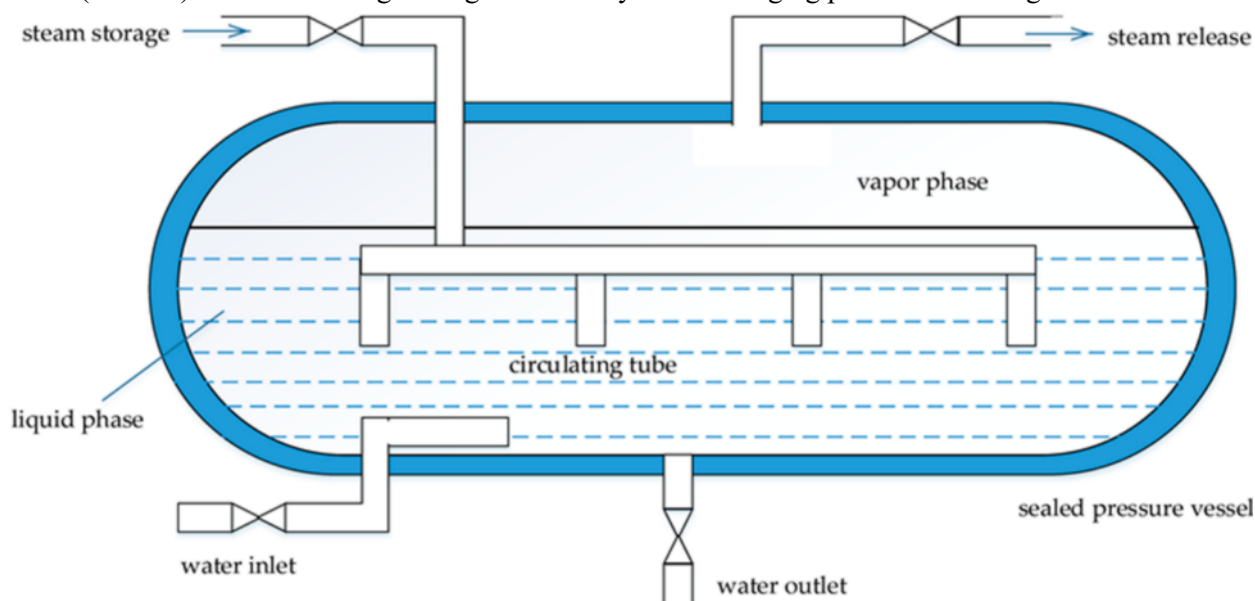


Fig. 8-6: Schematic of pressure-drop steam accumulator vessel for steam storage¹⁹⁶

One option is to use steam accumulators (Fig. 8-6) to store excess steam from the charging process until it is needed for the discharging process. Steam accumulators are able to ‘store’ steam by injecting surplus steam into pressurized water, bringing it up to saturation temperature; the steam can be recovered on demand by dropping the pressure of the system to controllably flash steam from the pressurized water. The use of steam accumulators has been demonstrated at CSP facilities¹⁹⁵ and is an ongoing area of development^{196, 197} with advanced designs incorporating concrete capable of 24 hours of steam storage^{198, 199}. The calculated parasitic load of the steam accumulator system, presented in Table 8-2, is $\sim 4.7\%$ reducing the peak RTE to $\sim 87\%$ assuming a storage efficiency of 99%. This should be revisited when first-hand storage efficiency data is available for the advanced steam storage designs.

Table 8-2: Power generation from CaO hydration CSP-TCES plant for each TVP simulation scenario

Discharge output (MW)	Discharge time (h)	Total energy discharged (MWh)	Steam flowrate (kg/h)	Energy needed for steam (MWh)	Steam storage efficiency ¹⁹⁶	Parasitic load (%)
128	8	1024	107	46	0.99	6.5

Another option is using a more complex flowsheet involving both TCES and molten salt TES attached to a single CSP plant (Fig. 8-7). This is as molten salt TES stores sensible heat and so can be readily accessed. In this case the TES system would serve as a thermal buffer to facilitate high-temperature steam generation on-site from the condensed water stored from the charging process. It is known that molten salt TES can do so in current CSP plants to drive steam cycles ($\sim 560^{\circ}\text{C}$) and so is a well-understood practice. Fundamentally this would mean that the CSP plant would be relying on molten salt TES for inter-day buffering and operation, with the TCES capability facilitating inter-seasonal and baseload operation. This approach entails significant thermal inefficiencies and would result in much lower RTEs of $\sim 70\%$ as noted in Chapter 6.

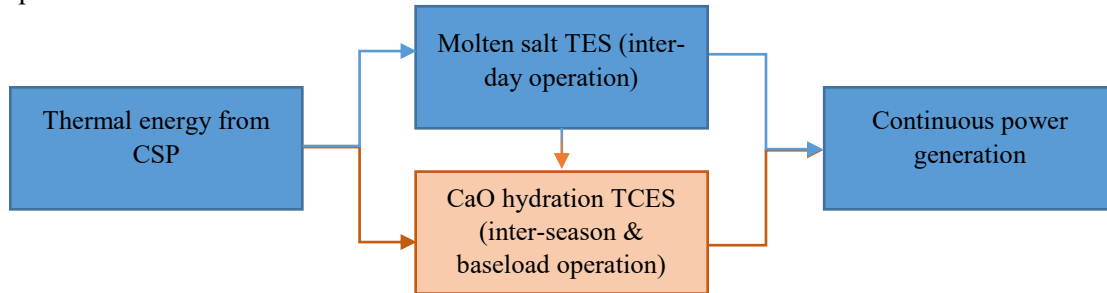


Fig. 8-7: Possible operating scheme for CSP-TES-(CaO hydration TCES) plant for baseload power

It is possible that detailed designs for CSP-TCES plants based on the CaO hydration system will need to consider either of these technologies in conjunction with either on-site steam generation or direct purchase of high temperature steam from the nearest available location. As the manifestation of high-temperature CSP technologies that are under testing become clearer, the suitability of these approaches can be better explored through future study. It is outside the scope of this initial work to explore more detailed techno-economics for flowsheet design variations that may be required with technology design advancements. However it is acknowledged that this consideration adds some complexity to the plant design and may result in less viable business cases in certain locations. For Chapter 9 the costs of buying 100% of the required steam volumes are considered as it would be the most expensive option to implement.

8.3 TVP Modelling Results – CaO Hydration System

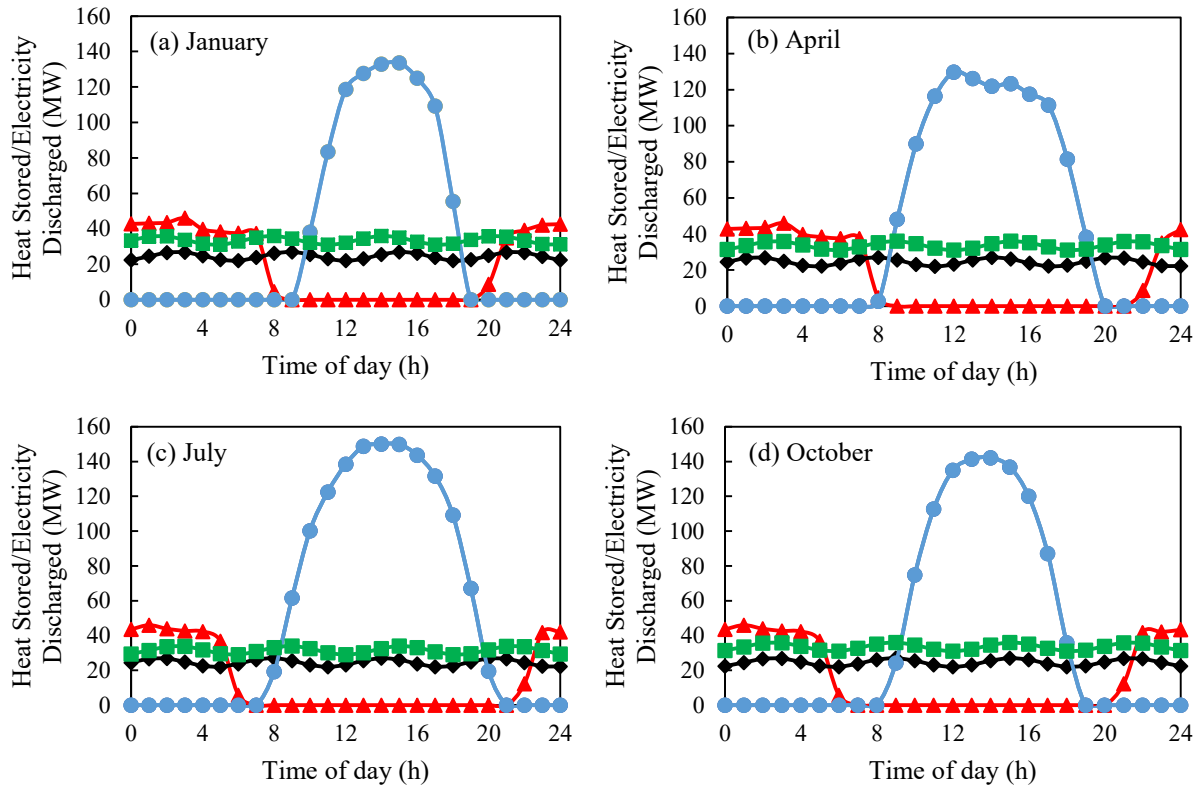


Fig. 8-8: Charging ($\circ$) and discharging loads of the CaO hydration CSP-TCES plant, operating in a TVP simulation according to scenarios S1 ($\triangle$), S2 ($\diamond$), and S3 ($\square$) throughout the year in (a) January, (b) April, (c) July, and (d) October based on a case study for Seville, Spain

From Fig. 8-8, it is observed that the time of year has a significant impact on the effectiveness of the charging process with 33% more energy stored in July than in January, while April and October offer middling performances. However, the steady-state charging capacity is only reached in brief periods throughout, showing that consideration of the TVP performance of the plant is important, as both the charging and discharging FBRs are operating at sub-optimal conditions for most of the time. Having a quantitative understanding of these trends also allows for planning the operation of the discharge cycle.

In Table 8-3, it is seen how the batch-wise discharge operation in scenario S1 results in a much lower average output compared to the alternatives despite their limited maximum capacity. However, while it may be more efficient to operate scenarios S2 and S3, this may not align with the local electricity demand. It is expected that in practice, plants of a similar design will use a mix of scenarios S1-S3 throughout its lifetime depending on local grid demands and the operational strategy chosen for this specific plant by the operator; such study is outside the scope of this work.

Table 8-3: Power generation from CaO hydration CSP-TCES plant for each TVP simulation scenario

Scenario	S1	S2	S3	S0
Maximum power output (MW _e)	48.9	25.7	32.3	20.5
Average power output in 24h (MW _e)	10.2	24.2	31.5	20.2

Table 8-4: Seasonal stored thermal energy quantities and required thermal energy discharge volumes required to achieve each operating scenario using the CaO hydration CSP-TCES plant in Seville, Spain; *italics indicative of monthly scenario being achievable purely through stored quantities. Annual values calculated on a 330-day basis*

Month	Jan	Apr	July	Oct	Annual
Thermal energy stored (GWh _{th})	27.9	33.0	40.9	30.3	363.3
S1 Thermal energy discharge required (GWh _{th})	37.5	<i>31.4</i>	<i>26.8</i>	<i>30.0</i>	<i>345.7</i>
S2 Thermal energy discharge required (GWh _{th})	39.9	39.9	39.9	39.9	438.9
S3 Thermal energy discharge required (GWh _{th})	62.8	62.8	62.8	62.8	690.8
S0 Thermal energy discharge required (GWh _{th})	33.0	<i>33.0</i>	<i>33.0</i>	33.0	<i>363.0</i>

In Table 8-4, the calculated monthly and annual energy storage and discharge quantities for each TVP operating scenario are presented. On a monthly basis batch-wise operation via scenario S1 can be fully met through stored energy volumes for 3 out of 4 seasons; in scenarios S2 and S3 this is only achieved once, in July for S2. This consideration is important where the primary objective of the designed plant is to be a net store of energy. These results are due to the 39% Rankine efficiency of the steam cycle (c.f. Chapter 6) resulting in larger volumes of thermal energy needed to produce the requisite amounts of electricity. If this were representative of a current CSP facility it would be cause for concern due to only short-term energy storage being available and thus scenarios S2 and S3 would be unviable by themselves. However as TCES systems have much greater storage times, on the scale of months, the annual basis is fair to consider. In this case only scenario S1 can be achieved on an annual basis if the plant is operated standalone.

This would mean that a mix of scenarios S1-S3 would need to be employed over a year if the designed plant is to operate on a standalone basis while providing baseline power to the grid during discharging hours. This is feasible from a technical perspective however the economics also need to be evaluated to grasp the financial viability of the potential operating scenarios; this is addressed later in Chapter 9.

What this also suggests is that the S2 and S3 discharging scenarios were overestimations of the capabilities of the designed plant when considering standalone performance. However, it is still of interest to investigate

the potential of the discharging process to operate on a continuous basis to resolve intermittency issues of traditional solar power – which is one of the main objectives of incorporating energy storage. It is observed that as both S2 and S3 require far more energy than is available within the plant, and as they operate with sub-maximal thermal outputs from the discharging reaction (50% and 75% respectively), then it is clear that a continuous operating scenario making full use of the stored energy can be achieved.

To this end, scenario S0 was added to the calculations in Table 8-4 such that annual thermal discharge requirements could be fully satisfied by the energy stored by the charging process. In this scenario, on a monthly basis the energy storage process can fulfil the required discharge volumes for half of the year while on an annual basis it can fully satisfy them. This scenario was calculated to require a continuous discharging process operating at 41.3% of optimal thermal output resulting in a constant production of 20.2 MW_e, thereby operating at a solar-to-electricity conversion efficiency of 16.8% on a standalone basis. Hence it is seen that, even with long-term cycling of the reactants and the associated deterioration in performance, a continuous discharging scenario can be achieved for a standalone CSP-TCES plant using the CaO hydration/dehydration TCES system that have comparable energy conversion efficiencies to current standalone CSP plants (13-22%)⁴⁵ that have minimal storage provisions.

The implications of these results are significantly positive from a technical efficiency and operability perspective. It means that the integration of a CaO hydration TCES system allows for maintaining the overall solar-to-electricity conversion efficiency of the base case CSP plant while radically changing its discharging schedule capabilities such that this conversion efficiency can be maintained alongside a continuous discharging operation for a baseline supply to the grid. Furthermore as this operating scenario only requires 41.3% of the maximum designed capacity, the plant retains the ability to significantly boost its power production levels over shorter time frames if needed to meet demand surges. This potential to operate in a ‘peaker plant’ mode (a role traditionally played by fossil fuel power plants) is suitable for future study and is not within the scope of the current work.

8.4 TVP Modelling Results – CMO Redox System

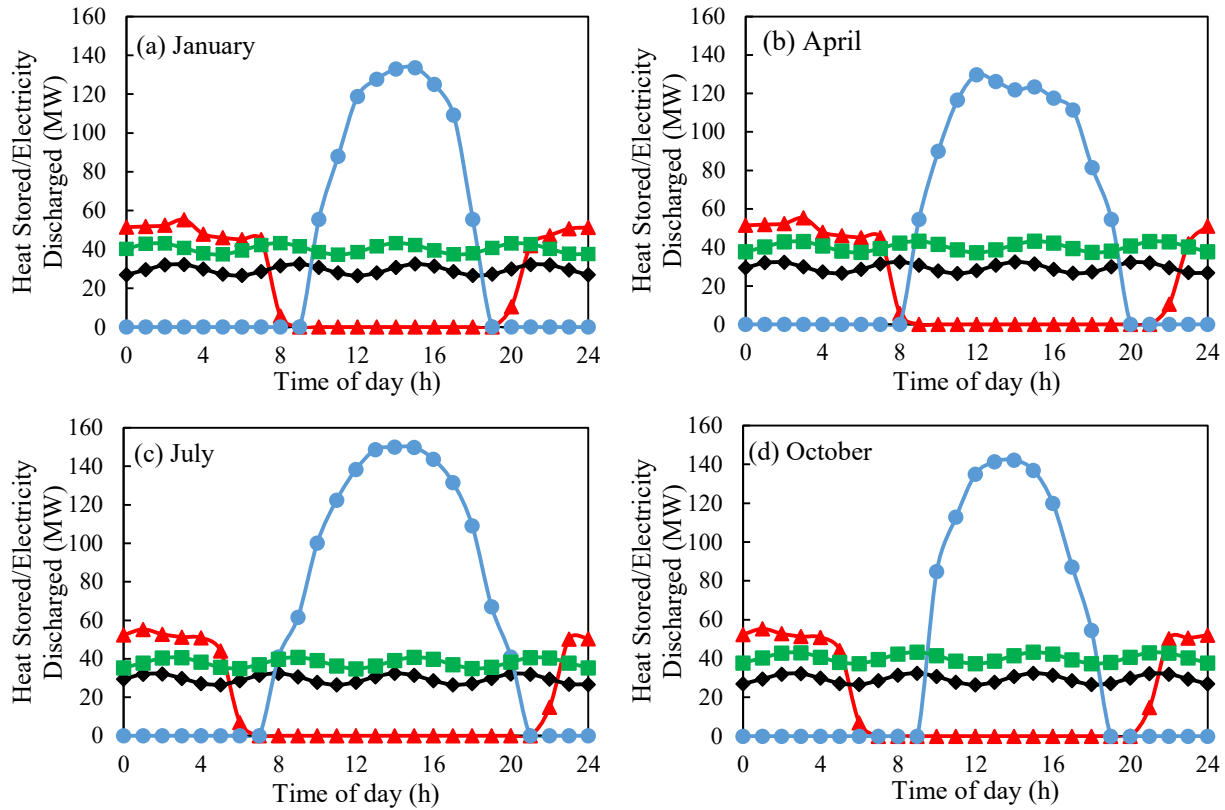


Fig. 8-9: Charging (○) and discharging loads of the CaO hydration CSP-TCES plant, operating in a TVP simulation according to scenarios S1 (△), S2 (◇), and S3 (□) throughout the year in (a) January, (b) April, (c) July, and (d) October based on a case study for Seville, Spain

Table 8-5: Power generation from CMO redox CSP-TCES plant for each TVP simulation scenario

Scenario	S1	S2	S3	S0
Maximum power output (MW _e)	58.8	30.9	38.8	25.7
Average power output in 24h (MW _e)	12.3	29.0	36.7	25.4

A similar analysis was conducted for the TVP modelling results of the CMO redox system. In Fig. 8-9 the outcomes of the TVP operation scenarios are presented and the overall trends are observed to be qualitatively similar to those observed for the CaO hydration system. The results for the charging process are very similar overall; this was expected as both charging reactions were designed to operate to the same specifications. The main difference was the temperature of the HTF supplying the heat to the reactors and this was not observed to impact the effectiveness of the charging process at any bed loading quantity. For the discharging process across the four TVP operating schedules it was observed from Table 8-5 that the maximum and average power outputs in all cases are higher than for the CaO hydration system.

This is expected as based on the modelling of the power generation cycles conducted in Chapters 6 and 7, the thermal efficiency of the sCO₂ Brayton cycle employed for the CMO redox system is higher than that of the steam Rankine cycle used for the CaO hydration system (48% vs 39%); here this improved efficiency is now seen as translated into comparable results. As before, it is expected that in reality a combination of operating scenarios may be employed by the plant operators over time depending on external circumstances.

In Table 8-6 the monthly and annual energy storage and discharge quantities for the CMO system under each TVP operation scenario are presented. The overall trends again are similar to those observed in Section 8.4 for the CaO hydration system in that on an annual basis, only scenario S1 among the three originally proposed scenarios, which is a batch-wise discharging operation scenario, can be met via standalone operation of the plant at the chosen location of Seville. It is observed that the thermal energy discharge volumes required to meet scenarios S1 are slightly lower for the CMO system; this is again attributed to the higher thermal efficiency of the Brayton cycle used.

Table 8-6: Seasonal stored thermal energy quantities and required thermal energy discharge volumes required to achieve each operating scenario using the CMO redox CSP-TCES plant in Seville, Spain; italics indicative of monthly scenario being achievable purely through stored quantities. Annual values calculated on a 330-day basis.

Month	Jan	Apr	July	Oct	Annual
Thermal energy stored (GWh _{th})	28.4	33.8	42.1	30.4	370.5
S1 Thermal energy discharge required (GWh _{th})	36.1	<i>30.2</i>	<i>25.8</i>	<i>28.9</i>	<i>332.8</i>
S2 Thermal energy discharge required (GWh _{th})	39.9	39.9	<i>39.9</i>	39.9	438.9
S3 Thermal energy discharge required (GWh _{th})	62.8	62.8	62.8	62.8	690.8
S0 Thermal energy discharge required (GWh _{th})	33.7	<i>33.7</i>	<i>33.7</i>	<i>33.7</i>	<i>370.5</i>

In the case of the CMO system scenario S0 was found to require the discharging process to operate at 43.1% of the optimal thermal output. It was noted that although fundamentally both process should require the same fraction of maximum thermal output to fulfil scenario S0, the slightly higher value required here was a result of slightly more energy stored by the plant in the charging process, likely due to accumulation of slightly better charging efficiencies built up across multiple charging periods.

This produced a continuous output of 25.4 MW_e using the Brayton cycle, which gave the process a solar-to-electricity conversion efficiency of 21.1%.which was at the upper limit of reported efficiencies of existing CSP plants without TCES. Hence, just as for the CaO hydration system, the designed CMO redox TCES system was found to be suitable for implementation at the case study location both without compromising the energy conversion efficiency of the base case CSP plant (or even potentially improving it) and with the added bonus of being now able to produce a continuous and stable power output from the

combined CSP-TCES facility at only 43.1% of the maximum discharging capacity while as a result retaining spare capacity to temporarily operate at much higher discharging rates should the need arise.

8.5 Geographical Considerations for TVP Modelling

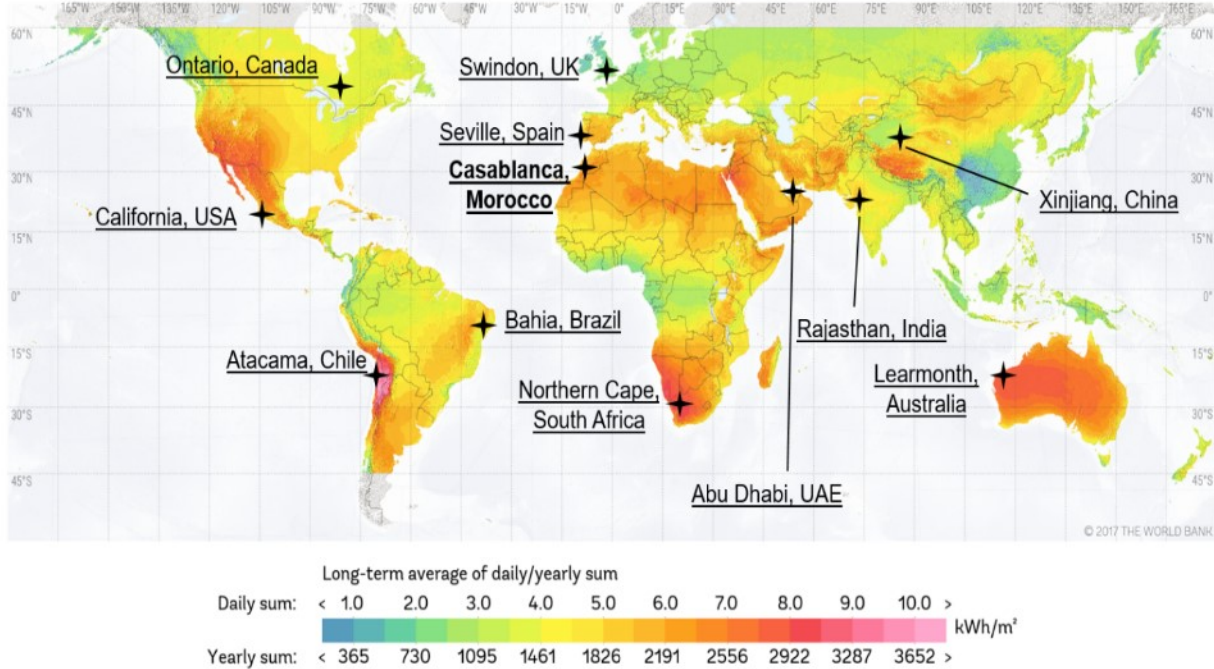


Fig. 8-10: Global normal solar irradiance map with case-study locations labelled²⁰⁰

11 further locations were selected for studying the techno-economic sensitivity of the plant to geographical location. These locations were chosen based on availability of reliable solar irradiance data, the extent of current deployment of CSP technology in the region, and the average annual and seasonal levels of solar irradiance experienced. Fig. 8-10 shows all 12 locations along with their average solar irradiance levels. Data for these locations were obtained from the SAM tool and pertinent location data is numerically presented in Table 8-7 for ease of comparison. It follows that having such variations in solar irradiance levels would mean that the hourly input energy into the CSP part of the plant from the heliostat fields for storage would vary differently compared to trends in the case study. However, the design specification for the TCES part of the plant for each location was not significantly changed as the target TCES process capacity is fixed at 130 MW_{th} and the processes were designed for handling the maximum load.

This means that the capital and operating costs pertaining to a TCES part of the plant for each location would not vary significantly, unlike the costs for the CSP part of the plant. Hence, the initially designed TCES plant specifications for Seville were used in conjunction with solar irradiance data from each location to scale the CSP part of the plant by varying the required heliostat field sizes. This was used to TVPally model the charging and (S0 and S1) discharging schedules for the 11 other locations.

8.5.1 Specifications for Considered Geographical Locations

Fig. 8-10 indicates that Bahia, Rajasthan, and California experience similar levels of annual irradiance but Bahia experiences more stable daylight hours as it is much closer to the equator. This translated into larger energy volumes for the Bahia plant as it more efficiently utilized the same level of solar resources compared to the other sites. This was also apparent when comparing Northern Cape to Abu Dhabi, with both having similar average irradiation levels but Northern Cape experiencing much larger fluctuations in daylight hours (Table 8-7) – up to 4 hours more daylight during December compared to June – resulting in almost 20% lower energy volumes compared to Abu Dhabi. The most effective locations were Atacama and Learmonth; they have the highest annual irradiance and experience smaller fluctuations in daylight hours.

Table 8-7: Weather data, location data, and level of existing CSP infrastructure for each studied location

Location	Min. day length (h)	Max. day length (h)	Avg. DNI (kWh/m ²)	CSP deployment	Latitude	Longitude
Seville, Spain	10	15	2120	high	37.389	-5.994
Casablanca, Morocco	11	15	2289	high	33.573	-7.589
Swindon, UK	8	18	474	very low	51.556	-1.780
Ontario, Canada	10	17	893	very low	51.254	-85.323
California, USA	10	15	2830	medium	34.052	-118.243
Atacama, Chile	10	15	3448	high	-22.369	-69.133
Bahia, Brazil	11	14	2471	medium	-12.579	-41.700
Northern Cape, S.A.	10	14	2849	low-medium	-29.047	21.857
Abu Dhabi, UAE	11	14	2370	high	24.454	54.378
Rajasthan, India	11	15	1735	medium-high	27.024	74.218
Xinjiang, China	9	15	1682	low-medium	42.525	87.539
Learmonth, Australia	11	13	2933	medium-high	-22.262	114.096

Following the approach used in Section 8.2.1, the minimum direct normal irradiation (DNI) levels for the 11 additional locations were calculated, allowing for estimation of heliostat field sizes. The calculated sizes are reported in Table 8-8 and it was observed that most locations required a field size in the 400,000-700,000 m² range although notably for Swindon, UK and Ontario, Canada, far larger field sizes were estimated. Such large field installations are unlikely to be cost-effective at these two locations and is something that is suitable for future investigation. Other options could also be explored for such locations – for instance the import of stored solar energy from other locations to operate the discharging process. In the subsequent sections, only discharging scenarios S0 and S1 were considered to evaluate standalone plant designs. Hence for scenario S1, the operating hours for the discharge processes at each location were based on the average night lengths inferred from data in Table 8-6 while for scenario S0 the operating scale of the discharging processes were informed based on the total stored heat volumes calculated for each location.

Table 8-8: Calculated minimum heliostat field sizes for all 12 CSP-TCES plant locations considered

Plant location	Minimum DNI (kWh/m²)	Heliostat field size (m²)
Seville, Spain	1692	552,721
Casablanca, Morocco	1736	511,913
Swindon, UK	371	2,472,086
Ontario, Canada	706	1,312,171
California, USA	2213	414,053
Atacama, Chile	2532	339,840
Bahia, Brazil	1893	474,208
Northern Cape, South Africa	2228	411,291
Abu Dhabi, UAE	1759	494,417
Rajasthan, India	1246	675,371
Xinjiang, China	1302	696,652
Learmonth, Australia	2317	399,512

8.5.2 Impact of Geography on TVP Performance of TCES Systems

The annual energy production and storage volumes reflected in Figs. 8-11 – 8-14 for these 12 locations show a direct correlation with annual solar irradiation levels, with the CMO redox system offering ~22% larger electricity production volumes due to more efficient power generation. Swindon and Ontario expectedly yielded the lowest annual storage volumes due to their low average annual irradiance levels and varying daylight hours. Due to this, the electricity production volumes were also limited by the need for standalone operation, although it would be possible to boost these volumes by importing stored energy materials from other locations for discharging purposes which would have further economic implications. Scenario S1 resulted in 9-11% higher annual electricity production compared to S0 however as S0 involves continuous discharging, the economics should be considered to better assess any trade-offs between the two scenarios.

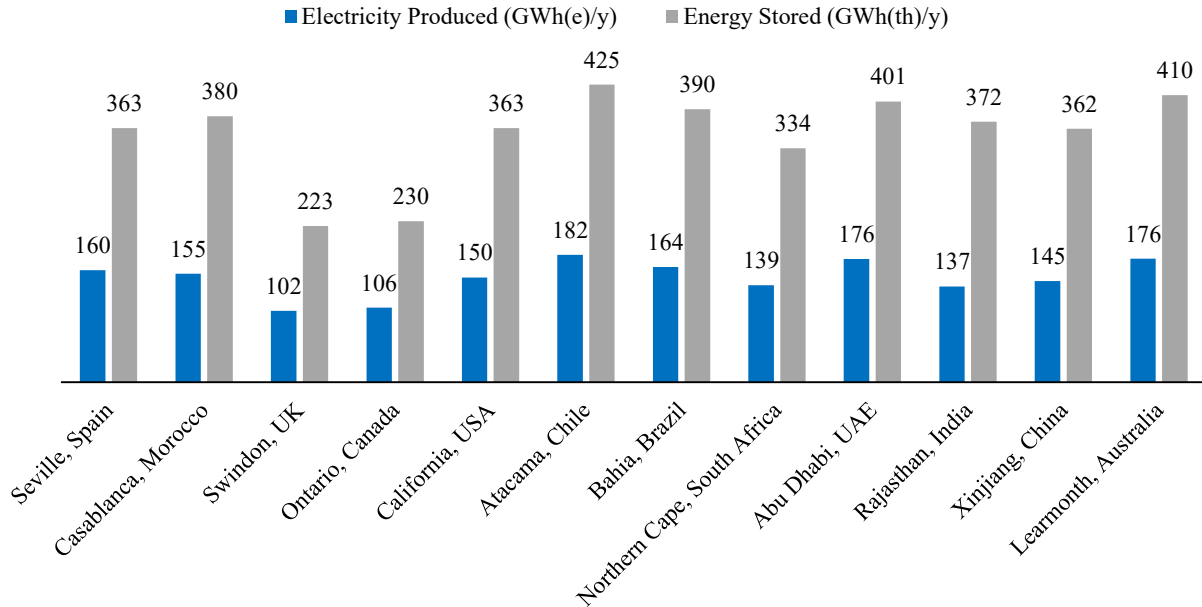


Fig. 8-11: Estimated energy storage and production capacities for a 130 MW_{th} CSP-TCES plant using the CaO/Ca(OH)₂ TCES system, operated TVPally on a continuous discharging schedule (scenario S0) at locations around the world with varying solar irradiance levels

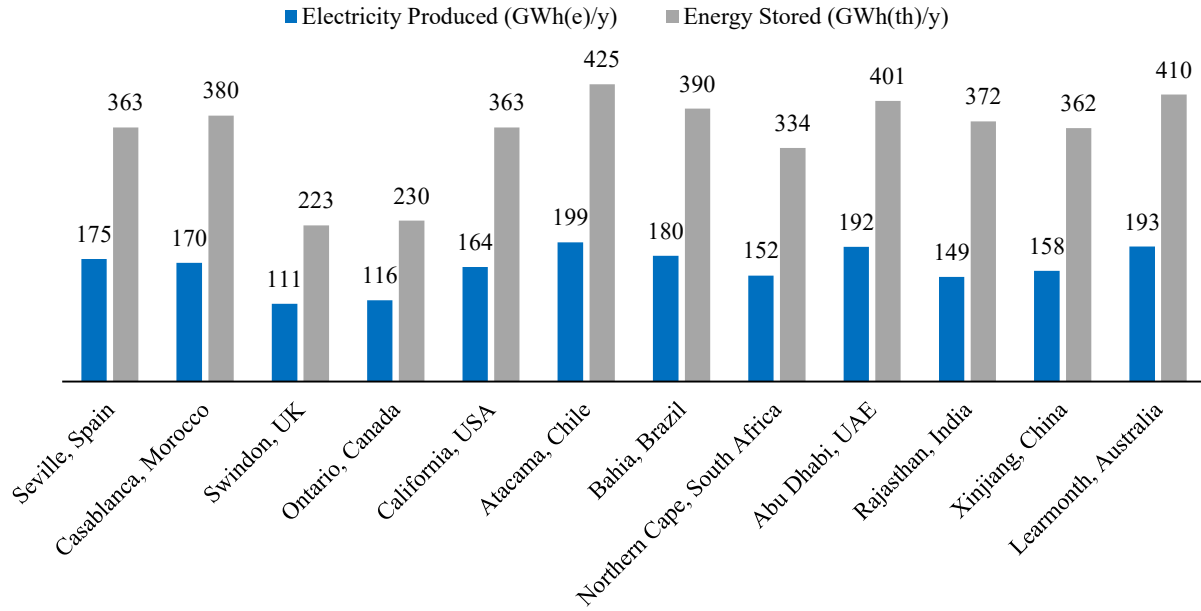


Fig. 8-12: Estimated energy storage and production capacities for a 130 MW_{th} CSP-TCES plant using the CaO/Ca(OH)₂ TCES system, operated TVPally on a batch-wise discharging schedule only at night (scenario S1) at locations around the world with varying solar irradiance levels

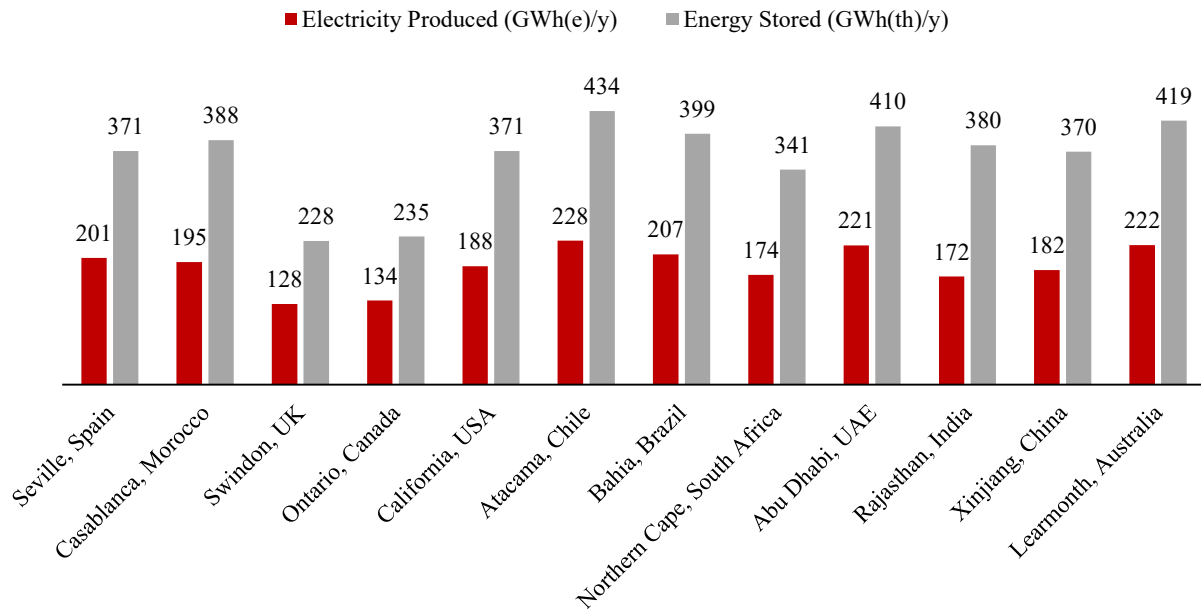


Fig. 8-13: Estimated energy storage and production capacities for a 130 MW_{th} CSP-TCES plant using the CMO redox TCES system, operated TVPally on a continuous discharging schedule (scenario S0) at locations around the world with varying solar irradiance levels

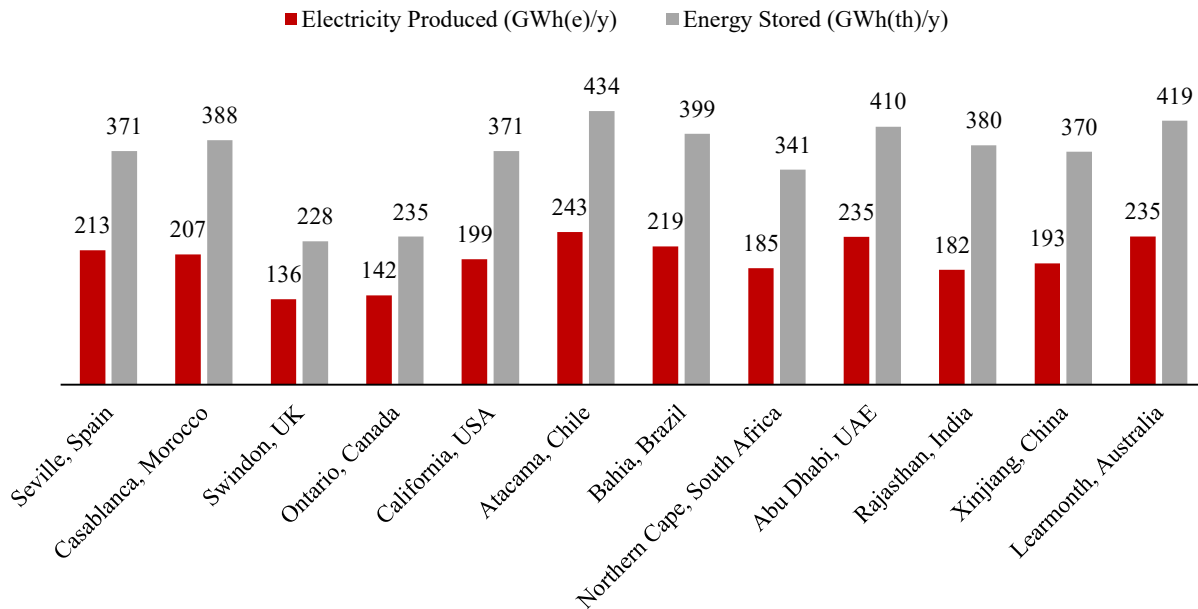


Fig. 8-14: Estimated energy storage and production capacities for a 130 MW_{th} CSP-TCES plant using the CMO redox TCES system, operated TVPally on a batch-wise discharging schedule only at night (scenario S1) at locations around the world with varying solar irradiance levels

8.6 Chapter Summary and Concluding Remarks

The results of the initial TVP modelling study for the CaO hydration system were discussed. For the discharging processes, scenario S1 was found to result in the highest maximum power output of 48.9 MW_e but the lowest time-based average power output of 10.2 MW_e as might be expected from a batch-wise operated process which was only run for limited periods of time. The average annual energy storage and electricity production volumes were calculated for each scenario and it was identified that only scenario S1 was achievable on an annual basis through standalone operation as it required 345.9 GW_{th} of energy discharged compared to the 363.2 GW_{th} annually stored by the designed TCES process.

An additional TVP operation scenario S0 was then introduced and specified in order to produce a continuous operation scenario that allowed for standalone plant operation through TVP simulation. It was found that scenario S0 could be achieved through operating the CaO hydration discharging FBR continuously at 41.3% of maximum capacity. This resulted in the capability for constant power generation at 20.2 MW_e which gave the plant an average solar-to-electricity conversion efficiency of 16.8% - this was in line with efficiencies for existing CSP setups and so it was found that incorporating the CaO hydration

TCES system did not negatively impact the potential energy conversion efficiency of a candidate CSP plant and furthermore enabled the possibility of continuous power generation.

In the fourth section the TVP modelling results for the CMO redox TCES system were considered through a similar approach. No discernible difference was found in the performance of the charging process compared to that of the CaO hydration charging system. For the discharging system it was found that all four TVP operating scenarios (now including S0) resulted in higher maximum as well as average power outputs with scenario S1 having maximum and average power outputs of 58.8 MW_e and 12.3 MW_e respectively. The higher power outputs calculated here were attributed to the higher thermal efficiencies of the sCO₂ Brayton cycle designed for and employed in the CMO discharging flowsheet.

It was once again found that only S1 among the three originally chosen TVP operating discharge scenarios could be fulfilled by the plant on a standalone basis and so scenario S0 was again evaluated here. It was found that operating a continuous discharge process through scenario S0 while operating the plant on a standalone basis required the discharging FBR to operate at 43.1% of its optimal thermal output. This resulted in the potential for continuous power generation at 25.4 MW_e due to the use of the sCO₂ Brayton cycle and the associated solar-to-electricity conversion efficiency for the CMO redox TCES system was found to be 21.1% which placed it at the very upper limit of efficiencies achieved by existing CSP plants. This further reinforced the attractiveness of installing TCES facilities alongside CSP plants in general and from a technical perspective the CMO redox TCES system seemed to offer better performance than the CaO hydration TCES system for the studied location of Seville.

As standalone operation was the preferred operating criteria only scenarios S0 and S1 were considered for these locations and it was found that the modelled annual energy storage and electricity production volumes had a direct correlation with the annual average DNI for each location. 10 of the 12 locations achieved performances that were within $\pm 20\%$ of those for the initial case study situated in Seville which suggested that the designed CSP-TCES plants were robust enough to perform adequately despite variations pertaining to geographical factors and that the plants would be technically viable at a wide range of locations.

When comparing the two TCES systems studied the CMO redox system was found to offer ~22% more electricity production than the CaO hydration system, while in terms of discharging operating scenario the batch-wise operation for scenario S1 yielded 9-11% more electricity production than scenario S0. For both factors it was recommended that an economic analysis be considered to ascertain any potential tradeoffs.

Chapter 9

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Techno-Economic Assessment of CSP- TCES Plants

Chapter Contents

Sections	Subsections
1. Techno-Economic Assessment Background	1. TEA Literature for CSP Plants with Energy Storage
2. Economic Costing Methodology	1. Base Case Costing Approach 2. Accounting for Dynamic Operation of Plant 3. Accounting for Geographical Variations
3. TEA Results for CSP-TCES Plants	1. Calculations for AOC, LCOE, and LCOS 2. Energy Storage and Production Costs for Designed CSP-TCES Plants
4. Benchmarking of CSP-TCES Costs	1. CSP-TCES versus other Renewable Energy Storage Options 2. CSP-TCES versus other Renewable Energy Production Options
5. Chapter Summary and Concluding Remarks	

9.1 Techno-Economic Assessment Background

In order to identify key economic variables, a brief review of existing literature results for TEA of CSP plants with energy storage was performed to identify known economic impacts of considering energy storage. It is to be noted that all reported cost are in U.S. cents based on currency rates as of 2016.

9.1.1 TEA Literature for CSP Plants with Energy Storage

In recent times more attention has been placed in the literature on analyzing the economic benefits of increased TES capabilities for CSP plants and these usually involve a model system with latent heat energy storage on the order of hours. Work by Costa and Neto²⁰¹ compared the economic benefits of 0-24 h of TES capacity versus a CSP plant hybridized with fossil fuel backup generation and reported that the incorporation of TES allowed for achieving annual energy production of up to 721 GWh_e from a 110 MW_e facility with an LCOE of 13.4 c/kWh which was the same cost as those borne by smaller plants with 452 GWh_e of energy produced by a 70 MW_e plant incorporating 26% of fossil fuel generation loads as backup.

Their findings suggested that the incorporation of additional energy storage capacity contributed little to the estimated LCOE of CSP plants while also allowing them to achieve much higher overall energy production levels annually which can only be seen as a considerable benefit. Furthermore doing so also economically discouraged the partial incorporation of fossil fuel power supplies as a backup mechanism to fulfil additional demand as a result of the stored extra energy available via TES. As this was achieved with just a maximum of 24h of storage capacity it is expected that having the much greater flexibility of a year of storage via the designed CSP-TCES plants in this study would make the LCOE even more attractive and allow for higher levels of overall power generation from a basic CSP plant.

The impact of geographical variations on the techno-economic performance of CSP plants with nominal (~5h) of TES were studied by Rea et al.²⁰² where the impacts of varying labor costs, annual solar irradiance levels, and geographical latitudes were considered. The estimated LCOE for a 20 MW_e plant (thus similar in scale to the design CSP-TCES plant in this study) was reported to be in the range of 13-15 c/kWh and unaffected by labor costs as locations in the US and India were compared with the labor cost multiplier for India being 0.047²⁰³ compared to that in the US. However the LCOE was reported to be significantly influenced by the geographical latitudes (and thus in a related manner, the solar irradiation levels) as a case study in location based in Alaska was found to have a much higher LCOE of 30.3 c/kWh.

These results suggested that when considering different locations for a CSP facility with energy storage, the consideration of variations in local labor costs made little impact on the LCOE of the designed plants. However the variations in average and seasonal solar irradiation levels at different locations did indeed

have a significant impact on the estimated economic performance of the plants as might be expected. For completeness, the costing approach here considers a brand new facility and so estimates of CSP field costs from the literature were used instead of performing detailed calculations. This was as detailed design of the heliostat field or tower receiver were not within the scope of this work. Hence, the main basis for detailed costing of the plant infrastructure was only the infrastructure required specifically for the TCES plant while the CSP infrastructure costs were estimated more broadly.

It was recognized that this was a simplistic approach to employ and more rigor could be employed especially in accounting for brand new setups that would incur higher infrastructural costs for both the CSP and TCES sides of the combined plant by incorporating backup thermal storage. This would require additional work and better understanding of the design requirements for CSP plants which was not well-aligned with the current focus of the study and thus was not included in the scope of this preliminary TEA.

9.2 Economic Costing Methodology

Upon identifying ballpark figures and metrics suitable for evaluating the performance of the designed CSP-TCES plants from an economic perspective and selecting a suitable basis for accounting for additional costs borne by the CSP facilities, a detailed TEA was performed for the processes across operating scenarios and locations. In order to do this an economic evaluation methodology was developed and standardized for use across all considered cases. In this section the development of the costing methodology is discussed and the relevant quantities and expressions identified. In addition, any specific considerations required and assumptions made for different operating scenarios and locations are discussed.

9.2.1 Base Case Costing Approach

The economics of the CSP-TCES process were evaluated adapting a commonly used approach by Seider et al.²⁰⁴ accounting for both capital and operating costs. This included utilizing Lang's 1947 'Simplified Approach'^{205, 206} for costing assets with an accuracy of $\pm 35\%$. First all TCES process units were costed using cost indexes provided by Seider et al.²⁰⁴ to obtain purchase costs C_p ; the sum total of these was then used to calculate the total depreciable capital (TDC) that accounts for delivery and installation costs, building and site infrastructure costs, contractor costs, and contingencies in Eq. 9-1. For all C_p calculations, the February 2019 value²⁰⁷ of the Chemical Engineering Plant Cost Index (CEPCI) was used – 603.1.

$$TDC = 1.05 f_{L,TDC} \sum_i \left(\frac{I}{I_b} \right) C_{P_i} \quad (9-1)$$

In Eq. 9-1, $f_{L,TDC}$ is the Lang factor (4.28 as determined by Peters, Timmerhaus and West for a solids-fluids processing plant²⁰⁸), I is the present-day CEPCI value, I_b is a baseline CEPCI value of 500 as of the year

2006, and the subscript i identifies individual process units. The estimated cost of land along with an estimated 10% factor of the TDC for startup costs were added to the TDC along with estimated CSP field and receiver costs to obtain the total permanent investment (TPI). The TPI was considered along with the interest rate and the plant lifetime to estimate an annualized cost of the total capital investment (TCI_{annual}) via Eq. 9-2. The Working Capital (WC) which covers the utilities and annual operating expenses was added to TCI_{annual} to obtain the annual operating cost (AOC). The Annual Operating Cost (AOC) was finally used to estimate the costs of energy storage and power generation (LCOE and LCOS) for the plant via Eq. 9-3.

$$TCI_{\text{annual}} = TPI \times (1 + i)^n \left[\frac{i}{(1+i)^n - 1} \right] \quad (9-2)$$

In Eq. 9-2, TCI_{annual} is the annual value of the total capital investment required for the plant (US\$/yr), i is the interest rate (%); and n is the project lifetime in years.

$$LCOE \text{ or } LCOS = \frac{AOC}{Q_{\text{generated or stored}}} \quad (9-3)$$

The TDC, TPI, TCI, and AOC (Table 7) were all calculated for scenarios S0 and S1 although only the AOC was found to vary between the two scenarios due to differing utilities and material costs.

9.2.2 Accounting for Dynamic Operation of Plant

It was decided in Section 9.1 that only dynamic discharging operation scenarios S0 and S1 were to be considered in this TEA as based on the results in Chapter 8, they were the only scenarios in which the designed plants could operate on a standalone basis over the course of a year (330 days). When considering the potential required purchased costs it was identified that, due to the steady-state specifications of the plants designed in Chapters 6 and 7 being sufficient to meet peak operating requirements even for the highest charging loads considered in the study (experienced in Chile), no differences in equipment specification and thus TPI were needed across either operating scenario.

Due to this, dynamic operation scenarios were accounted for by recalculating WC for either scenario as this would vary based on variations in flowrates required, operating schedules for both processes and the possible extents of energy integration. The annual electricity production volumes were also accounted for alongside the varying WC values for calculating LCOE and LCOS for either dynamic operating scenario.

9.2.3 Accounting for Geographical Variations

As identified in Section 9.1.1, location-based factors were not found to have any observable impact on the economic performance of CSP plants with energy storage facilities. To validate the literature findings, plant location was still accounted for in this study via location factors (pertaining to capital costs) and labour

factors (derived from labour costs and productivity rates) (Table 9-1)²⁰⁹; these geographical cost multipliers were employed to correct calculated values of labour costs, C_P , and TDC for each location.

Another consideration that was known to be location-specific was the cost of land used for calculating TPI. Land prices are known to vary significantly even within countries based on factors such as proximity to cities, accessibility, industrial demand, etc. and it was not possible within the scope of this study to determine specific suitable locations for each area studied and their accompanying land prices. As a guide a fixed land price based on data for Seville was used for each location in this initial study.

Table 9-1: Labour and location factors used for each considered location in the techno-economic analysis

Location	Labor Factor	Location Factor
Atacama, Chile	0.44	1.15
Learmonth, Australia	0.97	1.3
Northern Cape, South Africa	0.43	1.15
California, USA	1.21	1.1
Bahia, Brazil	0.41	1.1
Abu Dhabi, UAE	0.30	1.08
Casablanca, Morocco	0.44	1.05
Seville, Spain	0.83	1.1
Rajasthan, India	0.20	1.02
Xinjiang, China	0.30	0.9
Ontario, Canada	0.93	1.1
Swindon, UK	1.29	1.05

As the designed plant specification was standardized across all 12 locations, the TPI was easily modified based on the labour and location factors affecting the TDC for each location as mentioned earlier. The WC and AOC were recalculated based on specifications from the TVP simulation studies in Chapter 8. The various annual electricity production and energy storage volumes calculated in Chapter were also used alongside the recalculated WC and AOC values to calculate LCOE and LCOS for each location studied.

The main location-based costs considered in detail were those for the CSP plants. The cost estimation for these comprised of the heliostat field cost and the tower receiver cost; while the latter had a fixed rating and thus a fixed cost, the heliostat field size was calculated to vary significantly in Chapter 8 and thus the cost of the required field size for each location was incorporated here. Based on values from the SAM tool¹⁹⁴ and several TEAs in the literature considering locations such as Iran, USA,¹⁹⁴ Mexico,²¹⁰ and Pakistan,²¹¹ cost factors of \$175/m² for the heliostat field and \$160/kW_{th} for the receiver tower were used.

9.3 TEA Results for CSP-TCES Plants

The costing methodology developed in Section 9.2 was applied to all design cases produced in Chapter 8 in order to obtain estimates for the LCOE and LCOS of the designed plants. First the detailed economic calculations were performed for each dynamic operation scenario to obtain estimates for TDC for the standard plant designs which were fixed across locations. The WC and AOC were then evaluated separately based on TVP simulation data for each location and thus estimates of LCOE and LCOS were obtained.

9.3.1 Calculations for AOC, LCOE, and LCOS

Table 9-2: Calculation of the working capital (WC) required for the CaO hydration CSP-TCES plant

Utility category	Cost	Cost Unit	Consumption Rate (kg/day or kWh/day)		Annual cost (CaO hydration) (\$M)	
			S0	S1	S0	S1
Steam ²¹²	0.0135	\$/kg	108700	345600	0.485	1.541
Electricity ²¹²	0.07	\$/kWh	3240	11450	0.075	0.265
Cooling water ²¹²	0.00146	\$/kg	43800	43800	0.022	0.022
Process feed water ²¹²	0.000346	\$/kg	1007800	5529600	0.115	0.631
Fresh ^{213, 214} CaO & Ca(OH) ₂	0.10	\$/kg	425	425	0.018	0.018
Total (\$M)					0.735	2.460

Table 9-3: Purchased costs of all major process equipment for the CaO hydration CSP-TCES plant

Equipment	Purchased Cost, C _p (\$M)
Cyclones	0.39
Heat Exchangers	20.9
Pumps	0.11
Compressors	3.3
Turbines	5.3
Reactors	9.2
Storage Tanks	1.4
Total	40.6

In this section data is presented only for the case study location of Seville for brevity. Identical calculations were performed for the other 11 locations. Of note is the sorbent consumption rate for the CaO hydration TCES plant; this is due to pure Ca sorbents having poor cycling stability. Similarly the high material costs for the CMO redox TCES plant are a result of the high material volumes needed due to using an inert support. The calculated values of WC shown in Table 9-2 for the CaO hydration plant are significantly different between scenarios S0 and S1; this is due to the differences in steam consumption volumes. This is because the continuous operation in scenario S0 allows for much greater heat integration and circulating steam reutilization, reducing the need for additional heating using steam. Hence the bulk of the steam usage in S0 is for replenishing the steam cycle and resupplying the CSP facility with additional HTF flows. The steam volumes are a conservative estimate based on the assumption that the discharging cycle will need 80% of its steam needs freshly generated; this is based on discussions in Chapters 6 and 8. Among the purchased costs in Table 9-2, heat exchangers and compressors comprise 65% of the total costs due to the large compressors needed in the steam cycle and FBR exit gas streams and the heat exchangers used for the FBRs. The calculated values from Tables 9-2 and 9-3 were used to calculate TDC, TPI, and TCI_{annual} in Table 9-4. These values were fixed for the plants as the design specifications did not vary across locations or operating scenarios. These were then employed together with interest rates of 10%, plant lifetime of 20 years, and capacity factor of 0.70 to calculate the AOC, LCOE, and LCOS for the CaO hydration CSP-TCES plant based in Seville as reflected in Table 9-5. For a sensitivity analysis, these were also evaluated at interest rates of 15% to reflect the higher risk associated with newer technologies. Moreover, capacity factors between 0.30-0.70 were considered to account for variations in heliostat field sizing and choice of discharging regime as these factors limit the extents to which TCES can improve the capacity factor for the base case CSP plant. The lower and upper limits are based on similar studies for solar tower CSP plants incorporating up to 24-h molten salt TES^{193, 215}, with 0.70 estimated as the upper limit for an optimized plant based in Saudi Arabia which has DNI levels very similar to those for Seville as seen in Fig. 8-10.

Table 9-4: Major lifetime cost calculations for the CaO hydration CSP-TCES plant

Economic Cost Variable	\$M
CSP costs ^{194, 216}	96.7 @ \$175/m ² (Solar field); 20.8 @ \$160/kW _{th} (Tower)
TDC	210.2
<i>Land</i>	2.7
<i>Plant startup (10% of TDC)</i>	21.0
TPI (TDC + Land + startup)	233.9
<i>WC</i>	0.7 (S0); 2.4 (S1)
TCI_{annual}	22.1

Table 9-5: Key techno-economic metrics and assumptions for the CaO hydration CSP-TCES plant

Scenario	S0	S1
Solar Tower CSP plant capacity factor	0.70	0.70
Annual electricity produced (GWh)	160	175
AOC (\$M)	22.8	24.5
LCOE (c/kWh)	14.2	14.0
Annual energy stored (GWh)	363	363
Plant efficiency (%)	44	48
LCOS (c/kWh)	6.3	6.7
Interest rate (%)	10	10
Plant lifetime ²¹⁷ (years)	20	20

Table 9-6: Economic uncertainties for LCOE and LCOS estimates for the CaO hydration CSP-TCES plant

Scenario	S0 base estimate	S0 upper limit	S0 lower limit	S1 base estimate	S1 upper limit	S1 lower limit
Annual electricity produced (GWh)	160	88	160	175	96	175
Annual energy stored (GWh)	363	200	363	363	200	363
AOC (\$M)	22.8	31.7	19.3	24.5	34.8	20.5
LCOE (c/kWh)	14.2	36.0	12.0	14.0	34.8	11.8
LCOS (c/kWh)	6.3	15.9	5.3	6.7	16.7	5.7
Capacity factor	0.70	0.30	0.70	0.70	0.30	0.70
Interest rate (%)	10	15	10	10	15	10

From Table 9-5, the impact of operating scenario on the power output and economic performance of the CSP-TCES plant is apparent, most notably (considering the best case figures) in the LCOE which increased marginally by 2% if switching from batch mode to continuous discharge (S1 to S0). Doing this also positively affected the LCOS which decreased by 7% as a result of the lower AOC achieved through simultaneous continuous operation of both the charging and discharging processes. It was thus apparent that scenario S0 was the most attractive in terms of balancing both economics and capacity while also allowing for continuous power production. The capacity factor range of 0.30-0.70 and interest rate range of 10-15% were taken into account along with the inherent 35% uncertainty of the TDC calculation as noted in Section 9.2.1 to identify the uncertainties associated with the LCOE and LCOS in both scenarios. Table 9-6 shows that the AOC and therefore the LCOE and LCOS are significantly affected by this margin, giving an LCOE range of 12.0–36.0 c/kWh and an LCOS range of 5.3–15.9 c/kWh in the case of scenario S0.

The same calculation approach was employed for the CMO redox CSP-TCES plant. In Table 9-7 the calculations for the WC for each operating scenario show that overall the CMO redox system required a much higher cost for materials and utilities, most notably in the form of electricity consumption and fresh supply of CMO material. The electrical consumption was primarily due to the very high capacity compressors required for handling FBR exit gas streams and for power generation.

The cost of the supported CMO material was estimated from known costs for supported forms of the constituent metal oxides^{218, 219} and was also a major contributing factor to the cost that was partially mitigated due to the much better expected cycling stability of the material and thus the relatively lower replenishment rates assumed. Overall the WC needed for scenario S0 was 19% lower than that for S1 which was chiefly due to the lower electricity consumption incurred by running both processes continuously and thus facilitating a certain degree of energy integration within the plant.

In Table 9-8 the purchased costs required for the CMO redox plant design are reported and the estimated costs were significantly higher than for the CaO hydration plant. This was due to the much higher material flows and thus much larger vessels needed by the CMO redox system. As a result the costs for the reactors and storage tanks were larger by 60% and 360% respectively although the cost for compressors was lower by 24% due to smaller volumes of CO₂ used to operate the Brayton cycle compared to steam usage in the Rankine cycle. Overall the C_P for the CMO redox plant was 40% higher than for the CaO hydration plant and the impacts of this were seen in Table 9-9 where TDC, TPI, and TCI_{annual} were then calculated.

Table 9-7: Calculation of the working capital (WC) required for the CMO redox CSP-TCES plant

Utility category	Cost	Cost Unit	Consumption Rate (kg/day or kWh/day)		Annual cost (CaO hydration) (\$M)	
			S0	S1	S0	S1
Steam ²¹²	0.0135	\$/kg	24500	24500	0.109	0.109
Electricity ²¹²	0.07	\$/kWh	113000	151000	2.610	3.465
Cooling water ²¹²	0.00146	\$/kg	37500	37500	0.004	0.004
Fresh ^{218, 219} CMO _{red} & CMO _{ox}	1.56	\$/kg	1220	900	0.618	0.463
N ₂ ²²⁰	0.07	\$/kg	200	600	0.004	0.014
O ₂ ²²⁰	0.12	\$/kg	6500	8800	0.257	0.349
CO ₂ ²²⁰	0.30	\$/kg	5000	5000	0.495	0.495
Total (\$M)					4.098	4.899

Table 9-8: Purchased costs of all major process equipment for the CMO redox CSP-TCES plant

Equipment	Purchased Cost, C_p (\$M)
Cyclones	1.73
Heat Exchangers	23.5
Pumps	0.05
Compressors	2.5
Turbines	4.2
Reactors	15.6
Storage Tanks	5.1
Total	56.6

The calculated TCI_{annual} and WC values from Table 9-9 were then used to calculate the AOC, LCOE, and LCOS of the CMO redox plant reported in Table 9-10 using the same assumptions for the interest rate, capacity factor, and plant lifetime. It was observed that scenario S0 resulted in a 3% higher LCOE compared to S1. This suggested that a batch-wise power generation mode was marginally more economically attractive for the CMO redox plant. However the calculated LCOS for scenario S0 was 2% lower than that for scenario S1.

On the whole it was apparent that the choice of operating scenario made little difference in the economic performance of the designed CSP-TCES plant where the CMO redox system was used. This was reinforced by observing the calculated uncertainty ranges of the estimated LCOE and LCOS in Table 9-11 which returned very similar ranges for both scenarios and so scenario S0 was considered the most attractive as it maintained the economic performance of scenario S1 while also achieving continuous power generation with an LCOE range of 14.3–39.9 c/kWh and an LCOS range of 8.0–21.6 c/kWh.

Table 9-9: Major lifetime cost calculations for the CMO redox CSP-TCES plant

Economic Cost	\$M
CSP costs ^{194, 216}	96.7 @ \$175/m ² (Solar field); 20.8 @ \$160/kW _{th} (Tower)
TDC	246.3
Land	2.7
Plant startup (10% of TDC)	24.6
TPI (TDC + Land + startup)	273.6
WC	4.1 (S0); 4.9 (S1)
TCI_{annual}	28.5

Table 9-10: Key techno-economic metrics and assumptions for the CMO redox CSP-TCES plant

Scenario	S0	S1
Solar Tower CSP plant capacity factor	0.70	0.70
Annual electricity produced (GWh)	201	214
AOC (\$M)	32.6	33.4
LCOE (c/kWh)	16.2	15.7
Annual energy stored (GWh)	371	371
Plant efficiency (%)	54.2	57.5
LCOS (c/kWh)	8.8	9.0
Interest rate (%)	10	10
Plant lifetime ²¹⁷ (years)	20	20

Table 9-11: Economic uncertainty margins for LCOE and LCOS for the CMO redox CSP-TCES plant

Scenario	S0 base estimate	S0 upper limit	S0 lower limit	S1 base estimate	S1 upper limit	S1 lower limit
Annual electricity produced (GWh)	201	110	201	214	118	214
Annual energy stored (GWh)	371	204	371	371	204	371
AOC (\$M)	32.6	44.2	28.8	33.4	45.0	28.2
LCOE (c/kWh)	16.2	39.9	14.3	15.7	38.3	13.8
LCOS (c/kWh)	8.8	21.6	8.0	9.0	22.0	8.2
Capacity factor	0.70	0.30	0.70	0.70	0.30	0.70
Interest rate (%)	10	15	10	10	15	10

The AOCs for the CSP-TCES plants based on Scenario S0 were subsequently calculated for the 12 locations factoring in the required heliostat fields. Fig. 9-1 suggests that the average DNI levels do not significantly influence the AOC if the location has a DNI of >2000 kWh/m², regardless of other geographical factors. However, for locations with DNI below 2000 kWh/m² the AOC increases significantly from ~\$30 million to ~\$75 million with corresponding drops in DNI levels. This far outweighs the impact of choosing between the two TCES systems, as the CMO redox system incurs \$9-10 million higher AOC independent of location.

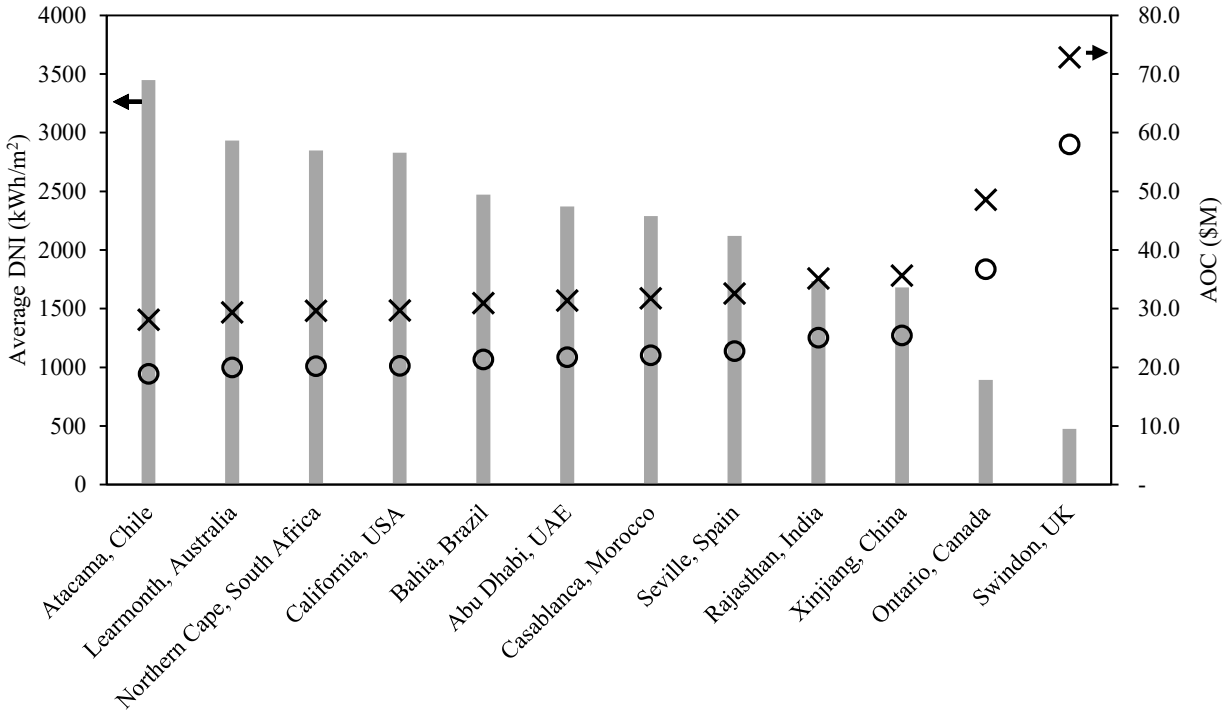


Fig. 9-1: Estimated AOC of CaO hydration (O) and CMO redox (x) CSP-TCES plants operated dynamically under scenario S0 at locations around the world with varying solar irradiance levels

9.3.2 Energy Storage and Production Costs for designed CSP-TCES Plants

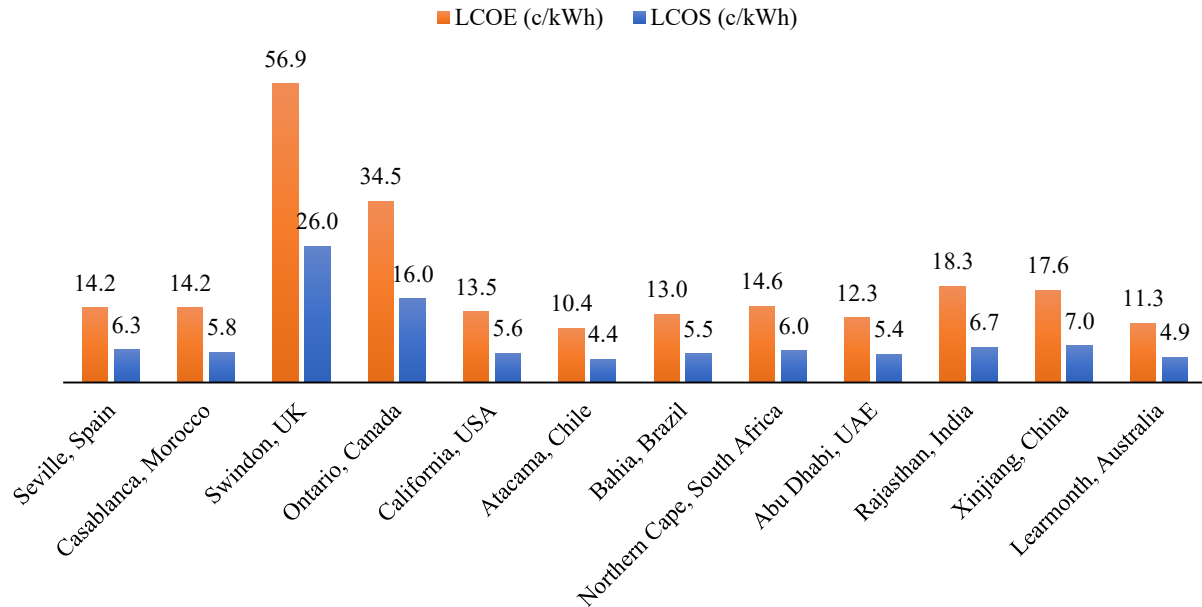


Fig. 9-2: Estimated LCOE and LCOS values for a 130 MW_{th} CaO hydration CSP-TCES plant operated dynamically under scenario S0 at locations around the world with varying solar irradiance levels

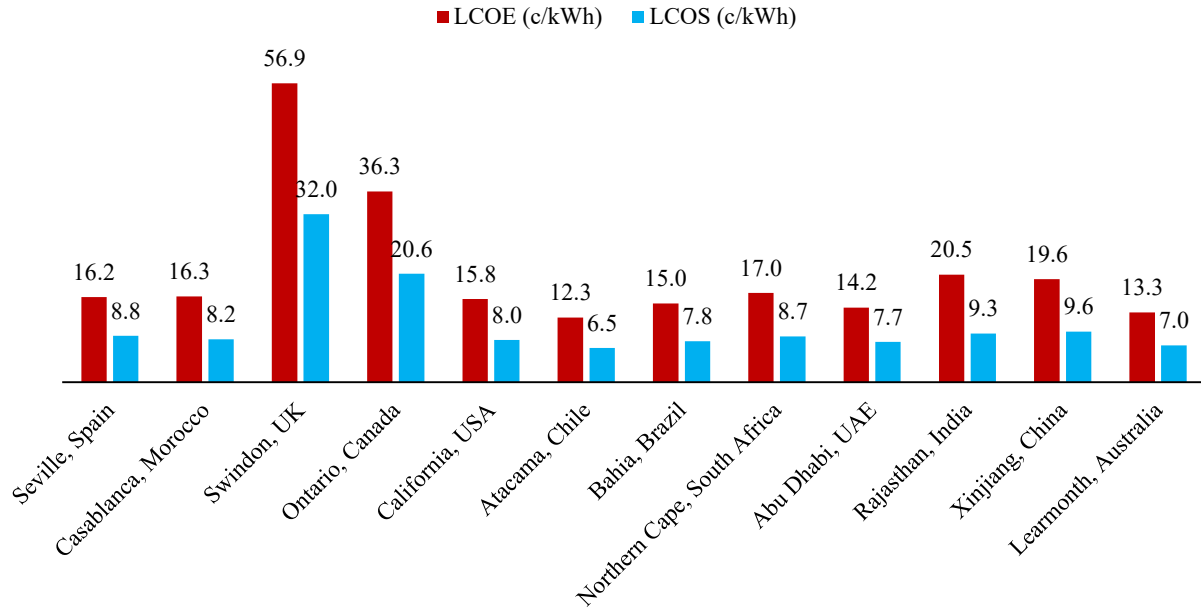


Fig. 9-3: Estimated LCOE and LCOS values for a 130 MW_{th} CMO redox CSP-TCES plant operated dynamically under scenario S0 at locations around the world with varying solar irradiance levels

The operating results of the CSP-TCES plants at the remaining 11 locations were also assessed and the associated LCOE and LCOS values for data from each location were calculated; only data for the base cases is discussed here. The techno-economic results for both the CSP-TCES plant were examined together as the qualitative trends displayed across plant designs and operating scenarios were very similar.

The LCOE and LCOS values obtained through scenario S0 in Figs. 9-2 and 9-3 and those for scenario S1 in Figs. 9-4 and 9-5 reflect the variations observed in the energy production and storage volumes across locations. It was observed that the CaO hydration CSP-TCES plant consistently offered lower LCOE and LCOS compared to the CMO redox CSP-plant and so was a more cost-effective design despite the technical advantages offered by the CMO redox process and plant design. In comparison to the Seville plant, superior cost performances were found possible at all locations except Rajasthan, Xinjiang, Swindon, and Ontario as expected by virtue of their lower annual solar irradiance levels. In fact, among all 12 locations only Swindon and Ontario offered costs that were outright unreasonable and unviable.

These results suggested that deploying the proposed CSP-TCES plant in the proposed configuration for both storing and producing power through standalone operation at higher latitudes with large variations in daylight hours and low annual solar irradiance levels would not be cost competitive with alternative renewable energy generation and storage technologies available in those regions. This is evidenced by very high investment into pumped hydro energy systems in Canada and offshore wind energy and batteries in the UK where the case for standalone solar energy technologies as a baseline power source is not attractive

and greater access to other sources of renewable power is available. However at most other locations considered which experience more stable daylight hours and greater solar irradiance, the proposed plant offers very competitive cost performances and achieves high volumes of storage and discharge throughout the year.

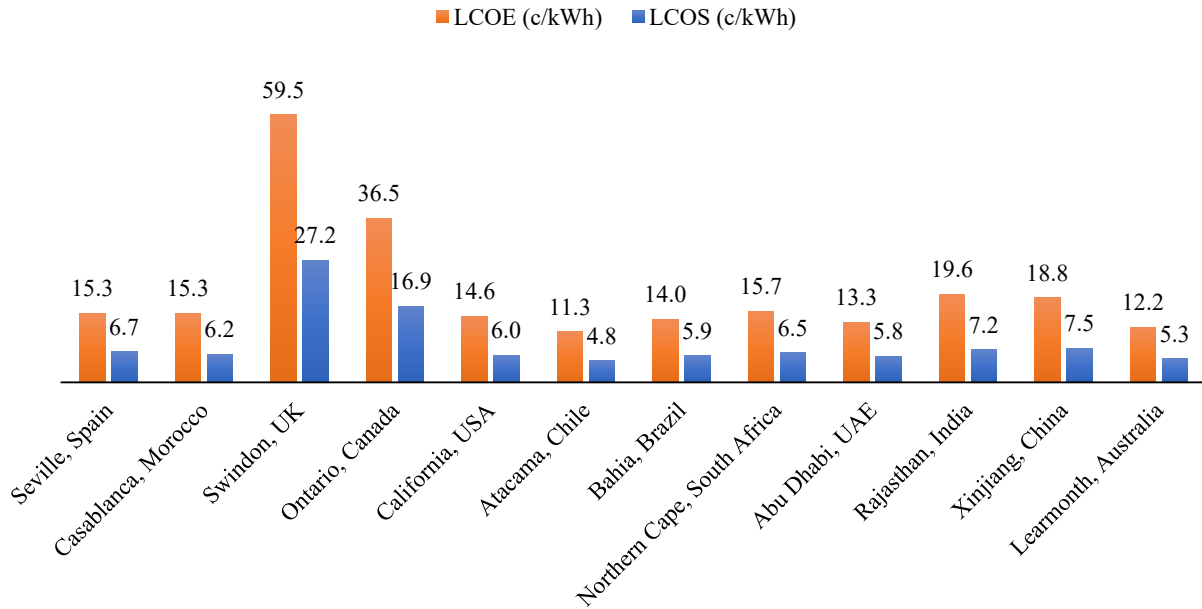


Fig. 9-4: Estimated LCOE and LCOS values for a 130 MW_{th} CaO hydration CSP-TCES plant operated dynamically under scenario S1 at locations around the world with varying solar irradiance levels

For several locations such as Rajasthan, Xinjiang, and Northern Cape, these numbers are encouraging as having an economically viable TCES-CSP setup could well lead to increased installation of CSP infrastructure in those areas while a combined storage/discharge plant design is piloted and developed for future use, driving down associated costs and allowing the local energy industries time to adapt to an increased adoption of solar energy technologies into both the storage and the power generation scenes.

At other locations where CSP technologies are already deployed to significant extents such as in Bahia, Atacama, Abu Dhabi, and Casablanca, the estimated costs are comparable to or lower than for Seville. Given that the designed plant in this study is not cost-optimized or technically optimized, there is a strong economic case for piloting and deploying TCES-CSP plants in such locations once other technological and economic aspects such as sorbent development and localized power generation scheduling progress further.

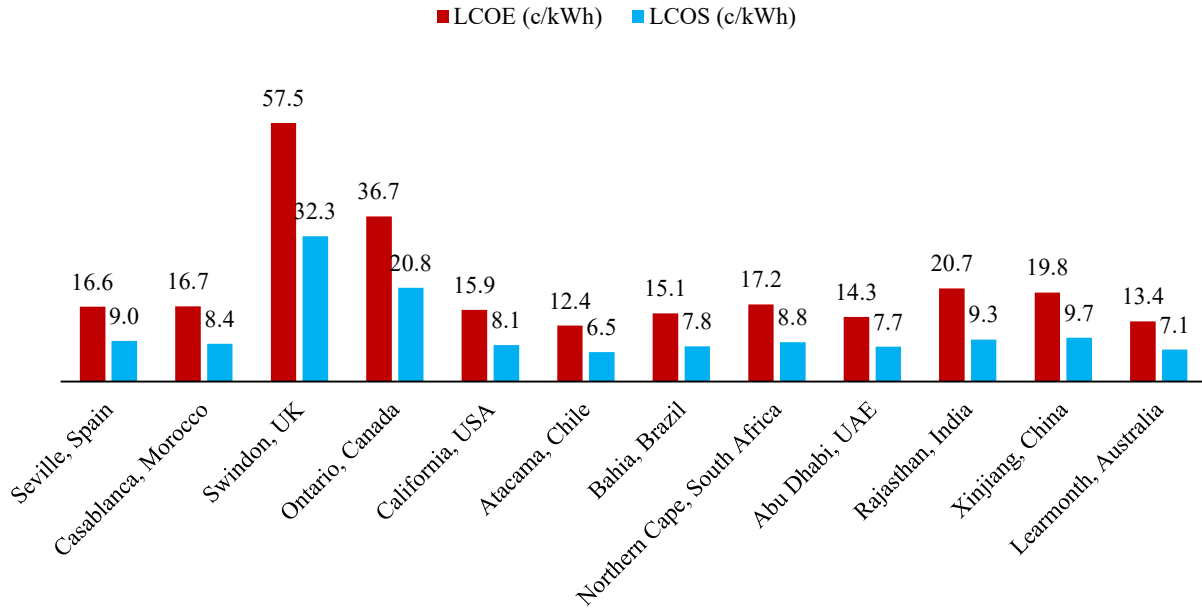


Fig. 9-5: Estimated LCOE and LCOS values for a 130 MW_{th} CMO redox CSP-TCES plant operated dynamically under scenario S1 at locations around the world with varying solar irradiance levels

9.4 Benchmarking of CSP-TCES Costs

In Section 9.3 the economic evaluation methodology was applied to the design cases for both designs of CSP-TCES plants and LCOE and LCOS values were calculated to establish the impacts of dynamic operation and geographical location on the performance of the plant designs. These results were then used in Section 9.4 to compare the techno-economic performance of the CSP-TCES plants to alternative clean/renewable energy storage and generation technologies commonly employed around the world.

9.4.1 CSP-TCES versus other Energy Storage Options

In Fig. 9-6 the LCOS for the two CSP-TCES plant designs were compared against values for alternative renewable energy storage technologies.^{221, 222} It was observed that in terms of energy storage, CSP-TCES is cheaper than molten salt storage and cost competitive with others including battery storage technologies. In considering long-term grid-scale storage options such as power-to-gas (P2G) technologies involving methane and hydrogen, CSP-TCES also comes in significantly cheaper – although this cost advantage would not be applicable in unfavorable regions for solar such as the UK and Canada as noted previously.

For inter-day storage, while CSP and TCES technologies continue to develop and mature in terms of material development, operation scheduling, and infrastructural improvements, batteries (such as vanadium redox and Li-ion) are also expected to undergo significant development in the coming decade. At large

scales, however, CSP-TCES retains higher energy storage densities and offer greater ease of energy transportation using CaO as a denser and more durable energy vector compared to batteries. Moreover, CSP-TCES is able to offer both inter-day and inter-seasonal energy storage which cannot be achieved using batteries. This means it will be more useful for grid balancing, strengthening business cases for its deployment at large scales.

While the practicality of realizing these benefits under various circumstances requires further study, the CSP-TCES energy storage system can offer economic and technical advantages over the state-of-the-art. These preliminary LCOS values suggest that CSP-TCES systems can offer inter-seasonal and grid-scale energy storage at lower costs than that of existing alternatives if deployed in suitable geographies, although its inter-seasonal storage capability may require periodic discharging and recharging due to heat losses. In addition, the use of TCES for long-term storage significantly enhances the viability of CSP which is one of the most mature energy technologies harnessing heat. For further study, assessing the economic impacts of optimization of integrated CSP-TCES plant design including heliostat field sizing and discharging operating scenarios will serve to narrow the cost uncertainties and provide a more accurate LCOS forecast.

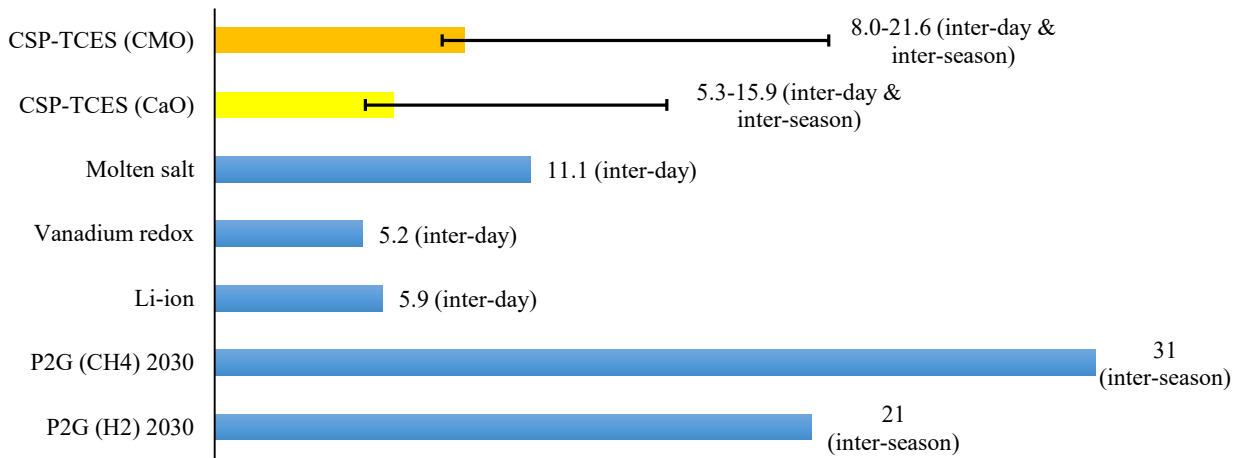


Fig. 9-6: A comparison of the economics of the designed CSP-TCES plants based in Seville with that of alternative storage and discharge technologies based on estimates of the LCOS

9.4.2 CSP-TCES versus other Energy Production Options

In Fig. 9-7, the cost-competitiveness of the CSP-TCES plant designs is compared to that of alternatives for power generation²²³⁻²²⁵ that are already deployed in the field or have been proposed for large-scale deployment and have low carbon or carbon-neutral footprints. The CSP-TCES plants are more economically attractive than solar PV using battery energy storage, but are not as cheap as most renewable alternatives or clean energy sources such as biomass, coal + CCS or hydro-electric energy generation.

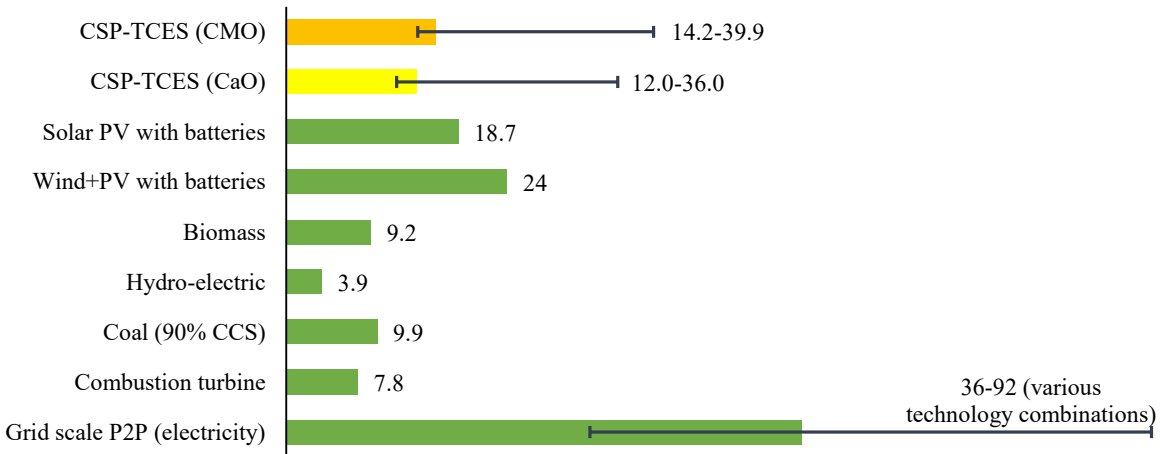


Fig. 9-7: A comparison of the economics of the designed CSP-TCES plants based in Seville with that of alternative discharge technologies based on estimates of the LCOE

However all three of these technologies are significantly more mature while CSP-TCES has ample room for technological development, particularly in the development of more robust storage and discharge materials. Impending improvements in power cycles and heat recovery systems may serve to reduce the LCOE for the designed plants. A footnote is that these LCOE values are also a result of achieving continuous electrical power generation. There is room to explore strategies for maximizing this capability to further reduce the LCOE for the designed systems. When considering renewables (PV or wind) + battery storage systems, the CSP-TCES systems are potentially slightly cheaper and also add hard-to-quantify intrinsic value due to bringing grid balancing capabilities.

When considering the grid-scale power-to-power (P2P) systems proposed by Yao et al.²²⁴, it is seen that even in the most stringent scenario CSP-TCES offers a cheaper option for grid-scale energy storage and generation due to significantly fewer unit processes being required, reducing energy conversion inefficiencies. While CSP-TCES still requires several technological advancements to be commercially deployable, the proposed P2P systems also face high technological uncertainties as they are dependent on the continued development of newer technologies such as direct air capture of CO₂ (DAC).

The designed CSP-TCES plants were thus considered to be economically competitive across most geographies as they are able to both store and produce energy on demand and more importantly maintain baseload power generation during off-sun hours. While they also can be suitable for grid balancing, further study incorporating grid data is needed to understand their techno-economic performance in such use cases. Successful deployment of CSP-TCES would make strides towards mitigating the intermittency concerns of solar energy generation although it would involve higher capital costs and be considered more financially risky early on. As part of the energy transition, a variety of technologies are needed globally and so it is

understood that in certain situations, electricity-based systems (such as P2P, Wind+PV with batteries) may be more attractive. Where this may not be possible and solar heat is accessible, CSP-TCES can offer a new capability: heat-based inter-seasonal and grid-scale energy storage and power generation options at costs in line with electricity-based alternatives. Further study of optimized CSP-TCES plant design including sizing of the heliostat field and storage capacities, along with continued technological developments, will serve to refine the estimated LCOE values.

9.5 Chapter Summary and Concluding Remarks

For the CaO hydration TCES plant design it was found that scenario S0 yielded higher LCOE (14.2 c/kWh) and lower LCOS (6.3 c/kWh) values than S1 (14.0 c/kWh and 6.7 c/kWh respectively) due to producing less electricity over the course of a year (160 GWh vs 175 GWh). This result suggested that for the CaO/Ca(OH)₂ plant scenario S0 was more economically attractive as well as operationally more desirable due to being able to maintain continuous power generation purely through stored energy volumes on a standalone basis. The inherent uncertainty in the approximations employed by the costing methodology and the variability in designed capacity factors and economic assumptions were evaluated and this resulted in the expected LCOE being in the range of 12.0–36.0 c/kWh with the LCOS having a range of 5.3–15.9 c/kWh based on scenario S0.

An identical evaluation was conducted for both scenarios using the CMO redox plant. While scenario S0 again required lower costs than S1 the difference was less pronounced in this system (\$4.1 million vs \$4.9 million). In terms of equipment costs the reactors, heat exchangers, and compressors accounted for the vast majority of the total required (\$56.6 million) as was expected due to the much higher solid and gas flowrates in the plant necessitating larger vessels and higher capacity equipment. The subsequent calculated TCI_{annual} was \$16.1 million which was 19% higher than that of the CaO/Ca(OH)₂ system calculated previously. The calculated LCOE and LCOS were found to be similar for both operating scenarios with that for scenario S0 being 16.2 c/kWh and 8.8 c/kWh respectively. When factoring in the uncertainty the LCOE was found to be in the 14.2–39.9 c/kWh range while the LCOS was expected to be within 8.0–21.6 c/kWh.

It was observed that the LCOE and LCOS for the CMO redox plant were in both cases higher than that of the CaO/Ca(OH)₂ plant and this trend was observed to hold across all locations considered. This meant that overall the CaO/Ca(OH)₂ plant was the more economically attractive option despite the superior technical performance potential of the CMO redox plant although it is acknowledged that significant advancements in reactant materials for either process could affect this comparison in the near future. The calculated LCOE and LCOS values across all 12 locations were then considered and it was observed that for 9 of the other locations the calculated costs fell within the uncertainty range of the Seville base case. It was found that for

the remaining 2 locations, Swindon and Ontario, the estimated LCOE and LCOS values were ~380% and ~450% higher than for the base case. With no cost savings offered at these locations the sole advantage of continuous power generation might not be a sufficient incentive for deployment.

In the fourth section the estimated LCOE and LCOS values were then compared with those of relevant alternative energy storage and power generation options based on clean and/or renewable energy technologies; here the values for Seville were used as the guideline. When compared with energy storage options, the CSP-TCES plant designs were found to be more economically competitive with most other technologies, providing an attractive cost for a technology capable of both inter-day and inter-season energy storage. In terms of assessing the LCOE of the plant designs the results were less distinct. While the CSP-TCES plants offered a slightly lower LCOE than solar PV/wind with battery storage, several other renewable energy generation technologies offered lower LCOS values such as onshore wind. However it was noted that most of these technologies are more mature than TCES and so there remains potential for lower future LCOS values for the designed plant especially in terms of developing more cost-effective and durable storage materials. Furthermore it was noted that CSP-TCES offered unique capabilities for heat-based inter-seasonal and grid-scale energy storage coupled with baseline power generation and grid balancing capabilities, at lower costs than otherwise possible in a variety of geographies.

Chapter 10

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Conclusions & Recommendations for Future Work

Chapter Contents

Sections	Subsections
1. Conclusions	
2. Recommendations for Future Work	

10.1 Conclusions

In the nine prior chapters in this thesis, two chemical reaction systems were studied and evaluated for their suitability for thermochemical energy storage (TCES) in the context of concentrated solar power (CSP) – the calcium oxide/hydroxide reaction system and the copper-manganese mixed metal oxide (CMO) redox reaction system. The development of processes for energy storage as a means of achieving greater versatility for renewable energy generation sources such as CSP was the main motivation for this study. The key findings from the experimental and modelling work as well as the simulation studies are reproduced and summarized in this chapter.

Kinetic behavior of calcium oxide hydration reaction with steam under fluidized conditions

Calcium oxide sample was used for kinetic studies with steam without any supporting materials in an atmospheric pressure bench-scale fluidized bed environment. It was observed that larger particles underwent slower maximum rates of reaction which is to be expected due to greater intra-particle diffusional resistances. It was also found that smaller particles experienced a kinetics-driven regime for larger extents of the reaction. In addition, the porosity of particles – something observed to be loosely correlated with particle size – did not appear to have an effect on the conversion behavior.

The influence of varying the hydration reaction temperature was assessed. It was found that only the lower steam concentrations of 10% and 15% and the largest particle size range of 500-710 μm offered reactions slow enough at 400°C to allow for precise kinetics measurements. The higher reaction temperature resulted in much higher maximum and average reaction rates throughout the entirety of reactions; however it was noted that going to temperatures higher than this would see a drop in reaction rate under these conditions as the dehydration reaction rate increases quickly in that temperature range. Several separate experiments were conducted at 250°C, 300°C, and 350°C for the purposes of estimating kinetic parameters for comparison with literature values studying the same reaction. The obtained estimates of $A = 6.45 \times 10^{-6} \text{ s}^{-1}$ and $E_a = -52 \text{ kJ/mol}$ fell in line with estimates in the broader literature suggesting that the FBR was well suited for conducting accurate kinetics experiments.

Kinetic modelling of calcium oxide hydration reaction with steam using the shrinking core model, the random pore model, and the grain catalyst model

Three bespoke kinetic models from the literature (the SCM, RPM, and GCM) were used to model the experimental data obtained for the calcium oxide hydration reaction to assess their suitability for modelling the reaction under fluidized conditions and to ascertain the impact of various physicochemical reaction phenomena upon the behaviour of the reaction.

A form of the SCM developed in this study (D-SCM) accounting for fluctuating bulk reactant concentrations and particle expansion was able to describe the system most accurately across the range of conditions tested as well as literature data. A form of the GCM developed in this study (D-GCM) also returned significantly improved predictions compared to the GCM by way of accounting for changing steam concentrations. It performed well at lower conversions where the kinetic rate was more dominant. However when tested at a higher reaction temperature of 400°C its predictions dropped off in accuracy and reliability suggesting that further work would be needed to develop this model. On both a qualitative and quantitative basis as a result of statistical testing, the D-SCM appeared to be the most useful and accurate model to study the hydration of calcium oxide, yielding modelling accuracy improvements of up to 25% compared to the best available model in the literature for modelling reactions under fluidized conditions. The analytical assumptions involved in the D-SCM are applicable in the study of doped sorbents, synthetic analogues, or derivative materials on the bench scale as well as more importantly for scale-up studies. This is as in the latter application, larger particle sizes and more sintered particles are often used – both conditions where the D-SCM has performed better in this study compared to other models considered.

Steady-state design of scaled-up fluidized bed reactors and associated process flowsheets for a CSP-TCES plant using the $\text{CaO}/\text{Ca}(\text{OH})_2$ reaction system

FBRs and process flowsheets for the proposed $\text{CaO}/\text{Ca}(\text{OH})_2$ TCES system were designed based on reference specifications from an analytical literature study at 100 MW_{th} scale. The FBR for the exothermic hydration reaction was then designed and optimized based on the aforementioned specifications. By assessing the sensitivity of the design it was determined that a minimum reactor height of 10 m with a diameter of 3.5-5 m would yield the most effective reaction performance while minimizing particle losses through elutriation, while a bed mass of ~7000 kg provided the best trade-off between maximizing reaction conversion and heat released. Similarly the dehydration FBR was then designed and studied; this resulted in an optimal reactor diameter of 4 m but a taller reactor height of 14 m to counter the additional expected elutriation effects in the bed, while a bed mass of ~6500 kg was enough to store the required amount of heat while maintaining reaction conversion performance. Process flowsheets were then designed for steady-state simulation to account for pre- and post-reaction process requirements such as heating, storage, solar energy input and power generation systems.

Lastly, the power generation block was modelled using a pressurized steam Rankine cycle as it was identified as the most suitable design for a TCES process within this temperature range. A 3-stage cycle was designed achieving a η_{Rankine} value of 39%; this was identified as close to the maximum possible for the designed system due to the below-average boiler temperature of 411°C for the process. This resulted in a net electrical power output at steady-state of 49.8 MW from the designed $\text{CaO}/\text{Ca}(\text{OH})_2$ CSP-TCES plant.

Steady-state design of scaled-up fluidized bed reactors and associated process flowsheets for a CSP-TCES plant using the CMO redox reaction system

FBRs and process flowsheets for the proposed CMO redox TCES system were designed based on the previous $\text{CaO}/\text{Ca}(\text{OH})_2$ CSP-TCES plant design as reference with a target scale of $100 \text{ MW}_{\text{th}}$. The optimization for the designed FBR for the endothermic (charging) CMO reduction reaction was then conducted. It was identified that a minimum reactor height of 22 m with a diameter of 6 m and a bed mass of $\sim 22000 \text{ kg}$ would fulfil the design constraints and maximize the energy uptake and reaction conversions. Similarly the designed FBR for the exothermic (discharging) CMO oxidation reaction was then considered and its optimization results discussed. The resultant specification for the FBR that met the stipulated design constraints required a reactor height of 15 m with a diameter of 5.3 m and a bed mass of $\sim 18000 \text{ kg}$.

The power generation block was then designed and modelled using a supercritical CO_2 Brayton cycle as it was expected to offer greater thermal efficiencies than a traditional steam Rankine cycle and because the operating temperatures of the discharging flowsheet made the thermodynamics favorable to do so. A basic recompression Brayton cycle was design and implemented with specifications based recommendations from literature studies involving expansion of sCO_2 at 250 bar. The designed power cycle resulted in a net power output of 59.3 MW and a corresponding thermal efficiency of 47% which could potentially be further increased to approach 57% with optimized and more advanced designs for the Brayton cycle.

TVP simulation of process flowsheets of hypothetical CSP-TCES plants using the $\text{CaO}/\text{Ca}(\text{OH})_2$ reaction system and CMO redox reaction system

For the discharging processes, night-time operation resulted in the highest maximum power output of 48.9 MW_e but the lowest time-based average power output of 10.2 MW_e . Only scenario S1 was achievable on an annual basis through standalone operation as it required $345.9 \text{ GW}_{\text{th}}$ of energy discharged compared to the $363.2 \text{ GW}_{\text{th}}$ annually stored by the designed TCES process. An additional scenario S0 was then introduced and specified in order to produce a continuous operation scenario that allowed for standalone plant operation through TVP simulation. It was found that scenario S0 could be achieved through operating the CaO hydration discharging FBR continuously at 41.3% of maximum capacity. This resulted in the capability for constant power generation at 20.2 MW_e which gave the plant an average solar-to-electricity conversion efficiency of 16.8%. In the case of the CMO redox plant, for the discharging system it was found that all four dynamic operating scenarios (now including S0) resulted in higher maximum as well as average power outputs with scenario S1 having maximum and average power outputs of 58.8 MW_e and 12.3 MW_e respectively. The higher power outputs calculated here were attributed to the higher thermal efficiencies of the sCO_2 Brayton cycle designed for and employed in the CMO discharging flowsheet.

It was found that operating a continuous discharge process through scenario S0 while operating the plant on a standalone basis required the discharging FBR to operate at 43.1% of its optimal thermal output. This resulted in the potential for continuous power generation at 25.4 MW_e due to the use of the sCO₂ Brayton cycle and the associated solar-to-electricity conversion efficiency for the CMO redox TCES system was found to be 21.1% which placed it at the very upper limit of efficiencies achieved by existing CSP plants.

11 further locations were used to perform the TVP simulation studies for the two TCES processes. As standalone operation was the preferred operating criteria only scenarios S0 and S1 were considered for these locations and it was found that the modelled annual energy storage and electricity production volumes had a direct correlation with the annual average DNI for each location. 10 of the 12 locations achieved performances that were within $\pm 20\%$ of those for the initial case study situated in Seville which suggested that the designed CSP-TCES plants were robust enough to perform adequately despite variations pertaining to geographical factors and that the plants would be technically viable at a wide range of locations.

It was also noted that for the 2 locations exhibiting low DNI levels and shorter average daylight hours overall, the performance of the plants dropped significantly and it thus remained to be seen whether it would be economically viable to operate the plant at these locations either. When comparing the two TCES systems studied the CMO redox system was found to offer ~22% more electricity production than the CaO hydration system, while in terms of discharging operating scenario the batch-wise operation for scenario S1 yielded 9-11% more electricity production than scenario S0.

Techno-economic assessment of hypothetical CSP-TCES plants using the CaO/Ca(OH)₂ reaction system and CMO redox reaction system

Initial techno-economic calculations were performed for the Seville case study. For the CaO/Ca(OH)₂ CSP-TCES plant it was found that scenario S0 yielded marginally higher LCOE (14.2 c/kWh) and lower LCOS (6.3 c/kWh) values than S1 (14.0 c/kWh and 6.7 c/kWh respectively) due to producing less electricity over the course of a year (160 GWh vs 175 GWh). This result suggested that for the CaO/Ca(OH)₂ plant scenario S0 was more economically attractive as well as operationally more desirable due to being able to maintain continuous power generation purely through stored energy volumes on a standalone basis. The inherent uncertainty in the evaluation methodology was considered and this resulted in the expected LCOE being in the range of 12.0–36.0 c/kWh with the LCOS having a range of 5.3–15.9 c/kWh based on scenario S0.

An identical evaluation was conducted for both scenarios using the CMO redox plant. The calculated LCOE and LCOS were found to be similar for both operating scenarios with that for scenario S0 being 16.2 c/kWh and 8.8 c/kWh respectively. When factoring in the uncertainty the LCOE was found to be in the 14.2–39.9 c/kWh range while the LCOS was expected to be within 8.0–21.6 c/kWh. It was observed that the LCOE

and LCOS for the CMO redox plant were in both cases higher than that of the $\text{CaO}/\text{Ca}(\text{OH})_2$ plant and this trend was observed to hold across all locations considered. This meant that overall the $\text{CaO}/\text{Ca}(\text{OH})_2$ plant was the more economically attractive option despite the superior technical performance potential of the CMO redox plant although it is acknowledged that significant advancements in reactant materials for either process could affect this comparison in the near future.

The calculated LCOE and LCOS values across all 12 locations were then considered and it was observed that for 9 of the other locations the calculated costs fell within the uncertainty range of the Seville base case.. It was found that for the remaining 2 locations, Swindon and Ontario, the estimated LCOE and LCOS values were ~380% and ~450% higher than for the base case; with no cost savings offered at these locations the sole advantage of continuous power generation may not be a sufficient incentive for deployment.

The estimated LCOE and LCOS values were then compared with those of relevant alternative energy storage and power generation options based on clean and/or renewable energy technologies; here the values for Seville were used as the guideline. When compared with energy storage options, the CSP-TCES plant designs were found to be competitive with battery technologies as well as P2G, providing an attractive cost for both inter-day and inter-season energy storage capabilities. It was noted that both TCES and battery technologies are still steadily developing technologies and thus the expected costs for both could be expected to keep reducing in the future and that they cater to different purposes as TCES is a heat storage technology while batteries cater to electricity storage.

In terms of assessing the comparative performance of the LCOE of the plant designs the results were less distinct. While the CSP-TCES plants offered a slightly lower LCOE than solar PV with battery storage and also came in cheaper than industrial P2P systems. It was noted that despite the slightly higher costs, the designed plants importantly offered the advantage of continuous power generation capabilities that are not achievable through other technologies such as standalone solar PV or wind.

10.2 Recommendations for Future Work

In this final section several avenues for further investigation into the considered reaction systems and TCES process designs are explored. These were not pursued in the current work due to being outside the proposed scope of study or potentially requiring significant additional investigation efforts to thoroughly evaluate.

Further development of kinetic models for CaO hydration reaction

Despite showing good responsiveness and closeness of fitting after the updating of X_B and the incorporation of particle expansion considerations, the D-SCM could be still further developed to take into account any sintering that occurs over the course of reaction. This would be especially helpful for cycled experiments

and could lead to more accurate predictions over longer periods of cycled reactions, such as in thermochemical energy storage applications. The diffusion and kinetics controlled versions of the RPM could be adapted and merged, by means of a prediction weighting factor or otherwise, in order to account for transitions between the two regimes that occur over the course of a reaction. The two versions showed very responsive fits to the experimental data across a range conditions and could point toward a possible more accurate combined model.

The D-GCM's theoretical development could be revisited to assess the author's definition for ΔP_h in order to improve the model's responsiveness to different steam concentrations as although efforts were made in this work, the results at higher reaction temperatures indicated significant room for improvement in this regard. This would supplement the fact that it already accounts for particle expansion and heat and mass transfer resistances in the fluidised bed which had not been treated significantly by the other models.

Development of supported CaO materials for hydration in fluidized beds

The superior cycling stability exhibited by the supported CMOs were observed to have significant impacts on the economic performance of the TCES process when the CMO redox reaction was used as a relatively low fresh material feed rate was required despite the high costs of the material. Conversely the despite the much lower costs of fresh CaO and Ca(OH)₂, relatively large fresh feeds were required by the designed TCES process to account for regular deactivation and deterioration of the unsupported material.

In the study and pilot-scale testing of CCS and TCES processes using the carbonation reaction of CaO, several supported forms have been prepared and tested on suitably large scales.²²⁶ There is thus scope to perform experimental studies to determine the stability of these and other potential supported forms of CaO when subject to the hydration reaction under fluidized conditions. These would then allow for techno-economic reevaluation of the CSP-TCES plant designs involving the CaO hydration reaction system using a more mechanically and chemically durable reacting material.

Influence of sensible heat re-integration on CSP-TCES plant performance

While considering the superior fundamental capabilities of TCES as opposed to more basic heat storage technologies it was realized that there may be further untapped potential for energy storage and discharge capabilities in TCES processes by way of effectively using the material streams in the discharging process for preheating feed streams in the charging process and thus increasing the volumes of heat stored. While energy integration within each process flowsheet has been considered and is a standard element of design, inter-process energy integration for TCES processes have not been explored until recently.

Recent exploratory studies by Wang et al.²²⁷ investigating this possibility using the CaO carbonation reaction for a combined CSP-TCES 100 MW_{th} plant design using plug flow reactor designs in a steady-state simulation and reported that thermal efficiencies for the charging and discharging processes could be improved by 45.1% and 32.1% respectively. Such efficiency increases if replicable for plant designs using FBRs and the CaO/Ca(OH)₂ or CMO redox systems studied in this work could result in significant improvements to their techno-economic performance and commercial viability.

Alternative and advanced power cycle designs for CSP-TCES discharging flowsheets

It was noted that non-optimized power generation cycle designs were implemented for producing preliminary techno-economic performance estimates. For the CaO/Ca(OH)₂ discharging process a pressurized steam Rankine cycle was employed which is a standard base case design. For the relevant operating temperatures, other power cycle designs are also known to be suitable such as a supercritical steam Rankine cycle that may potentially offer superior thermal efficiencies for the power generation step.

Likewise for the CMO redox discharging process, a basic recompression sCO₂ Brayton cycle design was used for the same reasons however it is known that a variety of more complex and more thermally efficient Brayton cycle designs can be employed such as with inter-stage cooling, reheating, and regeneration subsystems. The incorporation of these more advanced power cycle designs into the discharging flowsheets for the designed plants would yield significant improvements in their power outputs, thermal efficiencies but the economic implication of doing so is something that has not yet been evaluated in the literature.

Alternative discharge schedule scenarios for CSP-TCES discharging flowsheets

Although three batch-wise and continuous discharging scenarios were considered and evaluated in this work, it was acknowledged that they did not fully represent the wide range of realistic discharge scenarios often used by intermittent power generation sources to maximize their utility from a grid perspective. Additional batch-wise discharge scenarios such as pre-scheduled high-volume discharge based on consumer demand trends are often used to supply power to the grid during windows of high demand such as on weekday mornings and evenings; a role typically served by fossil fuel-consuming ‘peaker’ plants.

However as operating during these windows also offers greater revenue through increased electricity prices, there is significant scope for exploring the operation of the designed FBR-based CSP-TCES plants according to such operating schedules as well which could serve as a way to cost-optimize the balancing of a baseline continuous power output and windows of high-volume power generation.

Nomenclature

Roman letters

A	Pre-exponential factor [1/s]
A_E, B_E	Fitting parameters for mass flow elutriation
A_{HS}	Size of heliostat field [m ²]
$A_t(H_B)$	Cross-sectional bed area [m ²]
Ar	Archimedes number
C	BET constant
C	Concentration [mol/m ³]
C_P	Purchased cost [\$]
d	Diameter [m]
D_e	Effective diffusion inside particles
D_m	Gravimetric energy density [kWh/kg]
D_V	Volumetric energy density [kWh/m ³]
E_a	Activation energy [kJ/mol]
E_f	Effectiveness factor [m]
$f_{L,TDC}$	Lang factor
g	Acceleration due to gravity [m/s ²]
H_1	Heat of adsorption of the adsorbing gas species onto a surface
H_r	Specific heat of reaction [kJ/mol]
H_v	Heat of condensation of liquid adsorbate
HP	High pressure turbine
IP	Intermediate pressure turbine
k	Reaction rate [s]
k_a	Apparent reaction rate [/s]
k_g	Mass transfer coefficient [m/s]
L_o	Total overlapping pore length [m]

LP	Low pressure turbine
M	Relative molecular mass [g/mol]
$\dot{m}_{e,i}$	Elutriated mass flow [kg/s]
N	Cycle number
n	Number of moles [-]
N_A	Avogadro's number [-]
N_{Bi}	Biot number [-]
P	Pressure
P	Pressure [bar]
$p(O_2)$	Partial pressure of O_2 [bar]
Q	Heat energy transferred [kJ, MJ, GJ]
R	Universal gas constant [J/mol/K]
R	Radius [m]
R_{BI}	Beam Irradiance [W/m ²]
r_C	Unreacted core radius [m]
r_S	Particle shell radius [m]
Re	Reynolds number [-]
S	Specific surface area [m ² /g]
S_o	Reaction surface area [m ²]
T	Temperature [°C, K]
t	Time [s]
t_d	Dead time [s]
u	Gas velocity [m/s]
v	Volume of adsorbed gas per unit mass of adsorbant [cm ³ /g]
V	Volume of stored material [m ³]
W	Molar flux [mol/m ² /s]
X	Conversion [-]

Greek letters

α	Particle expansion ratio [-]
ε	Porosity [-]
η_{HS+R}	Combined efficiency of heliostat and receiver
η_p	Thermal efficiency [%]
θ	Fitting parameter for random pore model [$h^{0.5}$]
μ	Kinematic viscosity [m^2/s]
ν_o	Pore volume distribution
ρ	Density [kg/m^3]
σ_0	Total area of adsorption sites [m^2]
Φ_X	Thiele modulus [-]
Ψ_K	Pore structure parameter [-]
ω	Fitting parameter for random pore model [$1/h$]

Superscripts

0	Initial conditions
B	Bulk
$dehyd$	Dehydration
e, E, eq	Equilibrium
f	Fluid
H	High
h, hyd	Hydration
i	For species i
i, m	Mixed stream measurement for species i
L	Low
mf	Minimum Fluidization
N	Cycle number
ox	Oxidized

<i>p</i>	Partial Pressure
<i>po</i>	Pore
<i>R</i>	Heat releasing process
<i>r</i>	Residual
<i>red</i>	Reduced
<i>S</i>	Heat storing process
<i>s</i>	Solid
<i>sat</i>	Saturation
<i>w</i>	Water

Abbreviations

<i>AFBR</i>	Atmospheric pressure fluidized bed reactor
<i>AOC</i>	Annual operating cost
<i>BET</i>	Brunauer, Emmett, and Teller
<i>BJH</i>	Barrett, Joyner, and Helenda
<i>CCS</i>	Carbon capture and storage
<i>CCU</i>	Carbon capture and utilization
<i>CEPCI</i>	Chemical Engineering Plant Cost Index
<i>CFD</i>	Computational fluid dynamics
<i>CHP</i>	Chemical heat pump
<i>CMO</i>	Mixed metal oxides comprising of 1:1 molar ratio of CuO and Mn with an average molecular formula of $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$
<i>CSP</i>	Concentrated solar power
<i>CST, CSTR</i>	Controlled stirred tank
<i>DAC</i>	Direct air capture of CO_2
<i>DNI</i>	Direct normal irradiance
<i>EOR</i>	Enhanced oil recovery
<i>FBR</i>	Fluidized bed reactor
<i>GHG</i>	Greenhouse gas emissions

<i>GOF</i>	Goodness-of-fit testing
<i>HTF</i>	Heat transfer fluid
<i>ID</i>	Internal diameter
<i>IGCC</i>	Integrated gasification combined cycle
<i>LC</i>	Limestone from Longcliffe Quarries
<i>LCOE</i>	Levelized cost of electricity production
<i>LCOS</i>	Levelized cost energy storage
<i>MMO</i>	Mixed metal oxides of any description
<i>MOF</i>	Metal-organic framework
<i>OD</i>	Outer diameter
<i>OFC</i>	Oxyfuel combustion
<i>PC</i>	Post-combustion
<i>PID</i>	Proportional-Integration-Derivative
<i>PSD</i>	Particle size distribution
<i>PV</i>	Photovoltaics
<i>RH</i>	Relative humidity
<i>SEM</i>	Scanning electron microscopy
<i>TCES</i>	Thermochemical energy storage
<i>TCI_{annual}</i>	Total capital investment, annualized
<i>TDC</i>	Total depreciable capital
<i>TDH</i>	Transport disengagement height
<i>TES</i>	Thermal energy storage
<i>TGA</i>	Thermogravimetric Analysis
<i>TPI</i>	Total permanent investment
<i>TRL</i>	Technological readiness level
<i>WC</i>	Working capital
<i>XRD</i>	X-ray diffraction
<i>XRF</i>	X-ray fluorescence spectroscopy

Appendix

Appendix A.1 - Cross Flow Factor Calculations

Estimates of the cross flow factor were made to better understand the degree of mixing present in the AFBR setup; this was done according to a method presented by Zhang et al.¹⁵³. The cross flow factor was calculated according to Eq. A-1 and A-2 catering for a first-order reaction taking place in a two-phase reactor model of a bubbling fluidized bed – a model proposed by Davidson and Harrison²²⁸.

$$\frac{C_{out}}{C_{in}} = \beta_u e^{-X_f} + \frac{(1 - \beta_u e^{-X_f})^2}{k' + 1 - \beta_u e^{-X_f}} \quad (A-1)$$

$$\text{Where } \beta_u = 1 - \frac{u_{mf}}{u} \quad (A-2)$$

In Eq. A-1 and A-2, X_f is the cross flow factor, C_{in} and C_{out} are the reactor inlet and reactor outlet concentrations, respectively, Q denotes the volumetric flow, and k' is the velocity constant of reaction in dimensionless form.

To estimate X_f , the C_{out}/C_{in} ratio was calculated for reactions involving reactant samples of varying mass. For more readily relating the sample mass to the cross flow rate, Eq. A-1 was rearranged as Eqn. A-3.

$$\frac{C_{out}}{C_{in}} = \beta_u e^{-X_f} + \frac{(1 - \beta_u e^{-X_f})^2}{\frac{k_o w}{V_{pp} Q \rho_{CaO}} + 1 - \beta_u e^{-X_f}} \quad (A-3)$$

$$\text{Where } \frac{k'}{w} = \frac{k_o H_{mf}}{U} = \frac{k_o}{V_{pp} Q \rho_{CaO}} \quad (A-4)$$

$$\text{And } V_{pp} = \frac{w}{\rho_{CaO} H_{mf} A} \quad (A-5)$$

In Eq. A-3, k_o is the observed rate constant, w is the mass of reactant sample introduced into the bed, V_{pp} denotes the total volume of particles per unit volume of the overall particulate phase as per the two-phase model, and H_{mf} gives the estimated height of the fluidized bed at minimum fluidization conditions. The SOLVER functionality in Microsoft Excel was used to vary X_f until Eqn. A-3 yielded the best fit to the experimental data comparing C_{out}/C_{in} vs w . This made use of the least-squares fitting method and yielded a cross flow factor of 16.31, which indicates that the system in the AFBR undergoes a high degree of mixing during reaction.

Appendix A.2 – Rotameter and RH Probe Calibrations

Fig. A-1 shows the calibration curves for the two rotameters used in the set-up. While the curves provide important information by themselves, noting of the range of calculated flowrates was of consequence in determining the range of producible steam concentrations. Table A-1 shows the flowrates used and data obtained from the RH probe calibration experiments. Curve fitting was used to produce the correlation in Fig. A-2 which was then implemented as a calculation step in the reactor control programme. The probe temperature during the experiments was maintained at 113.3°C for consistency.

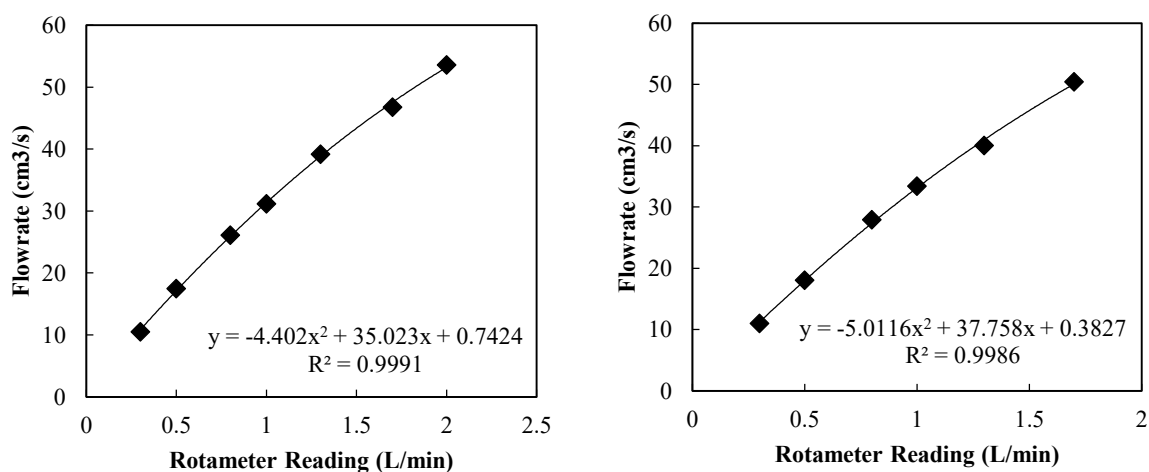


Fig. A-1: Calibration curves for rotameters to steam generator (left) and reactor (right)

Table A-1: RH probe calibration points and results

H ₂ O flowrate (g min ⁻¹)	N ₂ flowrate (cm ³ s ⁻¹)	Measured Voltage (V)
0.00	60.0	2049
0.09	57.7	2079
0.28	54.0	2179
0.49	48.0	2309
0.72	41.5	2444
0.97	35.2	2579

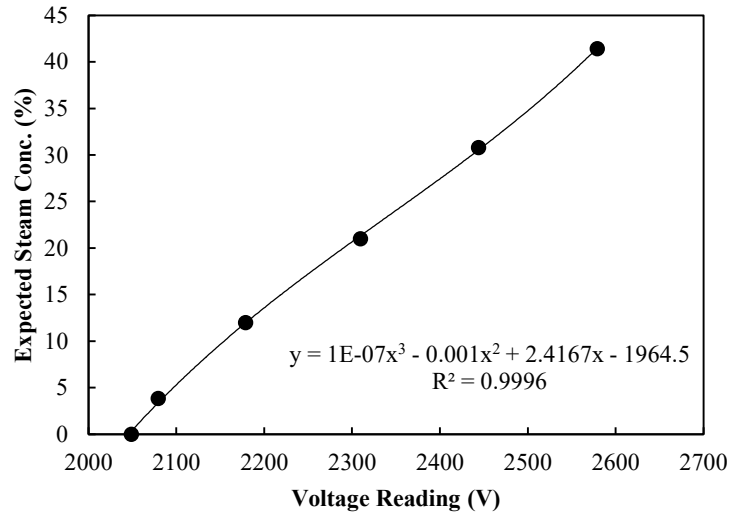


Fig. A-2: Calibration curve for RH probe

Appendix A.3 – MATLAB Scripts for evaluating the D-SCM

1. K2_fit.m

function output = k2_fit(k2,input)

output = (-1*k2) + (input(:,10) .* input(:,13) .* (1-input(:,14)) ./ (1-input(:,8)) ./ input(:,15) ./ input(:,12) ./ (input(:,18)-input(:,16))) ./ input(:,11);

This script determines the k_2 values from the data input from the user. This script is run automatically from the “SimplifiedModel.m” file.

2. Modelout2.m

function F = modelout2(vars,consts)

aX_S = vars(:,1);

aX_C = vars(:,2);

aX_CaO2H2 = vars(:,3);

ar_rat = (1 - aX_CaO2H2).^(1/3);

adXCaO2H2_dt = vars(:,4);

at = consts(:,3);

ak_g = consts(:,4);

aX_B = consts(:,5);

aD_e = consts(:,6);

ar_0 = consts(:,7);

```

aM_CaO = consts(:,11);
aC = consts(:,12);
arho_CaO = consts(:,13);
aeps_CaO = consts(:,14);
aS_0 = consts(:,15);
aX_E = consts(:,16);
ak_2 = consts(:,20);
a_XCaO2H2less1 = consts(:,21);
adXCaO2H2_dtless1 = consts(:,22);
atless1 = consts(:,23);
F(:,1) = ((-1) .* adXCaO2H2_dt) + (3 * ((1 - aX_CaO2H2).^(2/3)) .* aM_CaO .* aC .* aD_e .* log ((1 -
aX_S)./(1 - aX_C)) ./ (ar_0 .* (((ar_rat.^2)) - (ar_rat)))) ./ arho_CaO ./ (1 - aeps_CaO) ./ ar_0);
F(:,2) = ((ak_g .* (aX_B - aX_S))) - (aD_e .* log ((1 - aX_S)./(1 - aX_C)) ./ (ar_0 .* (1 - (1./ar_rat))));
F(:,3) = (-1 * ak_2) + (adXCaO2H2_dt .* arho_CaO .* (1-aeps_CaO) ./ (1 - aX_CaO2H2) ./ aS_0 ./ aC ./
(aX_C-aX_E)) ./aM_CaO;
F(:,4) = a_XCaO2H2less1 + trapz([atless1 at], [adXCaO2H2_dtless1 adXCaO2H2_dt]) - aX_CaO2H2;

```

This script solves the 4 ODEs by using the data created from the “*SimplifiedModel.m*” file which is used to create the model data for SCM. This script is run automatically by the “*SimplifiedModelPredictions.m*” file.

3. SimplifiedModel.m

```

%% Create variable 'data_exp' and copy Excel data into it!
data_vars = zeros (length(data_exp),2);
data_vars(:,1) = data_exp(:,5) - 0.0001;
data_vars(:,2) = 0.0001;
%% Introduce the model
% For fsolve:
%options = optimset('TolFun',1e-14);
options = optimset('TolFun',1e-14, 'MaxFunEvals', 1000000000000);
%options = [];
[tempdat1 , fv1 , exitfl1 , outp1] = fsolve (@scmeqs2012_1,data_vars,options,data_exp);

```

This script runs the “*K2_fit.m*” program to evaluate the K_2 for each data point this is a value used to evaluate the equations in the ODE solver provided in “*Modelout2.m*” script.

```

t_f = length (data_out)-1;
t_int = 1;
options = optimoptions('lsqnonlin','MaxFunEvals',40000,'TolFun',1e-14);
data_model = zeros((t_f/t_int)+1,27);
for i = 1:length (data_model)
    data_model (i,1:20) = [data_out(i,:) k2];
end
data_initialrate = data_model (1,20) * data_model (1,11) * data_model (1,15) * data_model (1,12)*
(data_model (1,5) - data_model (1,16))/ data_model (1,13)/ (1-data_model (1,14));
data_model (1,21:27) = [0 0 0 data_model(1,5) data_model(1,5) 0 data_initialrate];
j = 2;
while j <= ((t_f/t_int)+1)
    data_model (j,3) = (j-1)*t_int;
    data_model (j,21) = data_model (j-1,26);
    data_model (j,22) = data_model (j-1,27);

```

```

data_model (j,23) = data_model (j-1,3);
lb = [0 0 0 0.00001];
ub = [1 1 1 1];
x0 = [0.1 0.1 0.1 0.1];
[tempdat2] = lsqnonlin(@modelout2,x0,lb,ub,options,data_model(j,:));
data_model (j,24) = tempdat2(1);
data_model (j,25) = tempdat2(2);
data_model (j,26) = tempdat2(3);
data_model (j,27) = tempdat2(4);
data_model_outputs.tempdat (j,:) = tempdat2;
%data_model_outputs.fv (j,:) = fv2;
%data_model_outputs.exitflags (j,:) = exitfl2;
%data_model_outputs.outputs (j,:) = outp2;
%data_model_outputs.iterations (j,:) = outp2.iterations;
%data_model_outputs.funcCount (j,:) = outp2.funcCount;
%data_model_outputs.firstorderopt (j,:) = outp2.firstorderopt;
%if data_model (j,26) >= 0.95
% data_model = data_model (1:j,:);
% j = ((t_f/t_int)+1);
%else
%end
j=j + 1;
end

```

This script runs the ODE solver and generates the output values and stores it in the variable `data_model`. The ODE solver, least non-linear (`lsqnonlin`), was used to ensure that the ODEs were being solved to a complete set of iterations (an issue observed in the standard `fsolve` ODE solver). It is an algorithm that allows the user to set the upper and lower bounds to a solution allowing the ODE solver to function in a more defined range. The initial guess of the ODE is recommended to be 0.1 first 3 variables, but for ‘dx/dt’ a value of 0.06 ± 0.03 is recommended to produce curves that maintain a stable curvature, comparable to the experimental data set.

Appendix A.4 – AFBR support structure

In addition to the newly-designed system components in Sections 3.1.1 and 3.1.3, a new support frame for the reactor and its downstream process was also designed and constructed as visible in the schematic in Fig. A-3. The reactor with attached electrodes and cabling weighs over 10 kg hence ensuring a sturdy support is in place was deemed vital for safety purposes as well as reducing maintenance concerns. This new profile suspended the reactor using L-profiles mounted atop the frame and secured directly by the electrodes.

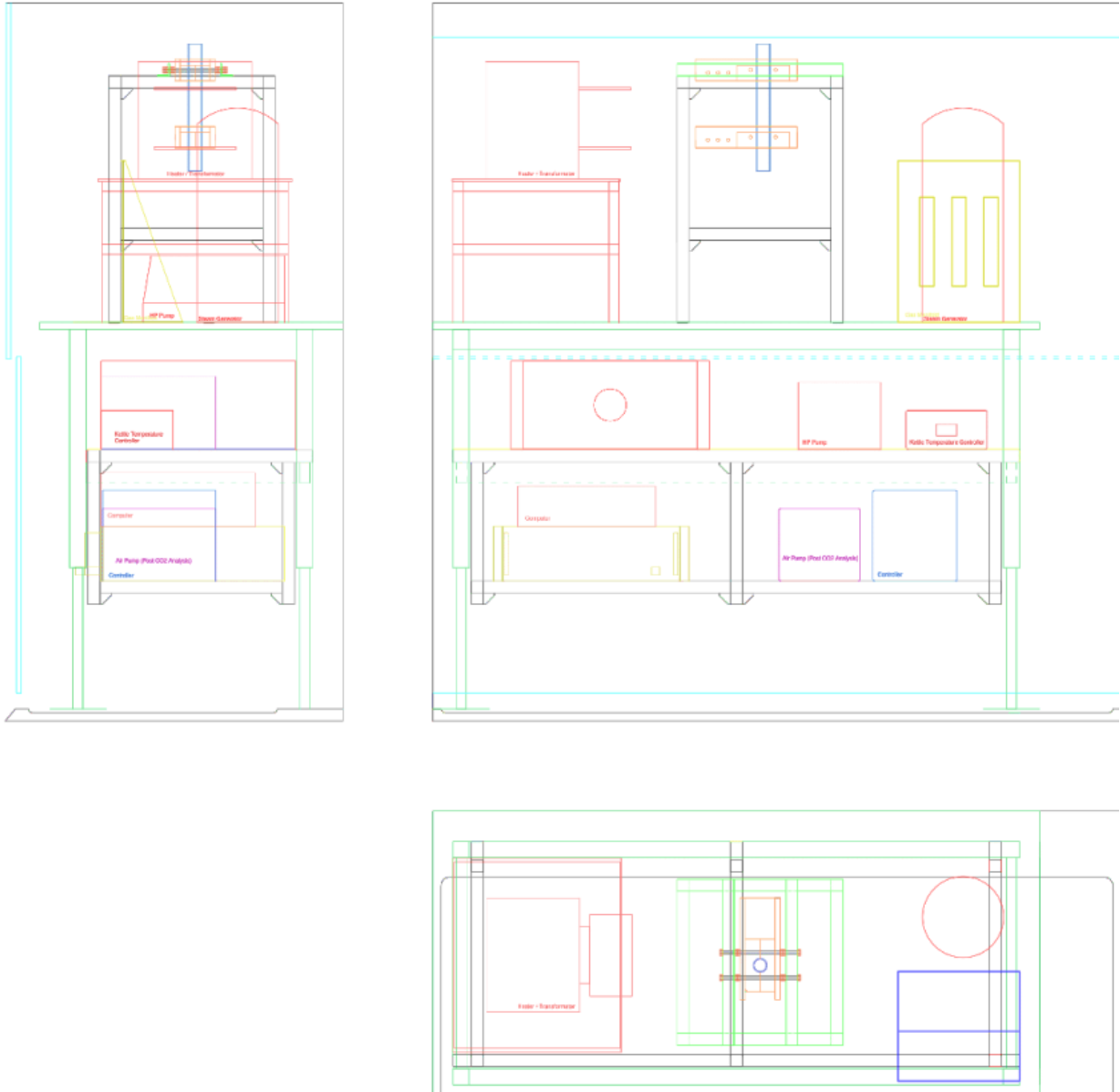


Fig. A-3: Layout of the AFBR, structural support, and associated experimental equipment³¹

Appendix A.5 – Heat capacity estimation for CMO and CFO materials

The Neumann-Kopp rule (NKR)^{229, 230} is often used to obtain estimates of the specific heat capacity of metal-based compounds and alloys. A developed form of the NKR (Eq. A-6 and A-7) specifically for MMO applications involving two individual precursor oxides (aAO and bBO) was produced by Leitner et al.¹⁸⁵ to account for the increased contributions from lattice dilation and variations in thermal expansion and compressibility coefficients (collectively represented by ΔC_{dil}), thus making it more suitable for high temperature calculations. In Eq. A-6, α and β represent the thermal material expansion and compressibility coefficients respectively.

$$\Delta C_{dil} = -T x_A x_B \left(\frac{\beta_A \beta_B}{\beta_{AB}} \right) \left(\frac{V_{m,A} V_{m,B}}{V_{m,AB}} \right) \left(\frac{\alpha_A}{\beta_A} - \frac{\alpha_B}{\beta_B} \right)^2 \quad (A-6)$$

$$C_{p,m}(A_{x_A} B_{x_B} O_z) = x_A C_{p,m}(AO_a) + x_B C_{p,m}(BO_b) + \Delta C_{dil},$$

$$z = x_A a + x_B b, \quad x_A + x_B = 1 \quad (A-7)$$

Comparisons with experimentally measured heat capacities of several MMOs showed only a ~4% deviation¹⁸⁵ in the predicted values from the developed NKR even at temperatures above 1000 K. Due to the high accuracy of these calculations, the modified NKR was also employed here to estimate the heat capacity of the CMO material and compared with estimates for the CFO material treating them to be formed from equimolar mixtures of CuO and MnO or FeO respectively. Pertinent thermochemical data for pure oxide materials were obtained from various literature datasets.^{231, 232}

Appendix A.6 – The correlations used for the calculation of the viscosity and density of gas mixtures

For the conditions used in the CMO oxidation process, the density of pure N₂ was modelled by Eq. A-8:

$$\rho_{N_2}(kg/m^3) = -0.33685 \left(T/T_0 \right)^3 + 1.3745 \left(T/T_0 \right)^2 - 2.0803 \left(T/T_0 \right) + 1.3837 \quad (A-8)$$

In Eq. A-8, T is the temperature of the gas in K and T_0 is the reference temperature of 1000 K.

The density of the mixture containing O₂ and N₂ ρ_g , was correlated by Eq. A-9:

$$\rho_g(kg/m^3) = 1 + a_1 y_{O_2} + \frac{a_2 y_{O_2}}{T/T_0} + a_3 y_{O_2} (T/T_0) + a_4 y_{O_2} (T/T_0)^2 \quad (A-9)$$

In Eq. A-9, y_{O_2} is the molar fraction of O₂, and a_i with $i = 1$ to 4 are unique coefficients which are listed in Table A-2. The values for a_i were sourced obtained from calculations by Patzschke.²⁷

The calculations for dynamic viscosity of the oxidizing gas mix were done similarly. Firstly, the viscosity of pure N₂ was correlated by Eq. A-10 with $T_0 = 1000$ K.:

$$\eta_{N_2}(\mu Pa \cdot s) = -5.2375 \left(\frac{T}{T_0} \right)^2 + 37.704 \left(\frac{T}{T_0} \right) + 9.0743 \quad (A-10)$$

The viscosity of the gas mixture containing O₂ + N₂, η_g , was then correlated by Eq. A-11:

$$\eta_g(\mu Pa \cdot s) = 1 + a_1 y_{O_2} + a_2 y_{O_2} \left(\frac{T}{T_0} \right) + a_3 y_{O_2} \left(\frac{T}{T_0} \right)^2 + a_4 y_{O_2}^2 \quad (A-11)$$

The parameters for Eq. A-11 were also calculated by Patzschke²⁷ and are reported in Table A-2.

Table A-2: Parameters for Eq. A-9 and A-11 to correlate the density and viscosity of the gas mixtures containing O₂ or N₂.

Property	Mixture	Parameter			
		a ₁	a ₂	a ₃	a ₄
ρ	N ₂ + O ₂	$1.4091 \cdot 10^{-1}$	$4.8109 \cdot 10^{-4}$	$1.9290E \cdot 10^{-3}$	$-9.1980 \cdot 10^{-4}$
η	N ₂ + O ₂	$2.0783 \cdot 10^{-1}$	$-3.8712 \cdot 10^{-3}$	$-5.9836 \cdot 10^{-3}$	$-1.6331 \cdot 10^{-2}$

Appendix A.7 – N₂ Porosimetry Background

Fig. A-4 shows the sorption analyser unit used. Fig. A-5 shows a typical nitrogen adsorption isotherm in the case of calcined limestone, presenting the volume of gas adsorbed by the sample against the proportion of actual gas pressure versus the vapour pressure of the adsorption species, with temperature kept constant at -196°C.

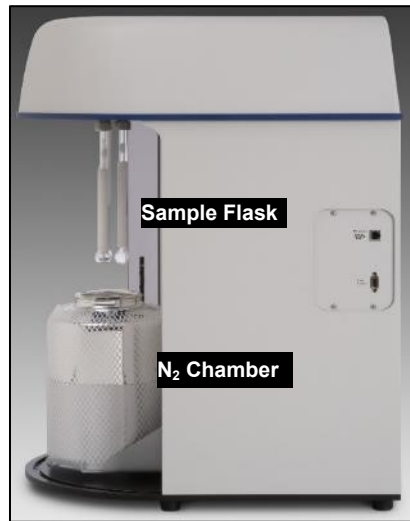


Fig. A-4: Tristar 3000 Unit used for N₂ porosimetry of calcined limestone samples

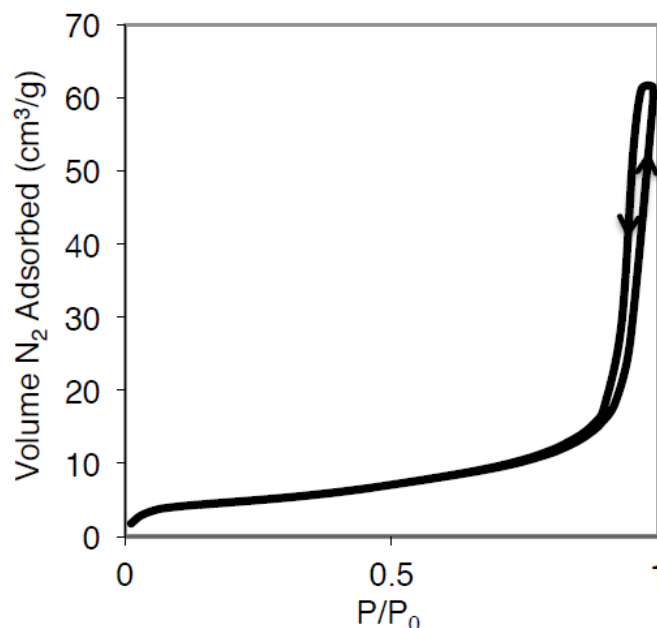


Fig. A-5: Sample nitrogen adsorption isotherm for calcined limestone¹¹⁶

The behaviour illustrated by the adsorption isotherm for calcined limestone is consistent with one of the six common patterns described by Brunauer²³³, in this case Type 4, usually corresponding to a sample of a porous adsorbant that possesses relatively large pores. The adsorption process is always exothermic, with an increasing amount of material adsorbed with increasing pressures and decreasing temperatures. In practice, nitrogen adsorption isotherms can be produced by gradually increasing the pressure of nitrogen gas immediately above a sample and measuring the resultant volume of adsorbed gas, until the vapour pressure of nitrogen is reached; after which the nitrogen pressure is gradually decreased in the same manner. For a material exhibiting a Type 4 isotherm, the initial trend observed is that for low pressures, the adsorbed gas volume increases rapidly as the gas pressure increases due to a monolayer of adsorbed nitrogen forming on the surface of the material; the rate of adsorption decreases as this monolayer fills up. This is only observed for a small pressure range; usually for $p/p_0 \leq 0.1$. Subsequently for a large pressure range (typically $0.1 \leq p/p_0 \leq 0.8$) a more steady increase in the volume of adsorbed nitrogen is observed as multilayers of adsorbed gas form on the material surface; following this a sharp increase in adsorbed volume is brought about due to the onset of bulk condensation of the adsorbing gas into the liquid phase.

The discrepancy in the latter stage of adsorption visible in Fig. A-5 is a hysteresis loop indicative of a porous material where capillary condensation of the adsorbing gas takes place; gas adsorption onto a pore accumulates on the pore walls forming a liquid condensate with decreasing diameter, while gas desorption initially begins from the surface of the condensed liquid which has a different curvature to the pore walls.

This results in evaporation being inhibited which causes the desorption curve to lag compared to the adsorption curve up until the point when all pores in the material have been emptied of previously adsorbed gas. The hysteresis loop is not in fact a closed loop – in this case the upper limit is solely a result of deliberately switching the operation from adsorption to desorption – which implies that there is no upper limit on pore size for such materials²³⁴. Estimates for the porosity and the surface area of a material can be calculated directly from the data available in the adsorption isotherm; in this case the BET and BJH approaches were used for doing so.

Appendix A.8 – Brunauer-Emmett-Teller (BET) Surface Area

The work done by Brunauer, Emmett, and Teller²³⁵ in this area built upon prior work by Langmuir²³⁶ which assumed that gas adsorption onto a surface stopped upon completion of a monolayer, by expanding it to describe a multilayer adsorption process. In Langmuir's work the two fundamental assumptions are that the evaporation rate is directly proportional to the number of occupied adsorption sites, and that the condensation rate is directly proportional to the number of unoccupied adsorption sites – with both being at equilibrium. In developing this, Brunauer et al.²³⁵ considered the condensation and evaporation rates onto each layer separately. Using the assumptions that the heat of adsorption and the adsorption rate constants to be identical for every layer except the initial monolayer – in essence, excluding the only instance where the adsorbing gas molecules interact with the adsorbant surface instead of other adsorbed molecules – they produced Eq. A-12 – A-13.

$$\frac{v}{v_m} = \frac{n}{n_m} = \frac{cp/p_0}{(1-p/p_0)[1+(c-1)p/p_0]} \quad (\text{A-12})$$

$$c = e^{(H_1-H_v)/RT} \quad (\text{A-13})$$

In Eq. A-12, v is the volume of adsorbed gas per unit mass of adsorbant, n is the number of moles of adsorbed gas per unit mass of adsorbant (for both quantities, the subscript m denotes the adsorbed extent on a complete layer per unit mass of adsorbant), p is the actual gas pressure, p_0 is the condensation pressure of the adsorbing gas, and c is the BET constant described by Eq. A-13 where H_1 is the heat of adsorption of the adsorbing gas species onto the surface in the case of the initial monolayer and H_v is the heat of condensation of the liquid adsorbate.

By inspecting Eq. A-12 a straight line plot is directly obtainable by plotting $(p/p_0)/n(1 - p/p_0)$ against p/p_0 which would then allow calculation of n_m , v_m , and thus also c . These quantities can then be used to calculate the specific surface area of the solid, S , using Eq. A-14.

$$n_m = \frac{S}{N_A \sigma_0} \quad (\text{A-14})$$

In Eq. A-14, σ_0 refers to the total area of an adsorption site and N_A is Avogadro's Number. The BET calculation method to obtain a surface area estimate typically returns the best results when considered for the range $0.05 \leq p/p_0 \leq 0.3$ according to previous findings (230). In this analysis, the BET method has been applied to all data for the more conservative range $0.05 \leq p/p_0 \leq 0.2$ to ensure that only the monolayer is being considered. This caution is necessary as exceeding this range increases the chance of overestimation of the surface area by inadvertently considering the multilayer adsorbed deposits of gas.

Appendix A.9 – Barrett-Joyner-Halenda (BJH) Pore Volume Distribution

Separately, work done by Barrett, Joyner, and Halenda²³⁷ produced a method to calculate pore volumes and surface area distributions directly from adsorption isotherms by investigating the desorption data contained in them. In this method, step-wise decreases in p/p_0 and the corresponding changes in volume of adsorbed gas are both related to two adsorption mechanisms: physical adsorption taking place on pore walls and capillary condensation occurring in the inner capillary volumes. For mathematical simplicity, the pore shapes are considered as cylinders. Through doing this, the adsorption layer thickness on the pore walls can be determined by an equation proposed by Halsey²³⁸ and subsequently the capillary thickness can be determined through an equation proposed by Lord Kelvin²³⁹.

Appendix A.10 – FBR Analytical Models

A variety of approaches have been taken in the literature for analytically modelling fluidized beds specifically in the context of TCES, based on FBR fundamentals and various assumptions made to simplify their treatment. Sometimes this results in considering them as completely different reactor designs by name which offer greater ease of computation due to their fundamental equations.

One popular approach for bubbling FBRs are the use of K-L-models.¹⁵⁹⁻¹⁶¹ In these models, the reactor is considered to comprise of two phases: a dense phase (emulsion) and a lean phase (bubbles), and heat and mass transfer take place within either phase and across both phases. Being a mass transfer-focused model, the K-L-model is well-suited for handling reactions where the gas phase composition varies across the emulsion and bubble phases, such as in the $\text{CaO}/\text{Ca}(\text{OH})_2$ system under certain conditions.

The K-L-model as introduced in Chapter 6, is among the most widely-used, however it is not always suitable. If there are no variations in the gas phase compositions, however, then the main advantage of the K-L-model becomes redundant and if homogeneous gas and solids temperature distributions are assumed, it effectively becomes a continuously stirred tank (CSTR) model which is a fundamentally different reactor design compared to the FBR. The assumptions further incorporated through this approach are: that the bed is always perfectly mixed with no local fluctuations; that there is no temperature gradient in either the solid or gas phases; and that the reaction is operating at steady-state. These assumptions are significant ones to

make and importantly are not representative of reactions performed under TCES conditions; the regular startup and shutdown required for running a TCES process for CSP mean that significant portions of the reaction regimes are going to involve non-homogeneous temperature and concentration gradients in the system and thus non steady-state operation. However they were a first step towards tackling the complex computation of FBR systems.

Another increasingly common approach is the use of computational fluid dynamics (CFD) via various modelling software packages. This is a heavy duty and rigorous approach used for modelling a wide variety of complex fluid mechanics scenarios such as for aviation aerodynamics modelling, weather simulation, biological flow modelling, and combustion engine modelling. With the high level of specificity involved in models used in CFD, detailed description and modelling of individual particles within a fluidized bed can be done, and various studies in the literature have employed this to model FBRs in a variety of contexts such as biomass gasification²⁴⁰, catalytic cracking²⁴¹, and chemical looping²⁴².

Given the availability of sufficient computational power, the assumptions made in using the K-L-models do not need to be made and thus fundamentally more accurate models of FBRs can be produced through the use of CFD which also account for physical reaction phenomena such as particle elutriation and the production and travel paths of bubbles within the bed, in addition to more complex considerations such as the spatial distribution of intermediates and side-products in more complex reaction systems.

However the required computational power to perform CFD for fluidized beds with ease is not yet commonplace and every instance requires bespoke mathematical models adapted specifically for the particular phenomenon being modelled which increases the complexity of this approach if used for exploratory study of a range of reaction systems such as that conducted in this work. Furthermore, while well suited for detailed and rigorous study of the reaction within the reactor unit itself, CFD simulations are difficult to connect with and integrate into other process design tools where the study of the overall process is desired. This means that though CFD simulations can handle non-steady-state reactors, it is impractical to simulate non-steady-state processes incorporating those reactors and thus at present this approach is best suited purely for studying the reactor unit.

Appendix A.11 – FBR Approximations in Aspen Plus Simulations

Most commonly in the literature, coal and/or biomass gasification²⁴³⁻²⁴⁶ are the main processes which have been most often studied using FBRs as their complex reaction systems mean that more conventional reactor designs are not as suitable and their industrial deployment already involves such a reactor configuration. To this end, Aspen Plus, which is a process simulation software has been used for this approach consistently for two decades as it is an industry-standard flowsheeting tool which can perform both steady-state and

dynamic process simulations and handle solids, liquids, gases, and mixed-phase process streams and allows for customizable kinetics and process units to be integrated through *Fortran* coding blocks. This makes it a suitable compromise between the rigorous but sandboxed reactor simulation capabilities of CFD and the simplified but widely-employable results of analytical reactor models, especially with the added convenience of flowsheet integration for studying the complete process.

While for conventional reactor types (plug flow reactors, CSTRs, etc.) the use of Aspen Plus is relatively straightforward, it has often been much more cumbersome to simulate FBRs in this software as no unit process options for doing so were available until recently due to the complex nature of the required underlying calculations. However, it was still used for such studies likely due to its overall flowsheeting convenience where studying the complete process was of significant importance for various studies. In doing so, FBRs have often been approximated and broken down into several sub-processes attempting to describe separate reaction phenomena in isolation.

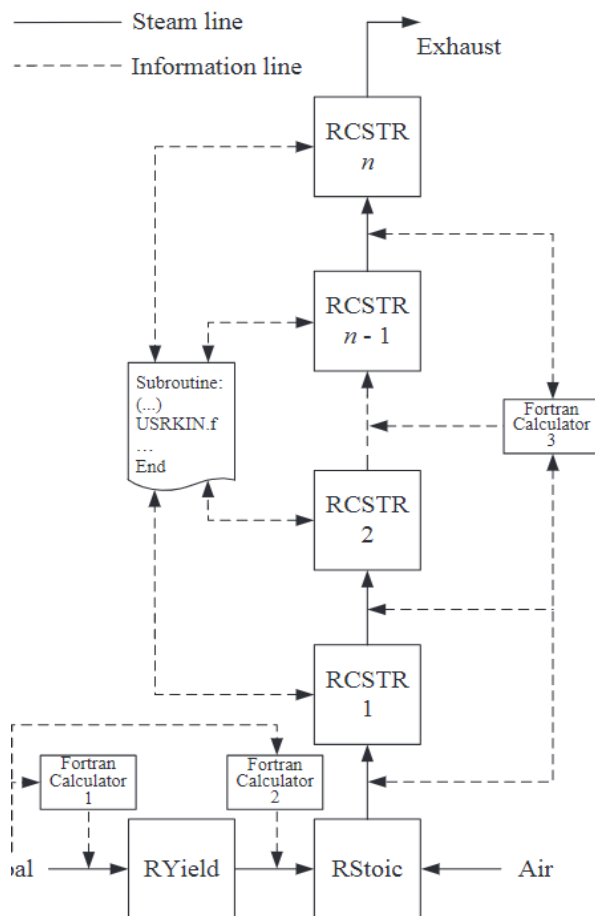


Fig. A-6: Typical Aspen Plus flowsheet section approximating a fluidized bed reactor process (in this case for coal combustion)²⁴⁷

Fig. A-6 illustrates this for the case of coal combustion. The *RYield* block is first used to break down the solid inflow material into elemental substances for ease of subsequent kinetic description; after which the *RStoic* block can be used to describe the initial reactions taking place that are assumed to occupy only a small fraction of the bed (in this case the combustion of volatiles). Subsequently the bulk of the reaction (char combustion) is simulated using a series of *RCSTR* blocks which is essentially a replication of the analytical CSTR models discussed earlier. However this typically is not the complete simulation of the reactor as additional analytical modelling is subsequently done using hydrodynamics models to describe the free board region of the FBR where fine particulates tend to be distributed, and subsequently overall mass and energy balance checks need to be performed for the entire chain of reactor blocks used.

Based on the preceding description and the multiple manual *Fortran* calculation inputs visibly required in Fig. A-6, the modelling of FBRs in Aspen Plus typically has been a painstaking and complex process with many separate calculation procedures that have to be constantly checked and reconciled with each other. Another example is considered in Fig. A-7 where an FBR design was studied in the literature using Aspen Plus for a chemical looping system which is a simpler process and more similar to the systems studied here. In this case, the series of plug flow reactors (PFRs; *RPlug*) are used to represent the gas flowing through a bubble phase while the series of CSTRs are for the gas flow through an emulsion phase. Again it is seen that many checks are required between the individual calculation steps.

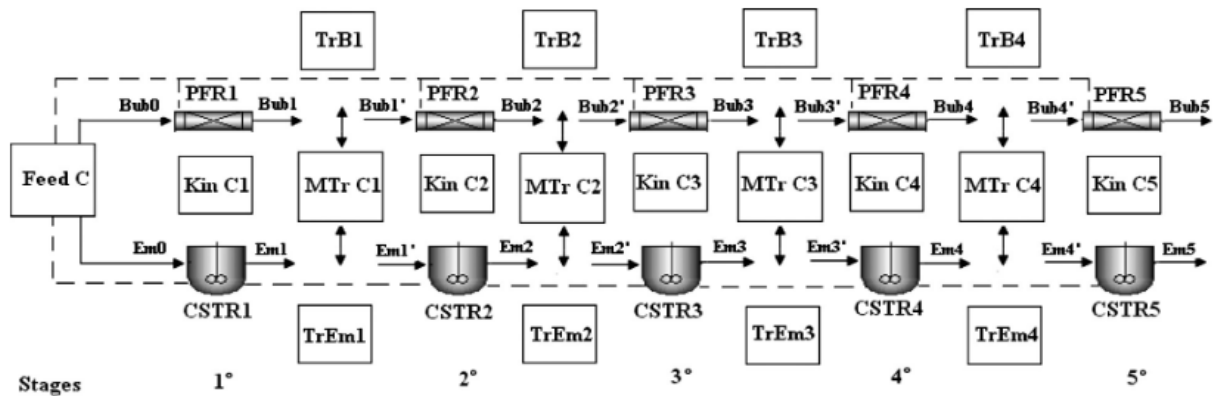


Fig. A-7: Typical Aspen Plus flowsheet approximating a bubbling fluidized bed for chemical looping²⁴⁸

Appendix A.12 – Additional FBR Simulation Considerations

While for an initial reactor design for steady-state consideration computationally simpler modelling approaches may be satisfactory, they are unable to consider additional physical considerations of reactor design such as its dimensions, the elutriation behavior of fluidized particles, the design and placement of the internal heat exchanger among other things, and the effect such factors have on the true behavior of the reaction systems and the reactors themselves. In contrast, the more computationally rigorous analytical

models can account for some of these factors but their unwieldy nature make it difficult to perform the design and optimization of the reactor in the context of the wider process which incorporates consideration of upstream and downstream unit operations as part of the plant flowsheet, meaning that the results of such models are often better suited as standalone reactor design studies. Intermediate software packages such as Aspen Plus have typically offered a combination of most of the capabilities of the aforementioned tools and have been used prominently for a wide variety of industrial process designs; however until 2016 it was significantly unwieldy and complex to design FBRs in this software.

Appendix A.13 – Summary of Literature Screening of TCES Reactions

Andre et al.⁷² conducted a thermodynamic assessment of the remaining reaction families (carbonates, hydroxides, sulfates, and redox systems) by estimating reaction enthalpies and turning temperatures (the temperature at which the standard Gibbs free enthalpy of the system is zero) of individual systems. Fig. A-8 presents the findings of their survey; it is noted that several systems investigated operate at low temperatures and/or have low mass energy storage densities thus ruling them out. It is also observed that reactions in the sulfate family are significantly more attractive than the rest based on their very high gravimetric storage densities and high turning temperatures. To this end, bench-scale studies involving them have been carried out in the literature to assess reaction kinetics^{249, 250}. However, reaction systems involving sulfates were not considered for further review due to the corrosive and toxic nature of SO_x gases involved that would cause additional mechanical design problems and operational safety issues when scaling up. The subsequent sections of this review thus only consider reported experimental results for carbonate, hydroxide, and redox systems. An initial illustration of the general chemistry for these families of systems is shown in Fig. A-9 along with a brief comparison of their traits for a high-level understanding of the phenomena considered; hydrides are included as they are also solid-gas systems potentially suitable for TCES but are not considered in this work due to their generally low operating temperature range as noted earlier in this section.

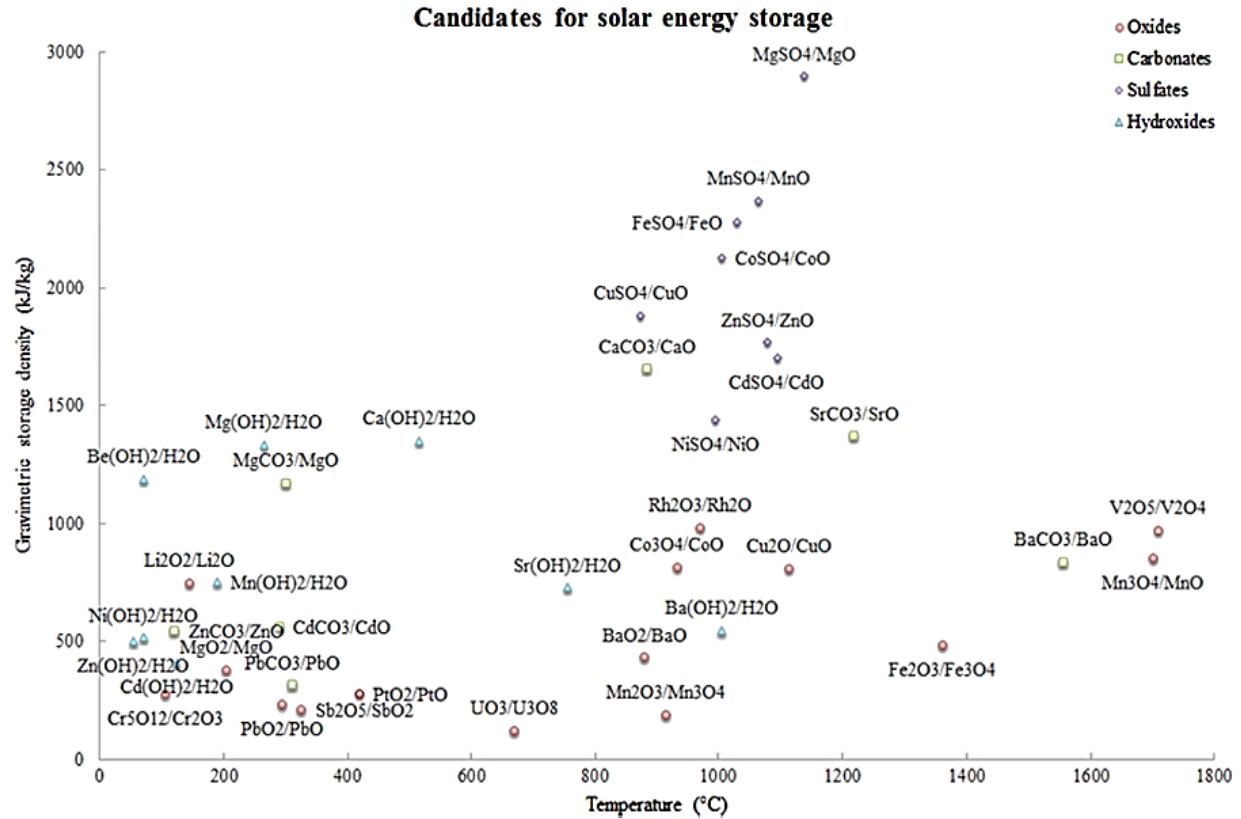


Fig. A-8: Energy storage density versus system turning temperature (surveyed systems for TCES)⁷²

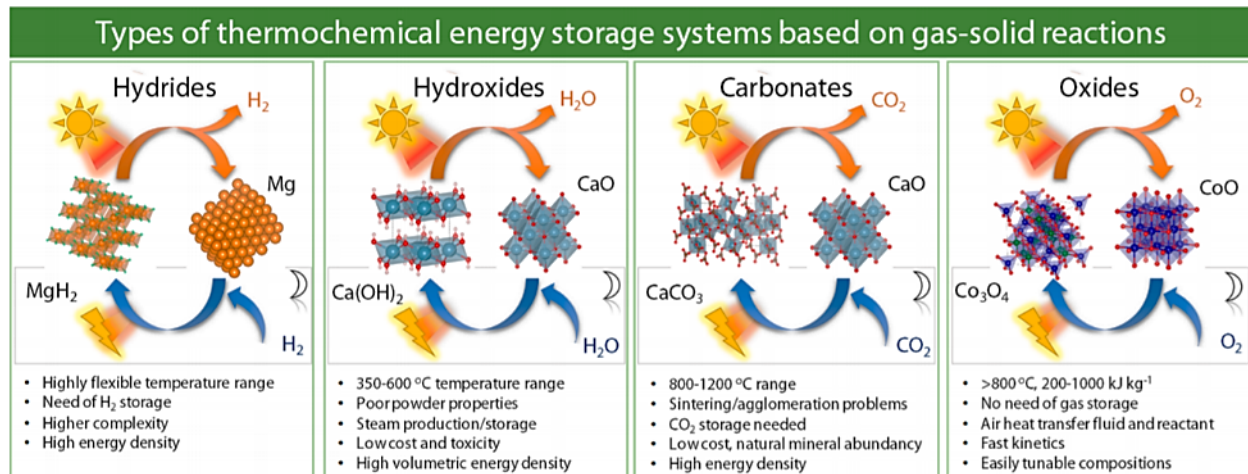


Fig. A-9: Summary of reaction schemes, advantages, and disadvantages of TCES reactions involving solid-gas chemistry⁷⁹

Metal Carbonates

Metal carbonates have been heavily investigated primarily for CCS applications as they use CO₂ for reaction. The general form is shown in Eq. A-14:



Due to CCS research, a wealth of literature data is available focusing on CaCO_3 systems. However, results have also been reported for PbCO_3 , MgCO_3 and SrCO_3 systems. Results from carbonate systems have been promising as several of them possess high reaction enthalpy and gravimetric storage densities^{74, 251-254}. The kinetics of systems involving CaCO_3 , SrCO_3 , MgCO_3 , BaCO_3 , and PbCO_3 has been previously studied^{255, 256}. Relevant thermodynamic data pertaining to carbonate systems is summarized in Table A-3.

Table A-3: Thermodynamic properties of selected metal carbonate systems relevant to TCES⁷²

Chemical material	Turning temperature (°C)	Reaction enthalpy (kJ/mol)	Gravimetric energy density (kJ/kg)
CaCO_3/CaO	885	165.832	1656.8
SrCO_3/SrO	1220	202.349	1370.65
MgCO_3/MgO	300	98.984	1174
BaCO_3/BaO	1555	165.096	836.6
CdCO_3/CdO	290	96.573	560.1
ZnCO_3/ZnO	120	68.326	544.9
PbCO_3/PbO	310	83.906	314

A screening study by Feng et al.²⁵⁷ for CO_2 capture materials concluded that CaO was one of the most promising materials for high temperature capture processes due to its superior energy densities, high turning temperature and large reaction enthalpy. However the phenomenon of sorbent deterioration is currently a major challenge hampering scale-up efforts. One recent technique developed more in line with CSP (and so untested for CCS applications) was developed by Nikulshina et al.²⁵⁸ wherein $\text{Ca}(\text{OH})_2$ is used as a proxy CO_2 sorbent to counter the loss in capacity experienced by CaO involving a three-step reaction (Eq. A-15 – A-17):



The impacts of particle calcination temperature, particle size, gas temperature, gas concentration, and the presence of steam on the long-term reactivity of the natural sorbent have also been studied^{259, 260}. In addition, synthetic Ca-based sorbents have been found to reduce sorbent agglomeration and sintering; CaZrO_3 ²⁶¹, Zr-stabilised CaO ²⁶², Ca-Al- CO_3/TiO_2 ²⁶³, $\text{CaTiO}_2/\text{Nano-CaO}$ ²⁶⁴, CaO-SiO_2 ²⁶⁵ among the more promising substances.

As demonstrated by Table A-3, the SrCO_3 system also has attractive thermodynamic properties and as such was tested by Miccio et al.²⁶⁶ in 2015 by cycling it under 50% CO_2 at 1100-1200°C. The base material (SrO) was found to experience a drop in carrying capacity due to sintering, much like CaO. More recently, Rhodes et al.²⁶⁷ also investigated this system and demonstrated that 40 wt% of yttria-stabilized zirconia, when used as a support, significantly reduced sintering of SrO while retaining close-to-maximum energy storage densities. However when testing with prolonged cycling, sintering was found to occur more pronouncedly. MgCO_3 systems have also been investigated particularly for CCS applications^{268, 269} however they have not received as much attention for CSP due to the relatively low temperatures involved²⁷⁰.

Metal Hydroxides

For metal hydroxide systems, the heat transfer fluid involved is steam which is cheap to produce and has a high gravimetric heat capacity, making these systems attractive for CSP energy storage. The general form of the reaction system is shown in Eq. A-18:



Relevant thermodynamic data is summarized in Table A-4. It is observed that the majority of the systems can only operate at temperatures that are too low for serious consideration for TCES applications. Of the remaining reactions, the standout candidates are those involving Ca(OH)_2 and Mg(OH)_2 due to their superior gravimetric energy densities. Unsurprisingly, the Ca(OH)_2 system has been widely investigated due to the additional attraction of the cheapness and accessibility of the material^{271, 272}.

Table A-4: Thermodynamic properties of selected metal hydroxide systems relevant to TCES⁷²

Chemical material	Turning temperature (°C)	Reaction enthalpy (kJ/mol)	Gravimetric energy density (kJ/kg)
Ca(OH)₂/CaO	515	100.177	1352
Mg(OH)₂/MgO	265	77.745	1333
Be(OH)₂/BeO	70	51.276	1191
Mn(OH)₂/MnO	190	67.072	754
Sr(OH)₂/SrO	755	88.581	728.3
Ba(OH)₂/BaO	1005	93.462	545.47
Ni(OH)₂/NiO	70	47.846	516
Zn(OH)₂/ZnO	55	49.609	498.86
Cd(OH)₂/CdO	125	59.952	409.4

Schaube et al.²⁷³ investigated the kinetics and thermodynamic behavior of the charging/discharging processes of the Ca(OH)₂ system at lab scales and achieved positive results even after 100 cycles, maintaining full conversions at atmospheric pressures. Larger-scale studies have also recently been conducted with Schmidt et al.¹³⁷ achieving reversible conversions of 77% while using several kilograms of material; meanwhile Azpiazu et al.²⁷⁴ found that the base material significantly deteriorates in carrying capacity after 20 cycles as a result of carbonation in air. Most recently in 2017, Rouge et al.¹⁵⁹ successfully cycled the Ca(OH)₂ system in a 20 kW pilot-scale setup using fluidized bed reactors with a continuous feeding and particle extraction system and developed a kinetic model of the reactor.

Separately, the effect of introducing additives to the system has been studied²⁷⁵. The use of powdered Al₂O₃ as an additive in a fluidized bed reactor by Pardo et al.²⁷⁶ showed that high energy densities could be maintained for longer cycles. In addition, Yan and Zhao²⁷⁷ tested CaO doped with Li and Mg and found that the reaction times and the dehydration reaction temperature could be reduced with no obvious detriment to particle reactivity.

Magnesium hydroxide systems have also received some attention, with L'vov et al.²⁷⁸ investigating the reaction mechanism. However it was reported that the base system could not operate at sufficiently high temperatures for TCES; as a result Shkatulov et al.²⁷⁹ tested both doping for both Mg(OH)₂ and Ca(OH)₂ systems – LiNO₃ and KNO₃ were found to be the most effective dopants for the respective systems in terms of improving their reaction rate and kinetic behavior.

Redox Systems

Various metal oxide systems have been investigated for TCES applications²⁸⁰ due to their high reaction temperatures and energy storage densities, making them viable for scale-up due to the small inventories required. The general form of the redox reactions is presented in Eq. A-19:



As observed from Table A-5, not all reactions operate in a temperature range suitable for TCES; while several systems involve too low temperatures, a good many (such as TiO₂, Fe₃O₄, and ZnO) were discounted from consideration due to the temperatures involved being impractically high for a CSP application. One key difference of redox systems is the use of air as the heat transfer fluid, thus eliminating the need to store the gaseous reactant. This allows for an open loop configuration while other systems require closed loops.

A preliminary investigation by Wong et al.²⁸⁰ found that only several systems exhibited suitable kinetic and thermodynamic behavior for further investigation for TCES: Co₃O₄, Mn₂O₃, BaO₂, CuO, Fe₂O₃, and V₂O₅. Of these, cobalt oxide reportedly demonstrated the most attractive kinetic behavior.²⁸⁰

Cobalt oxide is a controversial material, due to it being expensive and potentially carcinogenic. However due to its attractive reaction properties, it has received significant attention and tested in various reactor configurations (irradiated rotary kiln and powder-coated honeycomb designs)^{81, 92} with good cycling performance. Further work using a foam formulation for cobalt oxide also showed superior mechanical integrity and conversions when compared to traditional pellets²⁸¹. The kinetics of the system when using pellets were found to be better and showed better cycling stability than using powdered material²⁸².

Table A-5: Thermodynamic properties of selected pure metal oxide redox systems relevant to TCES⁷²

Chemical material	Turning temperature (°C)	Reaction enthalpy (kJ/mol)	Gravimetric energy density (kJ/kg)
Rh₂O₃/Rh₂O	970	249.276	982.1
V₂O₅/V₂O₄	1710	176.594	970.9
Co₃O₄/CoO	935	196.532	816.1
Mn₃O₄/MnO	1700	194.63	850.6
CuO/Cu₂O	1115	64.446	810.2
Li₂O₂/Li₂O	145	34.225	745.9
Fe₂O₃/Fe₃O₄	1360	232.613	485.6
BaO₂/BaO	880	73.258	432.6
MgO₂/MgO	205	21.432	380.6
Cr₅O₁₂/Cr₂O₃	105	126.17	279.1
PtO₂/PtO	420	62.802	276.5
PbO₂/PbO	295	55.234	230.9
Sb₂O₅/SbO₂	325	68.064	210.4
Mn₂O₃/Mn₃O₄	915	90.038	190.1
UO₃/U₃O₈	670	35.232	123

Manganese oxide was also investigated by the same group in terms of pellet versus powder performance²⁸². The Mn₂O₃/Mn₃O₄ system was found to have relatively slow kinetics for the re-oxidation reaction due to a two-step process: initially during post-reduction cooling between 700-500°C, and subsequently during heating for full oxidation between 500-850°C. The cycling stability of the system was investigated by Carillo et al.²⁸³ through thermogravimetric analysis; it was highlighted that initial particle sizes significantly influenced the kinetic behavior and sintering extent of the material while cycling. Systems of greater complexity have also been studied intensively involving the mixing of metal oxides (MMOs) for a single application; this is so as to overcome the problems faced when using systems of the individual oxides alone

by reducing the lattice stability and thus the lattice vacancy density in the particles, resulting in improved intra-particle oxygen mass transfer. The presence of the secondary oxide species also helps to inhibit the growth of grains within the primary oxide particles, thus serving to maintain reactivity.

To this end, comparative studies were reported on to assess the performance of pure cobalt and manganese oxides versus a MMO of the form $\text{Mn}_{3-x}\text{Co}_x\text{O}_4$ ²⁸⁴; here the pure oxides and mixed oxides did not demonstrate any significant disparity in performance. Block et al.²⁸⁵ estimated that doping of pure cobalt oxide with 10 mol% of iron oxide would show improved reaction reversibility over the pure oxide alone. In line with this, Pagkoura et al.²⁸⁶ investigated the reversibility of redox reactions for cobalt oxide pellets with alumina, ceria, iron oxide, manganese oxide, and zirconia as additives in the 800-1000°C range. It was found that ceria doping did not have improve the performance of the pellets, the use of 10-20 wt% alumina or iron oxide doped pellets demonstrated improved mechanical stability and consistent conversions upon cycling. Carillo et al.²⁸⁷ more recently found that Mn_2O_3 particles doped with 20 mol% Fe exhibited the fastest and most stable kinetics while also improving the energy storage density over cycling; however the sintering issue was observed to still persist.

Appendix A.14 – Additional Options for AspenPlus FBR Design

When using Aspen Plus for FBR design, the heat exchanger section in *Fluidbed* can be specified with factors such as the effective heat transfer coefficient, HTF tube bundle dimensions and diameters, and physical positioning within the FBR. It is noted that multi-tube designs are the only available configuration for heat exchangers in this case as other designs are not practically suited for integration with FBRs. While these properties are important for designing an FBR with an integrated heat exchanger, their detailed optimization is not within the scope of this work so long as an adequate rate of heat transfer to/from the bed is achieved. It is acknowledged that doing so may offer economic improvements by affecting the fabrication costs of the heat exchanger and the volumes of HTFs required but these considerations were not deemed critical to the initial design study of the FBRs and the flowsheets.

Another element that can be specified in *Fluidbed* are the gas distributors at the bottom of the FBRs. The main functions of gas distributors are to aid with uniform fluidization across the FBR cross section, to maintain a constant pressure drop throughout the operation of the FBR, and to prevent solids flowing upstream (through the bottom of the FBR) at any time. Specifying their design affects the magnitude of the pressure drop created at the bottom of the bed and also the initial bubble size produced by the fluidizing gas based on how it enters through the distributors. While these considerations, in particular the initial bubble size, are usually important factors in designing fluidized beds, their impacts on the behavior of the bed vary significantly depending on the nature of the bed as well; smaller and less dense particles are more easily buoyed by bubbles which can affect the bed height, bed voidage, heat transfer within the bed, and

other considerations. However the CaO/Ca(OH)₂ materials are of suitably high densities and are being used at large enough particle sizes where this is not expected to be a significant concern. Hence, optimization of the design of gas distributors was not performed in this initial study.

Appendix A.15 – AFBR Fluidization Calculations

Prior to operating the reactor, theoretical calculations were carried out to predict how particles would behave within the system; for this the gas and solids densities and the gas viscosities were needed. The following relations known as the Wen and Yu correlations (Eq. A-20 – A-22) were utilized to ascertain the minimum flowrate of cold gas feed required for the system to achieve fluidization, given a known particle size, particle density, and reaction temperature.

$$Re_{mf} = ((33.7)^2 + 0.0408Ar)^{\frac{1}{2}} - 33.7 \quad (A-20)$$

$$Ar = \frac{d_p^3 \rho_f (\rho_s - \rho_f) g}{\mu^2} \quad (A-21)$$

$$u_{mf} = \frac{\mu Re_{mf}}{d_p \rho_f} \quad (A-22)$$

Wherein Ar is the Archimedes number, ρ_f is the gas density, ρ_s is the particle (solids) density, g is the gravitational constant, d_p is the mean particle diameter, Re_{mf} is the Reynolds number at minimum fluidization, u_{mf} is the minimum fluidization velocity, and μ is the dynamic viscosity. For a sample calculation using known literature fluid viscosities for N₂ gas, the u_{mf} for a system at 1 bar consisting of 355-425 μ m sand at 400°C is calculated to be 9.9 cm³/s. To ensure thorough mixing of particles and a stable, well-defined fluidized bed during reaction as well as to be able to accurately set rotameters to particular flowrates, all experiments were conducted using flowrates ensuring a u/u_{mf} of at least 2.5.

Minimum fluidization velocities were calculated using fluid viscosities for N₂ from the NIST Chemistry Webbook²⁸⁸. The bulk fluidized material was SiO₂ sand (silica) with a size fraction of 355-425 μ m and a density of 2650 kg/m³²⁸⁹. Fluidization of the material was observed under temperatures and flowrates used in experiments in this work through indirect visual inspection by use of a reflective mirror positioned immediately downstream of the reactor. Accordingly, all hydration experiments carried out in the FBR and presented here were performed using a total gaseous volumetric flowrate of 47.5 cm³/s under standard conditions.

For the reacting CaO material, the largest size fraction used was 500-710 μ m and mixed with the sand for all experiments and fluidization calculations for this size fraction have been carried out accordingly, as smaller particle sizes would have lower minimum fluidization velocities. During the course of an

experiment, the CaO underwent hydration resulting in particles of a higher volumetric density; fluidization calculations were also carried out for these particles assuming a constant particle size for simplicity. The density of Ca(OH)_2 was considered as 2210 kg/m^3 and that of CaO as 3320 kg/m^3 .²⁸⁸ Minimum fluidization flowrates and values of u/u_{mf} are shown in Table A-6.

Table A-6: Minimum fluidization flowrates (Q_{mf}) for sand, CaO, and Ca(OH)_2 , and values for u/u_{mf} with a total gas flowrate of $47.5 \text{ cm}^3/\text{s}$

Temperature (K)	Sand (355-425 μm)		CaO (500-710 μm)		Ca(OH) ₂ (initially 500-710 μm CaO)	
	Q_{mf} (cm^3/s)	u/u_{mf}	Q_{mf} (cm^3/s)	u/u_{mf}	Q_{mf} (cm^3/s)	u/u_{mf}
573	11.1	4.3	13.7	3.5	19.3	2.5
623	10.6	4.5	11.4	4.2	17.3	2.7
673	9.9	4.8	9.5	5.0	14.4	3.3

Appendix A.16 – AFBR Response Time Measurements

Due to the path length and gas velocities involved, any measurement made downstream of the reaction faces a time delay τ_a in being reported by sensors which is inherent in the equipment^{290, 291}. As a result of this time delay, the true concentration C_i within the bed differed from the reported measured concentration downstream $C_{i,m}$ at any time t as the gas continued to mix while flowing from the bed to the sensor.

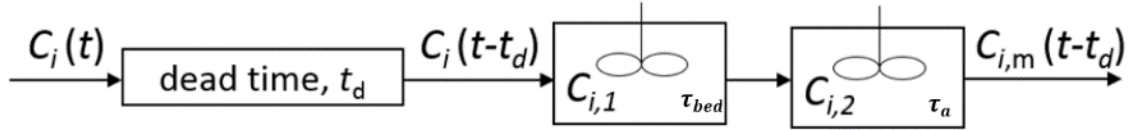


Fig. A-10: Schematic of the mathematical representation of the AFBR set-up in terms of lag times, used as reference for deconvoluting relative humidity measurements during hydration experiments, adapted²⁹¹

Moreover, there was a dead time t_d between the true concentration manifesting above the bed and the corresponding reported concentration being measured. In addition, due to the fluidized bed being well-mixed, there was a residence time τ_{bed} associated with the gas flow through the reactor up till the RH probe that is longer than the duration an identical gas stream would need to traverse the same distance unimpeded²⁹¹. Quantifying these time delays and residence times through deconvoluting the logged signals was necessary to obtain accurate time-based concentration information from the experiments. Here the method proposed by Fennell et al²⁹⁰ and used elsewhere^{153, 291} was employed to analytically obtain an expression to determine C_i from experimentally obtainable data. Fig. A-10 displays the discussed treatment of the system by using well-stirred tanks to represent τ_{bed} and τ_a and was used as reference in this method.

The model can be described by Eq. A-23:

$$C_i(t - t_d) = C_{i,m} + \tau_{bed} \frac{d(C_{i,bed})}{dt} + \tau_a \frac{d(C_{i,a})}{dt} \quad (A-23)$$

The individual response times can be treated as a single variable τ_m since no measurements are made in between, giving Eq. A-24:

$$C_i(t - t_d) = C_{i,m} + \tau_m \frac{d(C_{i,m})}{dt} \quad (A-24)$$

This is then integrated and rearranged to produce the linearized Eq. A-25:

$$\ln\left(1 - \frac{C_{i,m}}{C_i}\right) = \frac{t - t_d}{\tau_m} \quad (A-25)$$

Experiments were performed to obtain measurements for τ_m , the AFBR system's residence time. The RH probe's response time was assumed as $\tau_a = 0.3$ based on the supplier's technical documentation²⁹². Fig. A-11 shows a sample graph of data processed according to Eq. A-25 to determine τ_m .

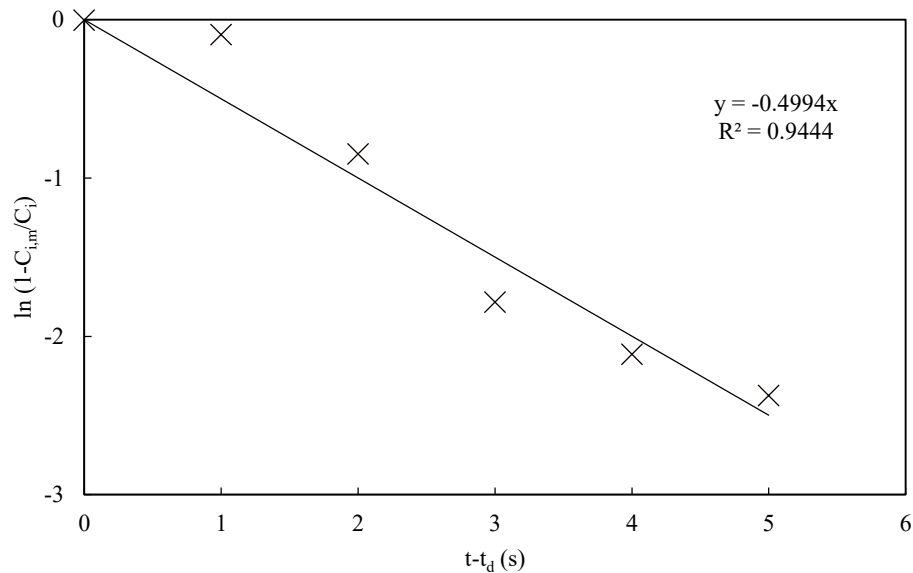


Fig. A-11: Plot of processed data to estimate τ_m for deconvoluting data from the AFBR

Due to treating the reactor system as a controlled stirred tank (CST), an averaged response time for the system of $\tau_m = 2.0$ s was applied to the raw data through Eq. A-24 to produce deconvoluted profiles after accounting for the response time of the bed and the analyzer. In addition, t_d was obtained by running the steam generation at steady-state through a bed of pure sand, then switching off the steam flow using a gate valve and subsequently measuring the time taken for the RH probe to register a drop in concentration; an average value of $t_d = 3.0$ s was obtained.

Appendix A.17 – AFBR Commissioning Experiments

Although this work is concerned with the hydration of calcium oxide, several experiments were first conducted to verify repeatability of mass balances within the AFBR system based on CO₂ readings from the gas analyzer during the calcination of limestone. Testing the system through this reaction meant that any pre-calcined materials were not wasted in running hydration experiments and that testing of gas leakage and particle elutriation or mass loss phenomena could be carried out on a simpler section of the set-up by bypassing the steam generator. The effect of temperature and reactant mass were assessed (Fig. A-12 and Table A-7); in all cases 12 g of 355-425 μm sand were added to aid fluidization of the bed material. The cross-flow factor for the system was determined to be 16.31 suggesting that a high degree of mixing occurs within the AFBR; the methodology is supplied in Appendix A.1.

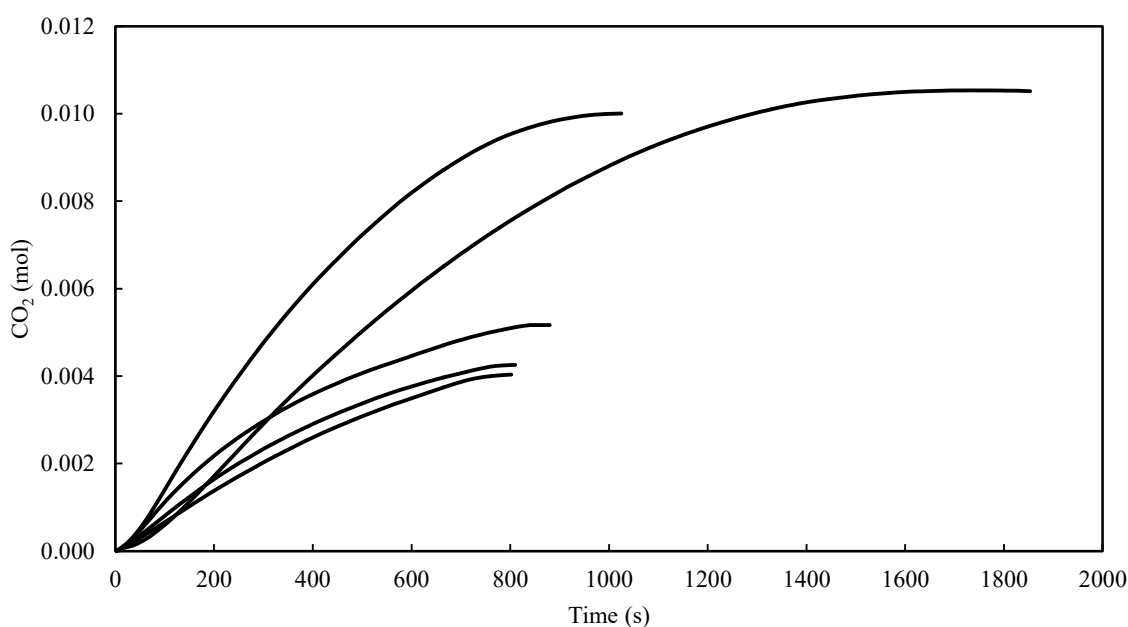


Fig. A-12: Limestone calcination experiments varying reaction temperature and amount of material fed

All of the reactions performed at the same temperature, regardless of reactant mass, took similar amounts of time to reach completion (data sets 2 – 5) which is expected behavior and demonstrates the reliability of the concentration readings. The total detected moles of CO₂ dropped significantly when the reactant mass was reduced from 1.0 g to 0.5 g, demonstrating the sensitivity of the analyzer to pick up on small differences even at low concentrations. In all cases, the mass balances between the overall CO₂ detected and the maximum possible released from reaction lined up with very good agreement; although the mass balance exceeded 100% for dataset 1, it is likely due to the much longer reaction time for these conditions (lower reaction temperature) leading to a larger accumulation of errors in the readings over that time.

Table A-7: Mass balance information for calcination experiments

No.	T (°C)	Limestone (g)	CO ₂ Measured (g)	CO ₂ expected (g)	Mass balance accuracy (%)
3	780	0.453	0.227	0.236	96
2	780	0.996	0.438	0.453	95
4	780	0.411	0.185	0.191	96
5	780	0.356	0.178	0.179	99
1	750	1.029	0.463	0.451	103

These results also indicated that there was no detectable gas leakage in the system and that the CO₂ analyzer was sensitive enough to accurately measure small volumes of gas; the setup in this regard was deemed satisfactory and so further tests involving steam for hydration reactions were undertaken. The subsequent commissioning experiments were to assess the suitability of data from the reactor for accurate fitting to kinetic models and the ease of operability of the setup. This depended on (i) the reliability of measurements for experiments conducted in quick succession without requiring shutdown of the process and (ii) the stability of the steam concentration during the reaction. The latter aspect is especially crucial as the new steam generation system had yet to be tested on this setup.

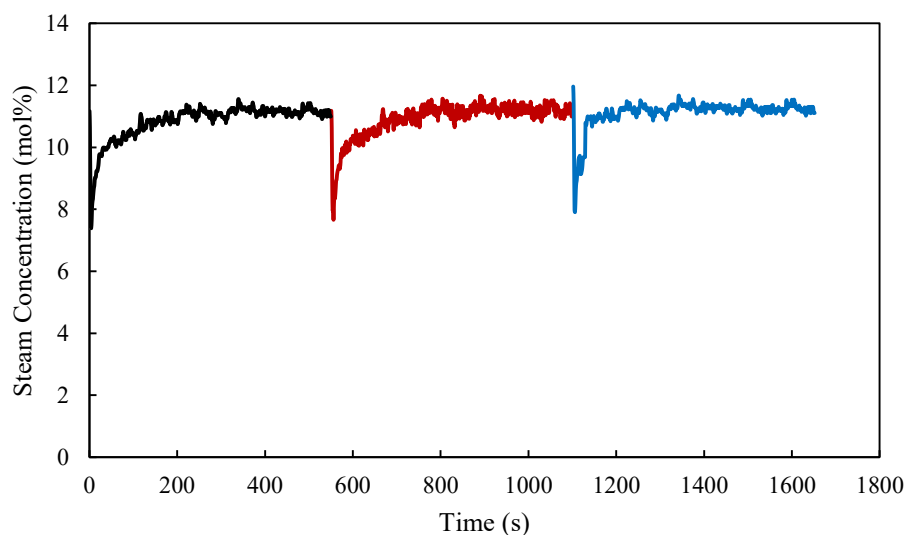


Fig. A-13: Steam concentration from tests (500-710 μm LC calcined at 850°C, $T_{\text{rxn}}=300^\circ\text{C}$, 10% steam)

To this end, several runs of CaO hydration using 0.5 g of calcined limestone and 12 g of sand were carried out in the AFBR under 10% steam generated in-situ. During the experiments, it was observed that the steady-state steam concentration readings before and after each reaction exhibited negligible differences,

with signal noise constituting $\leq 1\%$ of the measured values. Fig. A-13 illustrates the observed behavior in the calculated steam concentrations based on the measured relative humidity during the experimental runs.

The steam concentration consistently followed expected behavior during each reaction with a sharp drop during a fast initial reaction followed by a gradual recovery as the reaction approached completion. The steady-state concentration also consistently leveled out at $\sim 11\%$ after each reaction which meant that the measurement baseline did not drift over time – something that is known to occur for gas analyzers for instance. The consistent baseline meant that conducting experiments in quick succession without needing to fully shutdown the system would not compromise the reliability of the obtained data.

Appendix A.18 – Dynamic Modelling of CSP Energy Storage processes in literature

The prospect of performing dynamic modelling studies for solar energy generation is not a new one as many investigations of this nature have been performed in the literature in recent times pertaining to the various different CSP configurations, associated power generation systems, as well as thermal energy storage systems. Based on the chosen focus of this work on the TCES process, the literature pertaining to studies focusing on the latter aspect was considered in greater detail to identify possible suitable dynamic modelling approaches and strategies.

It was noted that far fewer studies were available that met this criteria, as most of dynamic simulation studies focused on modelling the direct power generation capabilities of CSP plants. This is most likely due to the thermal storage capacities of current CSP designs being very limited and so they are often simplified or neglected in such cases. Hence the approaches employed in those studies are naturally unsuitable for use here as they focus on traditional CSP plant configurations and have separate modelling criteria altogether which are incompatible with the scope of this study.

Current CSP designs typically incorporate only latent heat TES systems if at all, which typically only have storage durations of several hours. Due to this, various dynamic simulation studies in the literature have focused on studying the performance of such systems through computational CFD models^{25, 293, 294} coupled with experimental investigations^{25, 294} as such TES materials are often fluids or fluid-solid mixtures that are already at a high TRL and produced on large scales and so complementary pilot-scale testing facilities and simulation models for them have been developed over time. While the simulations and experimental approaches taken in these works are not necessarily applicable for this study due to the lack of suitable experimental data pertaining to fluidized bed setups for such applications, the variables studied and the selection of parameters to study their influence on did offer guidance on what aspects would be suitable for consideration in this work.

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