Morphological Property Variation and Ionic Transfer Behaviors of Solid Reactants in Fe-based and CaO-based Chemical Looping Processes

DISSERTATION

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By

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Abstract

Chemical looping technology aims at converting fossil fuels in an efficient and effective way with 100% CO₂ capture. As one of the most important factors to the success of chemical looping processes, the reaction properties of chemical looping particles have received a lot attention in the past decades. This dissertation explores the morphological properties and ionic transfer behaviors in Fe-based and CaO-based chemical looping processes with focuses on: 1) solid deactivation/reactivation mechanism, 2) sorbent activation & reactivation strategies, and 3) ionic diffusion mechanism in chemical looping related reactions.

Firstly, this work evaluates the deactivation mechanism for Fe-based and CaO-based solids in cyclic gas-solid reactions and finds that the widely believed the sintering theory for chemical looping particle deactivation is incomplete, which overlooks another important deactivating factor: irreversible pore opening-and-closing, which features a cyclic gas-solid reaction. Opposite to the conventional perspective, the temperature effect on solid morphology is conditional, depending on the dominating ionic transfer mechanism during the gas-solid reactions. Secondly, the HCl, COS, CO₂ captures by CaO-based sorbent are experimentally and theoretically studied on three aspects: 1) sorbent activation by precipitation approach, 2) sorbent reactivation by hydration, 3) dominating solid-phase ionic transfer mechanism. It is found that an optimized CaO sorbent with the most meso-pores has better HCl capture capacity than limestone-derived
CaO. Additionally, deactivated CaO sorbent after cyclic capture-and-release of CO₂ would restore its reactivity towards HCl capture after a hydration process. Inert marker experiment is used to determine the dominating ionic transfer mechanism during CaO reactions with HCl, COS, and CO₂. It is found that all the three reactions follow “inward diffusion mode”, meaning that the inward diffusion of gas-derived ionic species (e.g. Cl⁻ anion) and corresponding outward diffusion of O²⁻ anion dominate the three ionic diffusion processes. Thirdly, the mechanism of morphological enhancement of CaO by hydration is studied. In contrast to the previous works, this work focuses on the physical and chemical sub-steps that occur during a typical water hydration process. The widely believed “physical attrition theory” is experimentally disproved and a new multi-factor mechanism is proposed. Finally, pore structure change by structural ion diffusion is studied experimentally and theoretically, from which it is found that the solid-phase ionic diffusion is an independent factor that can affect the solid morphology variation in a gas-solid reaction.

Through the works as described in this dissertation, some misunderstandings in the previous studies on chemical looping particles are clarified. Additionally, more experimental and theoretical results are provided for better understanding of the Fe-based and CaO-based particles in chemical looping applications.
This document is lovingly dedicated to my mother, whose unshakable faith in God and unconditional love made me who I am today.
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I can still remember the first time I walked into Dr. Fan’s office and expressed my desire to be his student. Picture of that day is still vivid in my memory and will never fade. It is my life-time honor to work with Dr. Fan, who is a world-renowned professor in chemical engineering. During my five-years’ PhD study, Dr. Fan provided me with not only academic guidance but also how to be a valuable person to the society. I am very grateful that Dr. Fan found my gift in reaction mechanism of solid materials and gave me a lot of freedom in study and research. From him, I saw images of a knowledgeable professor, an enthusiastic chemical engineer, a strict advisor, and a loving father.

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Finally, I would like to praise to the mighty creator who made this wonderful world and gave me wisdom to appreciate that.
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**Fields of Study**

Major Field: Chemical and Biomolecular Engineering
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CHAPTER 1

Introduction to Fe-based and CaO-based Chemical Looping Processes for Fossil Fuel Conversion with CO$_2$ Capture

1.1 Introduction

With the fast-growing world-wide energy demand and growing global-warming concern, considerable attention and research efforts are put onto effective and efficient fossil fuel conversion with integrated carbon dioxide (CO$_2$) capture.$^{1,2}$ Chemical looping process for fossil fuel conversion and Carbon Capture and Sequestration (CCS) was conceptualized in the early 20$^{th}$ century and intensively developed after the late 1990s.$^3$ Compared with the conventional fossil fuel converting technologies, chemical looping process has several advantages, such as high process efficiency, low capital and operating costs, ease in CO$_2$ management, etc.$^3$ After years of intensive study, the basic process concept has been proved viable, and most recent research efforts are put onto large-scale demonstration and process optimization.$^{1,2,4}$ Currently, there are two types of chemical looping processes under development in the Ohio State University: CaO-based and Fe-based chemical looping processes, based on the primary reactive components. These primary reactive components go through cyclic gas-solid oxidation/reduction (for Fe) or carbonation/calcination reactions (for CaO).$^1$ It is been widely reported in the literature that most pure materials show steady deterioration of reactivity and recyclability over the cyclic gas-solid reactions.$^{1,5,6}$ Such deactivation is usually coupled with decayed
morphological properties (decrease in surface area and pore volume). Because the chemical reactions in chemical looping processes take place at elevated temperatures (>500 °C), a considerable volume of literature attributes this solid performance decay and morphological deterioration to the sintering effect, which fuses pore structure and agglomerates smaller particles (grains) into bigger ones by heat. A recent study, which is elaborated in a following chapter, shows that the cyclic pore opening-and-closing, which features in chemical looping processes, is an independent deactivating factor. To improve or rejuvenate the solids’ morphological properties, numerous research efforts are put onto optimizing the surface area and pore structure of chemical looping particles through solution combustion, precipitation, addition of physical support, anti-sintering doping, particle breaking, etc.\(^1\)\(^,\)\(^2\) Alternatively, some studies suggest adopting naturally-occurring materials with high intrinsic ionic conductive capability or artificially doping exotic atoms into primary solid crystal structure to create ion vacancies for enhanced ionic diffusion.\(^1\)\(^,\)\(^7\)\(^,\)\(^8\) In the previous studies of optimization of solid particles in OSU chemical looping processes, efforts were put on 1) enhancing/reactivating solid morphological properties, and 2) enhancing solid-phase ionic conductive capability.

Despite the difference in specific reaction schemes, all the chemical looping particles go through cyclic gas-solid reactions, which are first reviewed to better convey the experimental and theoretical works in the following sections.
1.2 Kinetics in Gas-solid Reactions

Given that the chemical looping processes always involve cyclic chemical capture-and-release of partial or entire gaseous reactant, the performance of solid reactant in each gas-solid reaction is determined by the intrinsic solid properties. Figure 1.1 shows the typical solid conversion curves during a gas-capture process and a gas-release process, respectively.

When a gas-capture process occurs, gas molecules diffuse to the solid grain surface either directly to solid’s outer surface or indirectly through internal gas channels (pore structure on solid grains and inner-particle voids). Initially, the gas reactant would first react with the solid reactant on the grain surface exposed to the gas phase, reaction rate of which is determined by the nature of intrinsic chemical reaction and reaction condition. And the overall solid conversion during the chemical-reaction-controlled step is generally determined by the overall solid surface area exposed to the gas-phase during the reaction. Because the gas-capture process often incurs volume expansion of the solid product layer, which may close the inner-particle voids and pore structure during conversion. Hence, the pore size distribution can also affect the overall surface area exposure to the gas-phase during the gas-capture process.

Simultaneously or after the solid surface is covered by solid product, direct contact of gaseous and solid reactants is hindered. Further solid conversion has to proceed through solid-phase ionic diffusion. Because of the ionic concentration gradients, solid reactant species tends to diffuse outward from the grain interior to the grain surface. Meanwhile, the ionic species derived from the solid product diffuses inward from the
grain surface to the grain interior. The overall diffusion process has to maintain charge neutrality. It means that, if cations diffuse inward or outward, corresponding anions and/or electrons with equal change can diffuse in a co-current mode, or cations with equal charge can diffuse in a counter-current mode. It is similar for anion diffusion. The ionic diffusion rate is determined by the intrinsic properties of solids and reaction conditions, which are elaborated in a following section. As illustrated in Figure 1.2, based on the dominating ionic transfer mechanism, an ionic diffusion step can be categorized into: “outward diffusion mode”, “inward diffusion mode”, and “mixed diffusion mode”. Inert marker experiment is usually used to characterize the dominating ionic transfer mechanism, which is elaborated in a following section.9,10

In the chemical-reaction-controlled step, the surface solid reactant is abundant for chemical reaction, so the ionic diffusion only plays an assisting role in the solid’s conversion. The chemical reaction rate is controlled by how fast the gaseous reactant can convert the solid reactant. However, when the surface solid reactant is mostly consumed by the gaseous reactant, further solid conversion rate is determined by how fast the solid reactant can be exposed or transferred to surface for direct gas-solid reaction through ionic transfer, which characterizes the ionic-diffusion-controlled step. Because the solid-phase ionic diffusion rate is usually much lower than the direct gas-solid chemical reaction rate, a transition from the fast chemical-reaction-controlled step to the slow ionic-diffusion-controlled step is noticeable on most solid conversion curves. In the chemical looping applications, the solid residence time in a reactor is usually limited, which means that the overall solid conversion in each gas capture/release process is mostly or entirely contributed by the first chemical-reaction-controlled step.1 This basic
two-step principle is valid in most gas-solid reactions, only with exception for some reactions in which the solid product layer disintegrated due to low mechanical strength. In this case, the gas reactant would circumvent the ionic diffusion resistance from the solid product layer and directly react with interior unreacted solid reactant at the fast chemical reaction rate.\textsuperscript{11}

Similar to the gas-capture process, the gas-release process usually has these two steps. Initially, the solid reactant (\textit{e.g.} CaCO\textsubscript{3}) decomposes into gaseous product and solid product on the grain surface spontaneously (\textit{e.g.} calcination of CaCO\textsubscript{3}) or by a gas reactant (\textit{e.g.} H\textsubscript{2} in Fe\textsubscript{2}O\textsubscript{3} reduction). This gaseous product then leaves solid surface area and diffuses into the gas phase. Because solid decomposition usually incurs volume shrinking, the produced solid (\textit{e.g.} CaO) cannot cover the entire grain surface, which would expose the inner solid reactant directly to the gas-phase.\textsuperscript{12} If the gas-release step involves inward ionic diffusion of solid product species, this inward diffusion will also contributed to the surface pore opening, which will be elaborated in a following chapter. As a result, direct chemical reaction can proceed in this manner until all the surface area is covered by solid product. The molar volumes of primary reactive components in Fe-based and CaO-based chemical looping particles are listed in Table 1.1. As soon as a solid product is formed, ionic diffusion would occur in a mode opposite to the gas-capture process.
<table>
<thead>
<tr>
<th>Name</th>
<th>Molar Volume (cm$^3$/mol)</th>
<th>Name</th>
<th>Molar Volume (cm$^3$/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>16.7</td>
<td>CaCO$_3$</td>
<td>36.9</td>
</tr>
<tr>
<td>Ca(OH)$_2$</td>
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<td></td>
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</tr>
<tr>
<td>Fe</td>
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<td>FeO</td>
<td>12.5</td>
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<td>Fe$_3$O$_4$</td>
<td>44.7</td>
<td>Fe$_2$O$_3$</td>
<td>30.5</td>
</tr>
</tbody>
</table>

* Molar volume reported in literature varies from study to study, based on different experimental and theoretical methods.

Table 1.1. Molar volume information of various chemical looping particles in different oxidation states.
Figure 1.1. Illustration of typical solid conversion curves of a gas-capture reaction (a) and a gas-release process (b).
Figure 1.2. Illustration of three ionic diffusion modes in a gas-capture reaction and principle of inert marker experiment. (a: original solid reactant, b: outward diffusion mode, c: mixed diffusion mode, d: inward diffusion mode)
CHAPTER 2

Solid Deactivation Mechanism for CaO-based and Fe-based Chemical Looping Particles

2.1 Introduction

Cyclic gas-solid reaction is a typical chemical reaction pattern, in which the solid reactant chemically carries partial or entire gas molecule between different reaction steps in a cyclic capture-and-release manner.\textsuperscript{2,4} A typical gas-capture reaction proceeds in two consecutive steps: the surface chemical-reaction-controlled step and the solid-phase ionic-transfer-controlled step.\textsuperscript{9,10,13,14} Gaseous reactant first reacts with the solid reactant on the solid surface and converts into solid product. After the product layer is formed (unless cracked), further conversion proceeds either through outward ionic diffusion of unreacted solid reactant and/or inward ionic diffusion of the solid product, which transfers and/or exposes fresh solid reactant to the gas-solid interface. Based on the dominating solid-phase ionic transfer mechanism, a gas-capture reaction can be categorized into “inward diffusion mode”, “outward diffusion mode”, or “mixed diffusion mode”.\textsuperscript{9,10,15} The ionic diffusion during the corresponding gas-release step is generally a reverse process of the capture step in principle. In the “inward diffusion mode”, the structural ions (e.g. Ca\textsuperscript{2+} in CaO/CaCO\textsubscript{3}) which define the solid structure, do not change by the inward and outward diffusion of the non-structural ions (e.g. CO\textsubscript{3}\textsuperscript{2-} in CaO/CaCO\textsubscript{3}).\textsuperscript{16} While in both “outward diffusion mode” and “mixed diffusion mode”,
the structural ions (*e.g.* iron cation in iron/iron oxides) diffuse though the solid surface. Because surface area and pore structure determine the solid’s exposure to the gas phase in the chemical-reaction-controlled step and also the width of the ionic diffusion pathway, solid morphological properties are regarded as one of the most important factors in a gas-solid reaction.

It was widely reported that these properties tend to deteriorate as the cyclic reaction proceeds, especially in high-temperature applications. A considerable volume of literature attributes the solid morphological property deterioration and corresponding reactivity decrease simply to the particle sintering/calcination at elevated temperatures, which would agglomerate smaller grains/particles into bigger ones and “fuse” pore structure. Therefore, numerous research efforts are devoted to the improvement of initial solid morphological properties, anti-sintering/calcination, and optimization of reaction condition. Such mechanism and efforts are valid in “one-time” gas-solid reactions and also catalysis which involves negligible solid conversion. However, the cyclic gas-solid reaction involves cyclic solid-phase ionic transfer and cyclic surface pore rearrangement, which are absent in catalysis and “one-time” gas-solid reactions. Hence, the previous understandings towards solid morphological and reactivity change in the cyclic gas-solid reactions should be re-evaluated.

In this chapter, cyclic carbonation-calcination reactions (CCR) of CaO (without structural ions diffusion) and cyclic reduction-oxidation reactions (Redox) of Fe (with structural ion diffusion) are used as two representative examples to discuss the mechanism of solid reactivity and morphological change in the cyclic gas-solid reactions. It is found that longer exposure to high-temperatures tends to deteriorate the
morphological properties and reactivities of both solid reactants. In contrast to the previous notion, the negative effect of a higher temperature on the solid’s morphological properties and resulting reactivity is conditional. If the structural ions participate in the solid-phase ionic diffusion, the solid reactivity can possibly decrease faster at a lower reaction temperature than at a higher temperature. A 2-D continuum diffusion mode is applied to simulate the effect of structural ion diffusion to the surface pore structure. With the effects of reaction temperature and reaction time excluded, the cyclic reaction *per se* shows a noticeable deteriorating effect on the solid reactivity. This effect can be attributed to the pore structure rearrangement due to cyclic molar volume expansion-and-shrinking and/or cyclic solid-phase ionic transfer.
2.2 Methods

2.2.1 Experimental Details

Materials

Naturally-occurring limestone power (CaCO₃) was obtained from Graymount (with about 2% impurities). Fe₂O₃ powder was obtained from NOAH Technologies. H₂, CO₂ and N₂ used in this chapter are 99.99% pure. Air was used as oxidant for Fe oxidation.

Tests of Effects of Reaction Temperature, Reaction Time, and Carbonation-Calcination Cycle on the Reactivity of CaO Solid

A Perkin-Elmer (Pyris 1) thermogravimetric analyzer (TGA) apparatus was used to prepare and test the CaO solids. The balance of the TGA can measure accurately up to 10⁻⁷ g. 30 mg limestone (CaCO₃) powder was used as the starting sample in each test. Total gas mixture flow rate for final carbonation reaction (γ section in Figure 2.1) was 120 ml min⁻¹, which consists of 10 % CO₂ and 90 % N₂. Gas composition for sample preparation steps (α and β sections in Figure 2.1) was elaborated in Table 2.1. The sample weight was continuously recorded for further analysis.

In order to identify independent role of reaction temperature, reaction time, and carbonation-calcination cycle to the reactivity of CaO solid in the cyclic CaO-CO₂ reaction, five representative samples were prepared and tested. Detailed information of sample preparation procedure was listed in Table 2.1. All the five samples were prepared and tested fully or partially through the cyclic reaction process shown in Figure 2.1.
Tests of Effects of Reaction Temperature, Reaction Time, and Reduction-Oxidation Cycle on the Reactivity of Fe Solid

A Perkin-Elmer (Pyris 1) thermogravimetric analyzer (TGA) apparatus was used to prepare and test the Fe solids. 40 mg Fe$_2$O$_3$ powder was used in each test as starting sample. Total air flow rate for oxidation reaction was 200 ml min$^{-1}$, which consists of about 21 % O$_2$ and 79 % N$_2$. Gas stream for reduction reaction consists of 30 ml min$^{-1}$ H$_2$ and 150 ml min$^{-1}$ N$_2$. Reaction condition for sample preparation steps ($\alpha$ and $\beta$ sections in Figure 2.2) was elaborated in Table 2.2. The reactivities of solid reactants after preparation steps at 800 °C or 900 °C are tested at 900 °C in air stream. The sample weight was continuously recorded for further analysis.

In order to identify independent role of reaction temperature, reaction time, and reduction-oxidation cycle to the reactivity of Fe solid in the final oxidation reaction, five representative samples were prepared and tested. Detailed information of sample preparation procedure was listed in Table 2.2. All five samples were prepared and tested fully or partially through the cyclic reaction process shown in Figure 2.2. Solid conversion at each reduction or oxidation step is above 95 %.
Morphology Analyses of CaO and Fe Samples

The morphological properties of CaO and Fe samples were tested in a NOVA 4200e analyzer (Quantachrome Company). The Brunauer Emmett Teller (BET) surface area and pore volume were measured at -196 °C using liquid N\textsubscript{2} as adsorbent.

Definition of Solid Reactivity for Gas Capture

The solid’s capture capacity is defined as weight capture percentage after 30 minutes’ carbonation in step 14 (shown in Figure 2.1) or 5 minutes’ oxidation in step (Shown in Figure 2.2):

Weight Capture Percentage: \( C_t = \frac{(W_t - W_0)}{W_0} \times 100 \) (%);

Where:

\( W_0 \): Sample weight after complete calcination/reduction. (mg)

\( W_t \): Sample weight at time \( t = 30 \) minutes (for CaO carbonation) or \( t = 5 \) minutes (for Fe oxidation). (mg)

On the basis of the definition of this parameter, a larger weight capture percentage \( C_t \) refers to a higher gas capture reactivity of a solid reactant.
2.2.2 Simulation Work

The effect of ionic transfer on surface pore structure during redox cycle was studied by the classic diffusion model:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D(C)\nabla C)$$

(1)

Where, $C$ is the concentration of iron or iron cation. $D(C)$ is the diffusion coefficient, which is a function of the local concentration $C$. In this chapter, only two-dimensional version of this equation is considered. A mesh with 81×81 grids is adopted in the simulations of both oxidation and reduction processes. Purpose of this simulation is to illustrate the basic physical idea of the effect of structural ion diffusion on the pore structure during the oxidation and reduction reactions rather than to give exact solutions of the redox process. Hence, in the following simulation results, all the parameters are dimensionless and the relative magnitudes of some parameters are not necessarily related to the real situation. A quantitative 2-D diffusion model for a more detailed analysis is elaborated in a following chapter.

For the oxidation process, the concentration of iron or iron cation decreases near the surface of the solid particle as the reaction proceeds. The internal iron thus diffuses outward under the driving force of iron concentration gradient. It is this diffusive behavior of iron that makes the solid surface gradually expand outward. To define a sharper gas-solid boundary, the diffusion coefficient is specified as

$$D(C) = D_e \exp(-a(1-C)/(C+b))$$

(2)
This equation gives smaller diffusion coefficient when the concentration decreases. It gives a constant $D_c$ when $C = 1$, which is the dimensionless concentration of the initial condition. Here, $D_c = 0.001$, when $a = 5$, $b = 1$ are used for the simulation.

For the reduction process, the concentration of iron on the solid surface is kept constant, which is $C = 1$ in this dimensionless simulation. This is based on the assumption that iron is steadily generated on the gas-solid interface and then diffuses inward into the solid. This process proceeds until the total inward flux of iron at the outmost solid layer reaches to a certain value, which means the outmost layer of solid surface has been fully consumed. Then, the gas-solid interface would shrink inwards. This change is demonstrated by denoting the next layer of grid as the new gas-solid interface, on which the reduction reaction occurs and new iron is produced for further inward diffusion. In order to determine when the surface retreat happens, diffusive flux of iron through the current surface is collected. If the summation of the collected flux reaches to a critical value, the operation of gas-solid interface change is executed. Here the diffusive flux can be described as:

$$j = -D(C) \nabla C$$ \hfill (3) \n
The criterion that permits the surface change is that

$$\sum j \cdot n dx dt > C_t dx^2$$ \hfill (4) \n
Where, $dx$ is the grid space, $dt$ is the time step, $n$ is the normal vector on local surface, and $C_t$ is the concentration of iron or iron cation in the unreacted Fe$_2$O$_3$ solid particle. In this simulation, $C_t$ is specified as 500.
2.3 Results and Discussion

2.3.1 Effect of Reaction Time

The effect of reaction time is studied by varying the time length of solid’s exposure to the reaction conditions. The “0 temp cycles + 0 CCR” sample is obtained immediately after the calcination of CaCO₃ is completed, while the “6 temp cycles + 0 CCR” sample goes through an extended cyclic temperature condition without any gas reactant introduced. Their CO₂ capture capacities (30 min weight capture percentage) are tested at the same condition. Preparation and testing of the “0 temp cycles + 0 Redox” and “2 temp cycles + 0 Redox” follow the same principle. As shown in Figure 2.3 (a) and (c), the “6 temp cycles + 0 CCR” and “2 temp cycles + 0 Redox” have lower reactivities than the “0 temp cycles + 0 CCR” and “0 temp cycles + 0 Redox”, respectively. At a longer time, sintering/calcination would have a greater deteriorating effect on a solid particle, which agglomerates smaller gains/particles and “fuses” pores to a greater extent. This greater sintering/calcination effect at a longer time is reflected on the particles’ lower surface areas and pore volumes (see Table 2.3).

2.3.2 Effect of Reaction Temperature

700 °C and 800 °C are compared to study the effect of reaction temperature on CaO solid, while 800 °C and 900 °C are compared for Fe solid. With other parameters fixed for a given solid, the difference in the resulting solid reactivity is caused by the temperature difference during the previous reaction step. As can be seen in Figure 2.3 (a) and (c), the resulting CaO reactivity after the 700 °C reactions is higher than that after 800 reactions, but this trend is opposite for the Fe solid. Please note that the resulting
reactivities for CaO or Fe are tested at the same conditions: 650 °C for the CaO samples and 900 °C for the Fe samples. The corresponding morphological properties show the same trend. This conditional temperature effect is against the conventional belief that a higher reaction temperature generally leads to worse morphological properties and lower reactivity by an enhanced sintering/calcination effect. It is true that, if the temperature is too high, the sintering/calcination can totally “fuse” pore structures and “ruin” the solid reactivity. However, if the reaction temperature is not too harsh to be a dominating deteriorating effect, other factors can determine the overall temperature effect on the solid properties in a cyclic gas-solid reaction.

Generally, the surface pore structure in cyclic gas-solid reactions can be affected by 1) mechanical interaction; 2) molar volume expansion-and-shrinking process, and possibly 3) diffusion of structural ions (if structural ions do diffuse). During the gas-capture process, because of the higher molar volume of solid product than the solid reactant, the product layer swells and pores are “squeezed” off as the reaction proceeds. When the gas component is released from the solid product, the pores are regenerated. This molar volume expansion-and-shrinking process is mainly determined by the inherent properties of the solid product and the solid reactant, which are only slightly affected by temperature. If the dominating solid-phase ionic transfer mechanism during the gas-capture step follows the “inward diffusion mode” such as in the CaO + CO₂ reaction. The non-structural ions (e.g. CO₃²⁻ in this chapter) “enters” and “leaves” the solid structure during the capture and release processes, respectively, while the layer arrangement of structural ions (e.g. Ca²⁺ in this work) is theoretically not affected by the ionic transfer process. In this case, reaction temperature can only affect
the sintering/calcination on the solid. This explains why 800 °C shows lower resulting solid reactivity than 700 °C for CaO (see Figure 2.3 (a)). This trend is also confirmed by the morphological information shown in Table 2.1. If the “outward diffusion mode” or “mixed diffusion mode” dominate the gas-capture process, the solid’s structural ions (e.g. iron cation in this chapter) diffuse outward through the gas-solid interface during the capture step which adds extra volume expansion, and diffuses inward during the gas release process which adds extra pore generation, compared to the “inward diffusion mode”. The effect of structural ion diffusion on the surface pores is elaborated in the following section. Given that ionic diffusivity increases “exponentially” with temperature, a higher temperature would generate more surface area and pore volume through enhanced volume expansion-and-shrinking process (see Table 2.3). These enhanced morphological properties then reflect in the Fe solid O₂ capture capacity, as shown in Figure 2.3(c).

2.3.3 Effect of Cyclic Gas-Solid Reaction

With the reaction temperature and reaction time fixed, the temperature-induced sintering effect on a solid particle should be the same (at least similar). The effect of cyclic gas-solid reaction is studied by comparing a solid reactant (CaO and Fe) that goes through a cyclic reaction and a solid reactant that only goes through the same temperature condition (time length and temperature) without any reactive gas introduced. As can be seen from Figure 2.3 (a) and (c), the cyclic reaction per se shows an obvious deteriorating effect on the resulting solid reactivity. To exclude the possibility that this deteriorating effect is due to the sintering/calcination on the product solid (CaCO₃ and Fe₂O₃), a product solid (CaCO₃ and Fe₂O₃) goes though the same temperature condition before
being converted to the reactant form (CaO and Fe). As shown in Figure 2.3 (b), the reactivities of “Sintered CaCO\(_3\) in CO\(_2\)” (“6 temp cycles + 0 CCR”) and “Sintered CaO in N\(_2\)” (“6 temp cycles + 0 CCR”) are both higher than that of the “6 temp cycles + 3 CCR”. Same conclusion is also valid for Fe and Fe\(_2\)O\(_3\) (see Figure 2.3 (d)). This comparison shows that the cyclic reaction is an independent deactivating effect in the overall solid deterioration which was almost unanimously attributed to the sintering/calcination effect in the previous studies.\(^1\),\(^4\),\(^18\),\(^19\)

When the gas-capture occurs, the overall surface pore removal can be contributed by volume expansion and possible solid-phase ionic transfer. As aforementioned, some pore volume of both bigger-pores and smaller-pores are “squeezed” off due to volume expansion of the product layer. This effect is mainly determined by the molar volumes of the solid product and the solid reactant. And if the solid-phase ionic transfer mechanism during the gas-capture step follows the “inward diffusion mode” (e.g. CaO + CO\(_2\) in this chapter), the non-structural ions (e.g. CO\(_3^{2-}\) in this chapter) would “enter” the solid structure without changing the arrangement of the structural ions (e.g. Ca\(^{2+}\) in this chapter). The overall pore removal is only contributed by the molar volume expansion. But if it follows the “outward diffusion mode” (e.g. Fe + O\(_2\) in this chapter) or “mixed diffusion mode”, the structural ion (e.g. iron cation in this chapter) would diffuse outward through the gas-solid interface. This outward diffusion rate is almost equal everywhere on the flat surface and its direction is perpendicular to the gas-solid interface. While on the surface with curvature, like the bottom part of the “valley” shown in Figure 2-4(b), the outward diffusion is much facilitated since the curvature gives larger diffusing areas. Because of this mechanism, the structural ions would diffuse more into the “valley” of
pores than that into the “top” of pores, which leads to pore burial. A reverse process occurs, when the gas component is released from the solid product and the structural ions diffuse backward. The effect of solid-phase transfer of structural ions to the porous structure was simulated by a 2-D continuum diffusion equation, using reduction and oxidation cycle of Fe as example. It can be seen from Figure 2.4, as the structural ions diffuse outward during gas capture, the pore volume decreases and the solid boundary expands. And as the structural ions diffuse inward during the gas-release, the pore volume increases and the solid boundary draws back.

It may raise a question that “if the pore closing-and-opening process was reversible, the overall morphological properties would not be affected by reaction cycles”. However, during the actual gas-release process, pores can be generated “everywhere” on the solid surface due to molar volume shrinking and possible inward diffusion of the structural ion, even on the flat surface area where no pore exists before the gas-capture step. The newly generated pores are generally smaller pores and “share” some pore volume of the bigger pores before the gas-capture process. Therefore, surface pore volume tends to be redistributed from bigger pores to the smaller pores, and the average pore diameter tends to decrease. In addition, there are some inner pores that are connected to the gas phase through surface pores before gas-capture step. Because of the irreversible pore closing-and-opening and decreasing pore diameter, some of such inner pores would be permanently closed or disconnected from gas-phase after cyclic reactions. As can be seen from Figure 2.5 (a), after three carbonation-calcination reaction (CCR) cycles, the pore volume of the bigger pores (20 ~ 100 nm) in CaO solid is greatly reduced while the pore volume of the smaller pores (< 20 nm) was relatively stable,
although smaller pores are more susceptible to sintering/calcination. And comparing the diameter ranges of the major pore volumes of “0 temp cycles + 0 Redox” and “2 temp cycles + 1 Redox” in Figure 2.5 (b), there is a general trend of pore volume drifting from larger ranges to smaller ranges. This average pore-size decrease for CaO and Fe confirms the mechanism described above.\(^1,9,22\) Therefore, through irreversible pore closing-and-opening by molar volume expansion-and-shrinking and possible structural ion diffusion, a cyclic reaction generally decreases the morphological properties of solid reactants, which is a unique and universal deteriorating factor in the cyclic gas-solid reactions. This mechanism does not apply to some special reactions, in which the product layer disintegrates due to low mechanical properties, such as steam/moisture hydration of CaO.

### 2.3.4 Discussion

Conventionally in heterogeneous catalysis reaction, the activity of a given solid catalyst is generally the reflection of its surface area and pore volume, which are mainly determined by its preparation process and working condition.\(^23\) Hence in the catalyst preparation, researchers use various approaches, such as physical support, sol-gel, impregnation, solution combustion, physical and chemical vapor deposition, etc., for the purpose of improving initial solid morphological properties. This practice is valid because, throughout an ideal catalysis process, a catalyst per se is not converted by any chemical reaction. And in a real process, the only factors that can possibly deteriorate the catalyst activity are extrinsic, e.g. poisoning, sintering, and etc.\(^24\) Such solid conversion is minimal. Therefore, good and long-lasting catalyst morphological properties can be achieved by good initial solid conditions, decent anti-sintering, up-stream feed clean-up,
and reasonable reaction condition control. It is similar for “one-time” gas-solid reactions, in which the fresh solid properties are the most important.25,26

However, when “cloning” this successful “optimizing-initial-morphology” strategy to a cyclic gas-solid reaction, most researchers overlooked an intrinsic nature of the solid reactant in this unique reaction pattern: the cyclic changes of solid structure and surface morphology. This cyclic structural change is a complex process which involves multiple factors in the cyclic reaction, such as the solid’s inherent properties, solid-phase ionic transfer, and reaction condition. As discovered in this chapter, this cyclic structural change tends to deteriorate the solid morphological properties. This independent role of cyclic reaction indicates that a large portion of effort for optimizing initial surface area and pore volume would eventually be wasted, regardless how well the reaction condition is controlled. Given that the solid morphological properties would inevitably deteriorate, the chemical-reaction-controlled step would become less important in the overall solid conversion. One approach to combat this morphological deterioration is to “destroy and reactivate” the decayed solid surface, such as applying hydration to the deactivated CaO sorbent during cyclic reactions with CO₂.27 However, this approach requires the solid to have some specific properties, e.g. low mechanical strength, which limit their general application. Alternatively, if the solid-phase ionic transfer capability could be enhanced, this inevitable reactivity loss by morphological deterioration might be compensated. It has been previously reported that, by doping certain exotic ions to the solid crystal structure, the ionic diffusion rate can be significantly enhanced, which would maintain stable solid reactivity and recyclability, despite a steady decay in surface area and pore volume.17 Because the enhanced ionic transfer capacity is relatively stable over cyclic
reactions and less susceptible to morphological deterioration, this approach should be more effective in maintaining the overall solid reactivity in the cyclic gas-solid reactions.

2.4 Concluding Remarks

In this chapter, we report the reactivity and morphological change of solid reactants in cyclic gas-solid reactions. Solid reactivity is studied as its gas capture capacity on a Thermal Gravimetric Analysis (TGA) test. The morphological properties are characterized by the surface area and pore structure from Brunauer-Emmett-Teller (BET) tests. Cyclic carbonation-calcination reactions of CaO and cyclic reduction-oxidation reactions of Fe are used to represent two types of cyclic gas-solid reactions: with only non-structural ion diffusion and with structural ion diffusion, respectively. Effects of reaction temperature, reaction time, and cyclic reaction on the solid reactivity and morphological properties are independently examined. It is found that longer exposure to reaction temperature would decrease the surface areas, pore volumes, and corresponding reactivities of both studied solid reactants, which is attributed to the extended sintering/calcination effect. In contract to the previous perspective, the effect of reaction temperature on the resulting solid reactivity is conditional, depending on the solid-phase ionic transfer mechanism. If the dominating diffusing ions in the cyclic reaction are all non-structural (“inward diffusion mode”), a higher reaction temperature induces greater sintering/calcination, which leads to greater solid morphological deterioration. If the structural ion participates in solid-phase ionic transfer (“outward diffusion mode” and “mixed diffusion mode”), a higher reaction temperature would lead to higher volume expansion during gas-capture and higher volume shrinking during gas-release. This enhanced volume expansion-and-shrinking is more beneficial to porous
structure at a higher temperature than at a lower temperature, which leads to a better solid reactivity. With the effects of reaction temperature and reaction time excluded, the effect of a cyclic reaction *per se* is independently examined, which shows obvious deterioration to the solid reactants. This independent deteriorating effect is attributed to the irreversible pore closing-and-opening, which is contributed by molar volume expansion-and-shrinking and possible solid-phase ionic transfer. In addition, a 2-D continuum diffusion modal is applied to simulate the surface pore structure change by structural ion diffusion during the gas-capture and gas-release steps, respectively. It is found that structural ions would “bury” the surface pore during gas-capture step and “enlarge” the surface pore during gas-release step. Elucidation of the mechanism of reactivity and morphological change of solid reactants would help re-evaluate the previous research efforts and re-build fundamental understandings towards cyclic gas-solid reactions.
Table 2.1. Detailed Information about Preparation Procedure of all the CaO Samples prior to the final CO\(_2\) Capture Capacity Tests.

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Initial Calcination ((\alpha))</th>
<th>Carbonation-Calcination Reaction (CCR) Cycles ((\beta))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calcination Time</td>
<td>Calcination Gas</td>
</tr>
<tr>
<td>0 temp cycles + 0 CCR</td>
<td>Stops after calcination completes</td>
<td>100% N(_2)</td>
</tr>
<tr>
<td>Sintered CaO in N(_2) (6 temp cycles + 0 CCR)</td>
<td>20 min</td>
<td>100% N(_2)</td>
</tr>
<tr>
<td>6 temp cycles + 3 CCR</td>
<td>20 min</td>
<td>100% N(_2)</td>
</tr>
<tr>
<td>6 temp cycles + 6 CCR</td>
<td>20 min</td>
<td>100% N(_2)</td>
</tr>
<tr>
<td>Sintered CaCO(_3) in CO(_2) (6 temp cycles + 0 CCR)</td>
<td>20 min</td>
<td>100% CO(_2)</td>
</tr>
<tr>
<td>Sample I.D.</td>
<td>Initial Reduction (α)</td>
<td>Reduction-Oxidation (Redox) Cycles (β)</td>
</tr>
<tr>
<td>-------------</td>
<td>----------------------</td>
<td>---------------------------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1st Oxidation</td>
</tr>
<tr>
<td>0 temp cycles + 0 Redox</td>
<td>Stops after reduction completes</td>
<td>N/A</td>
</tr>
<tr>
<td>Sintered Fe in H₂ 2 temp cycles + 0 Redox</td>
<td>20-260</td>
<td>N/A</td>
</tr>
<tr>
<td>2 temp cycles + 1 Redox</td>
<td>20-30</td>
<td>30-70</td>
</tr>
<tr>
<td>2 temp cycles + 2 Redox</td>
<td>20-30</td>
<td>30-45</td>
</tr>
<tr>
<td>Sintered Fe₂O₃ in N₂</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The time ranges listed in Table 2.2 correspond to the time axis in Figure 2.2

Table 2.2. Detailed Information about Preparation Procedure of all the Fe Samples prior to the final O₂ Capture Capacity Tests.
<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 temp cycles + 0 CCR @ 800 °C</td>
<td>18.576</td>
<td>0.134</td>
</tr>
<tr>
<td>6 temp cycles + 0 CCR @ 700 °C</td>
<td>20.259</td>
<td>0.157</td>
</tr>
<tr>
<td>6 temp cycles + 0 CCR @ 800 °C</td>
<td>14.273</td>
<td>0.149</td>
</tr>
<tr>
<td>0 temp cycles + 3 CCR @ 800 °C</td>
<td>8.293</td>
<td>0.056</td>
</tr>
<tr>
<td>Sintered CaCO$_3$ in CO$_2$ @ 800 °C</td>
<td>15.800</td>
<td>0.130</td>
</tr>
<tr>
<td>0 temp cycles + 0 Redox @ 900 °C</td>
<td>2.605</td>
<td>2.782×10$^{-3}$</td>
</tr>
<tr>
<td>2 temp cycles + 0 Redox @ 800 °C</td>
<td>0.793</td>
<td>1.302×10$^{-3}$</td>
</tr>
<tr>
<td>2 temp cycles + 0 Redox @ 900 °C</td>
<td>1.111</td>
<td>1.246×10$^{-3}$</td>
</tr>
<tr>
<td>2 temp cycles + 1 Redox @ 900 °C</td>
<td>0.754</td>
<td>1.444×10$^{-3}$</td>
</tr>
<tr>
<td>Sintered Fe$_2$O$_3$ in N$_2$ @ 900 °C</td>
<td>1.796</td>
<td>1.837×10$^{-3}$</td>
</tr>
</tbody>
</table>

Table 2.3. Morphological information of the CaO and Fe solid reactants
Figure 2.1. Detailed Information about Preparation Procedure of all the CaO Samples prior to the final CO$_2$ Capture Capacity Tests.
Figure 2.2. Schematic illustration of temperature sequence of Fe sample preparation and test. (α: initial reduction; β: Redox cycles; γ: final test).
Figure 2.3. Effects of reaction time, reaction temperature, and cyclic reactions on the gas-capture capacities (reactivities) of CaO and Fe solids. (a): 30 min CO₂ weight capture percentage of CaO; (b): control test of sintered CaCO₃; (c): 5 min O₂ weight capture percentage of Fe; (d): control test of sintered Fe₂O₃
Figure 2.4. Illustration of the simulated pore structure change by diffusion of structural ions (e.g. iron cation in this chapter) in (a): gas-release (reduction) and (b): gas-capture (oxidation) cycles of Fe using a 2-D continuum diffusion equation. (Effect of molar volume change is not included in this model)
Figure 2.5. Pore size distributions of the tested CaO and Fe solids. (negligible pore volume is present out of the displayed diameter ranges)
CHAPTER 3

Experimental Study of HCl Capture Using CaO Sorbents: Activation, Deactivation, Reactivation, and Ionic Transfer Mechanism

3.1 Introduction

Hydrogen chloride (HCl), which presents in coal-derived synthesis gas and coal-fired power plant flue gas, is a hazardous species to both process hardware and environmental health. The HCl concentration in these gas streams varies from 1 ppm to the order of several thousand ppm, depending on the coal composition and specific coal conversion process. Due to its corrosive and polluting nature, HCl needs to be removed from synthesis gas and flue gas to acceptable levels before downstream utilization and/or emission to the atmosphere.

Current HCl removal processes can be classified into either “wet processes” or “dry processes (including semi-dry processes).” Although wet processes are more widely used in industry, dry processes have several potential advantages over the existing wet processes, such as low capital requirement, low waste disposal, and ease in operation. Unlike the wet processes which are limited to low-temperature operations, dry processes, when performed at elevated temperatures with high-temperature sorbents, can increase the overall process efficiency. Among all the dry-process sorbents being used in industry
and under R&D, CaO sorbent is one of the most promising candidates, due to its low cost, high operating temperature, and relatively high chlorine capture capacity.\textsuperscript{35-38}

In the previous studies, most efforts were devoted to the investigation of kinetics, thermodynamics, and operating parameters of CaO sorbents in chloridation reaction. However, the effect due to the presence of other types of species such as SO\textsubscript{2}, H\textsubscript{2}S or CO\textsubscript{2} in CaO-based chemical looping processes,\textsuperscript{38-40} on the global sorbents’ chloridation reactivity has not been explored to date. In addition, there also lacks reaction mechanism information related to the ionic transfer in the CaCl\textsubscript{2} dense product phase in the earlier studies. Hence, understanding of sorbents’ chloridation reactivity change and reaction mechanism is of notable significance to the operation of such processes.

In this chapter, five aspects concerning the chloridation reaction and corresponding mechanism of CaO sorbents were investigated: 1) kinetics and operating parameters of CaO sorbents in chloridation reaction in TGA and fixed-bed setups; 2) the deactivating effects of some reaction/operating parameters on the chloridation reactivity of CaO sorbents, mainly in the context of CaO-based chemical looping processes; 3) using precipitation and hydration, respectively, to activate and reactivate CaO sorbents for the purpose of dry HCl capture; 4) explaining the deactivation and the effectiveness of activation and reactivation from the morphological standpoint; 5) identifying the dominating ionic transfer mechanism of chloridation reaction by inert marker experiment.
3.2 Chemical Reactions Involved in this Chapter

In this chapter, six major chemical reactions are involved, descriptions of which are listed below:

Synthesis of Precipitated Calcium Carbonate (PCC)

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (3-1)$$

In the chapter of sorbent activation, specially-tailored PCC is synthesized by precipitation of $Ca^{2+}$ cations and $CO_3^{2-}$ anions from Ca(OH)$_2$ slurry with a specially-designed procedure, which is elaborated in the experimental section.

Calcination of Limestone or PCC

$$CaCO_3 \rightarrow CaO + CO_2 \quad (3-2)$$

In reaction (3-2), naturally-occurring limestone or specially-tailored PCC is calcined to CaO for further reaction with CO$_2$ in a multi-cyclic CCR or capture of HCl in chloridation reaction (3-4).

Carbonation of CaO

$$CaO + CO_2 \rightarrow CaCO_3 \quad (3-3)$$

Reaction (3) occurs when CaO, calcined from reactions (3-2) or (3-6), reacts with CO$_2$ in the study of deactivation and reactivation, respectively.

Chloridation of CaO

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \quad (3-4)$$
Dry capture of HCl by CaO is the key reaction investigated in this chapter. The chloridation reaction rate (HCl capture capacity) is mainly dependent on reaction conditions and reactivity of CaO.

**Hydration of CaO**

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad (3-5) \]

In the study of reactivation, hydration is applied to reactivate the deactivated CaO.

**Calcination of Ca(OH)$_2$**

\[ \text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} \quad (3-6) \]

After hydration (3-5), Ca(OH)$_2$ is calcined back to CaO for further carbonation reaction (3-3) or chloridation reaction (3-4).
3.3 Experimental Details

Materials

Calcium hydroxide [Ca(OH)\textsubscript{2}] (for PCC synthesis only) and naturally-occurring limestone (CaCO\textsubscript{3}) were obtained from Graymont. Pure CaO powder for the inert marker experiment was from Aldrich Chemicals (99.95%). The procedure for the synthesis of Precipitated Calcium Carbonate (PCC) is outlined in the following section. Preparations of deactivated CaO as well as reactivated CaO are also described below. CO\textsubscript{2} and N\textsubscript{2} used for carbonation and calcination are 99.99 % and 99.999 % pure, respectively. HCl-containing gas stream was obtained by mixing gaseous HCl with N\textsubscript{2}. N40V is a sodium salt of a carboxylic acid, which was obtained from Allied Colloid and used in the synthesis of PCC.

Synthesis of Precipitated Calcium Carbonate (PCC)

It has been reported in the literature that morphological properties of CaO precursors can be tailored for enhanced acidic gases (CO\textsubscript{2} and SO\textsubscript{2}) capture using the synthesis procedure outlined in the previous literature.\textsuperscript{41,42} Figure 3.1 illustrates the schematic diagram for synthesis of this specially-tailored CaO precursor: Precipitated Calcium Carbonate (PCC). As shown in Figure 3.1, a slurry bubble column was used as carbonator, which consisted of a 5 cm O.D. Pyrex tube. In between slurry phase and glass beads was located a porous frit for the purpose of good distribution of CO\textsubscript{2} through Ca(OH)\textsubscript{2} slurry. A K-type thermocouple and a pH probe were inserted into the slurry to monitor the reaction temperature and pH change, respectively.
Similar to the previous studies, 0.5 l of distilled water and 0.0575 g of N40V were first filled into the reaction column in sequence. Then, 12.8 g Ca(OH)$_2$ was added to the solution to achieve a loading of 2.56 wt %, which corresponds to the concentration of 16 times the Ca(OH)$_2$ saturation solubility limit. In addition, the ratio of Ca(OH)$_2$ to N40V used here reached the exact point, at which no surface charge existed on the incipiently-formed CaCO$_3$ particles. After the slurry was ready, a CO$_2$ stream was introduced into the carbonator with the pH of slurry being constantly monitored. Hence, the Ca$^{2+}$ cations reacted with the CO$_3^{2-}$ anions derived from the dissolving CO$_2$ to form CaCO$_3$. The CaCO$_3$ then precipitated out due to its low solubility, which is the specially-tailored Precipitated Calcium Carbonate (PCC).

**Deactivation and Reactivation of CaO Sorbents**

Deactivated CaO sorbents were prepared using three methods: 1) multi-cyclic carbonation-calcination reaction (CCR); 2) high-temperature calcination; and 3) co-deactivation by combined 1) and 2) (in the fixed-bed tests only). Multi-cyclic CCR was carried out at 650 °C (carbonation step, 10% CO$_2$) and 700 °C (calcination step, inert condition). CaO sorbent deactivation by high-temperature calcination was conducted at 700 ~ 900 °C under 120 ml/min N$_2$. In the fixed-bed tests, the co-deactivated sample was inertly calcined at 900 °C and carbonated at 650 °C under 10% CO$_2$. Effects of sorbent deactivation on the chloridation reactivity are discussed in the following sections. Hydration was applied to the deactivated limestone-CaO at 400 °C with 100 % H$_2$O. Excessive H$_2$O was used to ensure complete hydration.

**Reaction Rate Test and Morphology Analysis**
A Perkin-Elmer (Pyris 1) Thermogravimetric Analyzer (TGA) apparatus and a fixed-bed reactor were used for chloridation reaction tests of CaO sorbents. The balance of the TGA can measure accurately up to $10^{-7}$ g. A small amount of sorbent sample (20 ~ 30 mg) was placed in a quartz crucible in each test. The sample weight was continuously recorded for further analysis. The design of the fixed-bed reaction system was shown in Figure 3.2, which consisted of three major components: 1) gas inlet system; 2) reactor & furnace; 3) gas analysis system.

The fixed-bed reactor was a 1 cm I.D. quartz tube. And the HCl analyzer is PureAire HCl analyzer, which could measure accurately to 0.1 ppm HCl. The morphological properties of CaO sorbents and their precursors were tested in a NOVA 4200e analyzer (Quantachrome Company). The Brunauer Emmett Teller (BET) surface area and pore volume were measured at -196 °C using liquid N$_2$ as adsorbent.

**Definition of Chloridation Reaction Rate of CaO Sorbents**

The chloridation reaction rate is defined as follows:

Weight Capture Percentage at time $t$: $$C_t = \frac{(W_t - W_o)}{W_0} \times 100 \text{ } (\%)$$

Weight Capture Rate (chloridation reaction rate of CaO sorbents): $$R = \frac{dC_t}{dt} \text{ } (\%/\text{min})$$

Where:

$W_o$: Sample weight after complete calcination. (mg)

$W_t$: Sample weight at a given time $t$. (mg)
Based on the definitions of these two parameters, larger $R$ refers to faster reaction rate. The weight capture rates reported in this chapter are initial reaction rates at the early stage of chloridation.

**Inert Marker Experiment**

In this chapter, inert marker technique was applied to identify the dominating ionic transfer mechanism in the reaction of CaO and HCl. CaO powder was first pressed into cylindrical tablets (diameter = 6 mm, height = 4 mm) by a 22226 N (5000 lb) hydraulic force. The tablets were sintered at 1200 °C for 48 hours under N$_2$ environment to remove the inner pore volume. The purpose of inner pore volume removal is to ensure that the growth of the product layer during the reaction is only a result of ionic diffusion of gases-reactant-derived species rather than the gas diffusion through porous structure. Then, the well-sintered CaO tablets were cooled down to the room temperature, and a strip of platinum paint (SPI supplies) was applied onto one side of the tablet. The platinum paint is a mixture of metallic platinum powder and organic solvents. Once heated, the organic solvents would vaporize, leaving only a layer of metallic platinum on the tablet surface as shown in Figure 3.3(a).

The platinum-marked CaO tablet was put into the TGA to react with gaseous HCl (50 ppm, balanced with N$_2$). The reaction was carried out at 500 °C for 30 days to ensure the partial conversion of CaO into CaCl$_2$. After the reaction was complete, the tablet was cooled down to room temperature and removed from the TGA. The tablet was post-treated for Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer
(EDS) analyses. As to the post-treatment, the tablet was first mounted in epoxy resin and then diagonally cut into two pieces, with the cross-section polished and exposed for SEM analysis (see Figure 3.3(b)). Energy Dispersive Spectrometer (EDS) was also used to obtain mappings of chlorine, platinum, and calcium on the same surface. The detailed results are presented in the following section.
3.4 Results and Discussion

Syngas and flue gas contain various acidic gases including CO$_2$, HCl, and sulfur-derived species, which can be simultaneously captured by CaO sorbent at elevated temperature.$^1$ Therefore, there may exist competing mechanism between co-capture of these gases. However, the current work focuses on the intrinsic reaction between CaO and HCl, excluding the influence of other acidic gases.

3.4.1 TGA Study 1 - Effect of Chloridation Temperature

The performances of limestone-CaO and PCC-CaO were first tested on TGA. External mass-transfer resistance was minimized by placing the tested samples in a thin layer in the TGA quartz sample holder. Limestone-CaO and PCC-CaO were obtained by calcining limestone and PCC at 700 °C under N$_2$, respectively. Introduction of HCl immediately followed the completion of calcination. Effect of temperature on chloridation reaction rate was investigated at four representative temperatures: 500 °C, 550 °C, 600 °C, and 650 °C, which is shown in Figure 3.4. As can be seen from Figure 3.4, the fastest HCl capture rate for both sorbents occurs at 550 °C. Similar results were reported in some previous studies. A reasonable explanation to the decrease of HCl capture rate above this optimal temperature is that, as chloridation temperature elevates further above 550 °C, the increase of HCl absorption by CaO is offset by the faster increase of HCl desorption from the CaCl$_2$.\textsuperscript{37,38} At each given chloridation temperature, PCC-CaO has higher capture capacity than limestone-CaO. The reason of the enhanced performance of this specially-tailored PCC-CaO sorbent can be explained by its more favorable morphology, which is described in a following section.
3.4.2 TGA Test 2 - Effects of HCl Concentration and Sorbent Precursor Particle Size

The effects of HCl concentration and sorbent particle size on the chloridation reaction rate were tested on the PCC-CaO sorbent. As to the effect of HCl concentration, three HCl concentrations (25 ppm, 500 ppm, and 1500 ppm) were obtained by mixing a 3000 ppm HCl stream and a pure N\textsubscript{2} stream at three different ratios. The effect of HCl concentration is given in Figure 3.5. Figure 3.5 indicates that, the higher the HCl concentration is, the faster the chloridation reaction of PCC-CaO is. This trend is very similar to the previously reported HCl capture by solid lime.\textsuperscript{39}

In addition, PCC solid was ground and screened into three size ranges: below 180 μm, 180 ~ 250 μm, and above 250 μm. At each given temperature shown in Figure 3.6, the chloridation reaction rate of PCC-CaO sorbent decreases as the particle size increases. Similar results were reported based on CaO sorbents from other precursors.\textsuperscript{43-46} This property can be explained by the fact that a smaller particle has a relatively larger surface area and pore volume, which leads to faster chloridation reaction rate.

3.4.3 TGA Test 3 - 1) Deactivation by Multi-Cyclic Carbonation-Calcination Reaction (CCR) and High-Temperature Calcination; 2) Reactivation by Hydration

A number of processes were proposed in recent years that use CaO sorbents (mostly derived from limestone) to remove CO\textsubscript{2} from flue gas or to produce H\textsubscript{2} from syngas. The main purpose of using CaO sorbents is to capture CO\textsubscript{2} into a CaCO\textsubscript{3} form and then to release it into a sequestration-ready CO\textsubscript{2} stream through a multi-cyclic carbonation-calcination reaction (CCR) process. Meanwhile, the HCl can be permanently captured in the form of CaCl\textsubscript{2} and disposed as solid waste along with the spent
sorbent. With the multi-cyclic CCR reaction, the sorbent property may change, which can potentially affect the chloridation reactivity of the recycled CaO sorbents. To better understand the effect of multi-cyclic CCR on the sorbents’ HCl capture capacity, chloridation reaction was conducted after the Nth CCR reaction (N = 0, 5, 10, 15). Take the (N = 10, R = 0.00128 %/min) point in Figure 3.7 for example, this exemplified process can be illustrated as \{[(\rightarrow\text{CaCO}_3\rightarrow\text{CaO}\rightarrow)\times10] \rightarrow\text{CaCl}_2\}. That is, limestone went through ten CCR cycles, and the resulting CaO then reacted with HCl. Weight capture rate of this resulting CaO is 0.00128 %/min. Figure 3.7 indicates that the multi-cyclic CCR demonstrates deactivating effect on the chloridation reactivity of both limestone-CaO and PCC-CaO. This may be attributed to pore closure by the CCR process. However, the specially-tailored PCC-CaO has higher reactivity than limestone-CaO at each given condition, and the trend of deactivation of PCC-CaO is much less notable than that of limestone-CaO. This can also be explained by the outstanding morphology of PCC, which is discussed in a following section.

Hydration was applied to the deactivated limestone-CaO sorbent to accomplish reactivation. Two hydration strategies were compared to find the possible mechanism of hydration reactivation. Hydration-1 is to apply hydration to recycled CaO only once after the Nth CCR. Take the (N = 10, R = 0.00185 %/min) point in Figure 3.7 for example, limestone first went through ten CCR cycles and ended up as limestone-CaO after the ten CCR cycles. After that, hydration was applied to this limestone-CaO. The hydrated sorbent was then calcined back to CaO and its chloridation reaction rate was measured (0.00185 %/min). This exemplified process can be illustrated as \{[(\rightarrow\text{CaCO}_3\rightarrow\text{CaO}\rightarrow)\times10] \rightarrow\text{Ca(OH)}_2\rightarrow\text{CaO}\rightarrow\text{CaCl}_2\}. Hydration-2 is to apply
hydration every time a calcination step is over. Take another point (N = 10, R = 0.00242 %/min) in Figure 3.7 for example, limestone was first calcined into CaO, and hydration was applied to this CaO. After that, the hydrated sample was further calcined back to CaO prior to a following carbonation step. This reaction cycle repeated for another nine times before the final reaction with HCl. This exemplified process can be illustrated as \[\{(\rightarrow\text{CaCO}_3\rightarrow\text{CaO}\rightarrow\text{Ca(OH)}_2\rightarrow\text{CaO}\rightarrow)\times10\rightarrow\text{CaCl}_2\}\]. As shown in Figure 3.7, both hydration strategies have obvious reactivating effect on the deactivated CaO sorbent. Nevertheless, hydration-2 can maintain and even improve the initial reactivity of fresh limestone-CaO even after fifteen CCR cycles, while the reactivating effect by hydration-1 decreases as the CCR number increases. A comparison of these two strategies implies that the activating effect of hydration is likely a result of the “hydration process” rather than the “hydration product”. The detailed hydration mechanism in discussed in a following chapter.

Another possible deactivating factor in the HCl capture process, the calcination temperature, was also studied. It has been discussed in the literature that high-temperature calcination (sintering) of CaCO$_3$-derived sorbents can lead to rapid deterioration of the sorbents’ CO$_2$ capture reactivity due to pore closure and pore size decrease as described in the previous chapter.$^{63-65}$ In order to study the effect of calcination temperature on the chloridation reactivity, limestone and PCC were calcined at five different temperatures: 700 °C, 750 °C, 800 °C, 850 °C, and 900 °C. Calcination time was fixed the same for all tests to exclude any influence of calcination time. Shown in Figure 3.8, as calcination temperature increases, the chloridation reactivities for both PCC-CaO and limestone-CaO decrease. This indicates that the pore closure resulting from high-temperature sintering
can adversely affect the chloridation reactivity. In addition, PCC-CaO demonstrates better sintering resistance compared with limestone-CaO in terms of both absolute value of reaction rate and the deactivation percentage. To study a possible reactivating method, hydration was applied to the calcined limestone-CaO samples. It can also be observed in Figure 3.8 that the chloridation reactivity of the sintered limestone-CaO sorbent was restored and even improved by hydration.

3.4.4 Fixed-Bed Test 1 – Effect of Chloridation Temperature

In order to have a better understanding of the properties of these CaO sorbents and further verify some results obtained from TGA tests, a fixed-bed reactor was used to study the effects of temperature, space velocity, activation, deactivation, and reactivation.

The effect of chloridation temperature on the HCl capture capacity of limestone-CaO was investigated first. As shown in Figure 3.2, an HCl analyzer was used at the end of the fixed-bed reactor and continuously recorded the HCl concentration in the outlet gas stream. The HCl breakthrough curves of five chloridation temperatures are shown in Figure 3.9, from which it can be seen that the HCl capture capacity increases from 450 °C to 550 °C and then decreases after 550 °C. This result is in good agreement with the one from the TGA study and can further consolidate the conclusion that the optimal temperature for high-temperature HCl capture is about 550 °C. 37,38

3.4.5 Fixed-Bed Test 2 – Effect of Space Velocity

The effect of space velocity on limestone-CaO HCl capture capacity was studied at 550 °C. Defined as the volumetric flowrate of HCl-containing gas disposed per unit of CaO sorbent, space velocity is one of the most important operating parameters in
industrial acidic-gas capture processes. The breakthrough CaO conversions of the studied space velocities are back-calculated and shown in Figure 3.10. As illustrated in this figure, the CaO conversion decreases as the space velocity increases. Although lower space velocity can achieve higher sorbent utilization, it could also lead to slower gas processing rate. Therefore, both breakthrough CaO conversion and gas processing rate should be taken into consideration in order to find an optimal operating condition for a specific gas-cleaning process.66

3.4.6 Fixed-Bed Test 3 – Effects of Activation, Deactivation, and Reactivation

To further study the effects of activation, deactivation, and reactivation, five representative samples were prepared and used in this fixed-bed study. Detailed information about these five samples as well as their preparation and chloridation procedures in this specific study is listed in the Table 3.1.

PCC-CaO (product from activation) and limestone-CaO were first compared in terms of breakthrough time. PCC-CaO shows better HCl capture capacity than limestone-CaO (see Figure 3.11). Five CCR cycles and high-temperature sintering (900 °C) were used to deactivate limestone-CaO. As can be seen from the same figure, both processes can lead to reactivity deterioration for the limestone-CaO sorbent. To study the reactivating effect of hydration, a co-deactivated limestone-CaO was hydrated. This co-deactivated limestone-CaO was prepared through five CCR cycles, in each of which the calcination temperature was kept at 900 °C. That is, this sorbent underwent both aforementioned deactivating processes. After hydration was applied to this sorbent, it can be seen from Figure 3.11 that the reactivity of the co-deactivated limestone-CaO is
restored and even improved, which further confirms that hydration is an effective reactivating method for combined CaO deactivation.

3.4.7 Characterization of CaO Sorbents and their Precursors

3.4.7.1 XRD Analysis of CaO Sorbents

Since CaO sorbents used in this study come from various sources, it is necessary to ensure that sorbent crystal structure and purity are not factors that dominate the HCl capture. Hence, XRD patterns were obtained for all the CaO sorbents tested in this study. As shown in Figure 3.12, all the CaO sorbents are pure and of same crystal structure. Therefore, the difference in their chloridation reactivity is mainly a reflection of their morphology rather than their crystal structures or purities.

3.4.7.2 Surface Area and Pore Structure of CaO Sorbents and their Precursors

In order to better explain the reason for sorbent deactivation as well as the improved/restored performance after activation and hydration, morphological properties of the studied CaO sorbents and some of their precursors were analyzed. Limestone-CaO and PCC-CaO were obtained by calcining limestone and PCC at 700 °C, respectively. CCR-deactivated CaO sorbent and sintering-deactivated CaO sorbent were prepared using procedures described in TGA test 3. Hydration followed the procedures described in fixed-bed test 3. Morphological properties of these samples are listed in Table 3.2. From Table 3.2, it can be observed that the surface area and pore volume of PCC are higher than those of naturally-occurring limestone. It has been reported by Gupta et al. that most of the pores of limestone lie in the range of micro-pores, while diameter of most pores of this specially-tailored PCC originates from 5 nm to 20 nm.22 The 5 ~ 20
nm is a meso-pore range which has been proved to be less susceptible to pore closure and sintering. Therefore, even though the PCC-CaO has lower surface area and pore volume than limestone-CaO, this unique structural advantage enables PCC-CaO with better HCl capture reactivity as well as good deactivation resistance than limestone-CaO, as demonstrated in the previous sections. Given the fact that both limestone and calcium hydroxide (hydration product) are of micro-porous structure, performances of their derived CaO sorbents are mostly determined by their surface areas and pore volumes. Based on this fact, deactivation and reactivation of these sorbents are explained by their changes in surface area and pore volume during the deactivation and reactivation processes. As can be seen from Table 3.2, surface areas and pore volumes of CCR-CaO and sintered-CaO exhibit a drastic decrease compared to those of the fresh limestone-CaO, which indicates that the multi-cyclic CCR and sintering processes lead to undesirable pore closure. This drastic decrease in both surface area and pore volume can be used to explain the loss of chloridation reactivity after these two processes. When hydration is applied, an obvious increase in surface area and pore volume occurs to the deactivated CaO sorbent, which indicates that the closed pore structure is re-opened by hydration. Combined with the result from TGA test 3, it can be inferred that the reactivating effect of hydration is likely a result of a physical process such as intra-particle attrition and inner-pore expansion rather than a chemical/crystal change from CaCO$_3$-CaO to hydration-CaO. Based on the experimental results and morphological analysis, it can be concluded that specially-tailored precipitation (activation) and hydration (reactivation) are two effective methods that can improve or restore CaO
sorbents’ morphological structure, which can subsequently lead to the enhanced HCl capture performance.

3.4.8 Inert Marker Experiment

Inert marker technique is an effective method to identify the dominating ionic diffusion mechanism in metal oxidation and other gas-solid or solid-solid reactions.\textsuperscript{67-70} This technique mainly utilizes inert metal in the form of a thin wire or a porous layer as a marker to indicate the relative location change of the original interface (gas-solid or solid-solid) after reaction. Accurate identification of this change could further help determine the dominating ionic diffusion mechanism.\textsuperscript{71} Taking the reaction of acidic gas with CaO for instance, a dense product layer CaX (X=S, SO\textsubscript{4}, etc.) is first formed on the surface of CaO as reaction takes place. In order to proceed the reaction, the reactant species derived from gas phase or/and the reactant species derived from CaO solid phase has to transfer through the dense product layer to make mutual physical contact by means of ionic diffusion.

As shown in Figure 3.13(a), when an inert marker is applied on the CaO surface before reaction, the original gas-solid interface is clearly marked as the product layer thickens. Generally, there are three possible scenarios for the relative location change of inert marker after reaction, each one of which characterizes a representative dominating ionic diffusion mechanism. If the inward migration of the reactant species derived from gas phase is much slower than the outward migration of the reactant species derived from CaO solid phase, the product layer grows outwards at the gas-solid interface. This is called “Outward Growth Mode”, which is characterized by the location change of inert
marker from the original gas-solid interface to the final CaX-CaO interface as indicated in Figure 3.13(b). If the inward migration of the reactant species derived from gas phase is comparable with the outward migration of the reactant species derived from CaO solid phase, the product layer grows both inwards and outwards. After reaction, the inert marker is buried in the product layer, which is called “Mixed Growth Mode” (see Figure 3.13(c)). If the inward migration of the reactant species derived from gas phase is much faster than the outward migration of the reactant species derived from CaO solid phase, the product layer grows inward at the CaX-CaO interface. This is called “Inward Growth Mode”, which is characterized by the unchanged location of inert marker at the gas-solid interface as indicated in Figure 3.13(d).

Figure 3.14 shows the scanning electron micrograph of the cross-section of the partially-chlorided CaO tablet. As shown in this figure, the CaCl\textsubscript{2} product layer is located between the platinum layer and the unreacted CaO bulk phase, which indicates that the location of platinum layer remained relatively unchanged during the reaction process.

In order to further confirm the relative location of platinum layer, CaCl\textsubscript{2} layer, and CaO bulk phase, Energy Dispersive Spectroscopy (EDS) was applied to obtain the mappings of platinum, chlorine, and calcium on the same surface. As can be seen from Figure 3.15, distributions of the three elements were brightened in their representative mappings, from which the relative location of platinum layer, CaCl\textsubscript{2} layer, and CaO bulk phase can be verified. That is, the platinum layer is located on the top surface of the tablet, and the CaCl\textsubscript{2} layer is “sandwiched” between the top platinum layer and the bottom CaO bulk phase. According to the layout of the three solid phases, the ionic diffusion mechanism can be identified as aforementioned “Inward Growth Mode”. That is, the
The dominating diffusion pattern is the inward diffusion of Cl\(^{-}\) anions concurring with the outward counter-current diffusion of O\(^{2-}\) anions. At the CaCl\(_2\)-CaO interface, the Cl\(^{-}\) anions replace the O\(^{2-}\) anions in CaO to form CaCl\(_2\). In order to satisfy local mass and charge balance, the replaced O\(^{2-}\) anions diffuse outwards through the CaCl\(_2\) layer and react with H\(^{+}\) cations at the gas-solid interface to form H\(_2\)O.

In order to have a better understanding of the ionic transfer mechanism in this solid system, it is helpful to review the crystal structures of CaCl\(_2\) and CaO. CaO is of simple cubic structure, in which each Ca atom has six equidistant O atoms as nearest neighbors and vice versa. CaCl\(_2\) is of orthorhombic crystal structure. The diameters of Ca\(^{2+}\), O\(^{2-}\), and Cl\(^{-}\) ions are of similar order (1.98 Å, 2.8 Å, and 3.62 Å, respectively). Because of the low probability of co-occurrence of a cation vacancy and a neighboring anion vacancy in this system, the co-current diffusion of Ca\(^{2+}\) cation and O\(^{2-}\) anion through CaCl\(_2\) layer is a less favorable diffusion pattern compared with counter-current diffusion of Cl\(^{-}\) anion and O\(^{2-}\) anion. In this manner, the CaCl\(_2\) product layer grows inwards to the CaO bulk phase as CaO is gradually converted into CaCl\(_2\), while the O\(^{2-}\) anions diffuse outwards through the CaCl\(_2\) product layer and react with H\(^{+}\) cations at the gas-solid interface.
3.5 Concluding Remarks

TGA and fixed-bed experiments were carried out on various CaO sorbents to study a number of factors that affect the HCl capture capacity and/or chloridation reactivity including operating parameters, deactivation, activation, and reactivation strategies. It was observed that the highest HCl capture capacity occurs at about 550 °C for both limestone-CaO and specially-tailored PCC-CaO, and this property is independent of HCl concentration or particle size. Higher HCl concentration and smaller particle size can both lead to higher chloridation reaction rate for PCC-CaO. Multi-cyclic CCR and/or high-temperature calcination can lead to deterioration of chloridation reactivity of CaO sorbents. PCC-CaO performs better than limestone-CaO, in terms of chloridation kinetics and deactivation resistance. The improved performance of PCC-CaO can be explained by its advantageous meso-porous structure, which has been previously studied for CO₂ and SO₂ capture. This result further confirmed the versatility and effectiveness of PCC-CaO in acidic gas capture from coal-derived flue gas and synthesis gas. Hydration was applied to reactivate the deactivated limestone-CaO sorbent, by which the sorbent’s chloridation reactivity was restored and even improved. The change in sorbent morphology explains the mechanism behind the deactivation and reactivation. In addition, a comparison of two hydration strategies indicates that the reactivating effect of hydration, in terms of HCl capture, is likely to result from the “hydration process” rather than the “hydration product”. These findings provide support for the possible application of precipitation and hydration to CaO sorbents in future HCl capture processes. In order to understand the dominating ionic diffusion mechanism of chloridation reaction in the absence of pores, inert marker experiment was conducted. It
was determined that inward diffusion of Cl\(^-\) anions concurs with outward diffusion of O\(^{2-}\) anions at stoichiometric ratio during the ionic transfer process. Since the movement of the relatively large Cl\(^-\) and O\(^{2-}\) anions is relatively slow in the solid phase, especially considering that the anion vacancies tend to be scarce, the rate of chloridation reaction tends to be low in the absence of porous structure. This further validates the importance of porous structure in the CaO sorbents.
<table>
<thead>
<tr>
<th>Sample Information</th>
<th>Activation/Deactivation/Reactivation Stage</th>
<th>Reaction Stage</th>
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<td>Sample ID</td>
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<td>5</td>
<td>Hydration-CaO</td>
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Table 3.1. Detailed information about the five samples as well as their preparation and chloridation procedures in fixed-bed test 3.
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<th>Pore Volume (cm$^3$/g)</th>
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<td>0.1314</td>
</tr>
</tbody>
</table>

$^a$ Surface area and pore volume.

$^\beta$ Hydration sample was prepared using method in the fixed-bed test 3.

Table 3.2. Morphological properties$^a$ of various CaO sorbents and their precursors.
Figure 3.1. Schematic diagram of the slurry bubble column used for the synthesis of specially-tailored Precipitated Calcium Carbonate (PCC).
Figure 3.2. Schematic diagram of the fixed-bed reaction system used for HCl capture capacity test.
Figure 3.3. (a) Illustration of layout of platinum layer on the CaO tablet; (b) Illustration of the half tablet after diagonal cutting.
Figure 3.4. Effect of chloridation temperature on the chloridation reaction rates of limestone-CaO and PCC-CaO sorbents. (HCl concentration: 1500 ppm; Particle size: below 180 μm).
Figure 3.5. Effect of HCl concentration on the chloridation reaction rate of PCC-CaO. (Particle size: below 180 μm).
Figure 3.6. Effect of PCC particle size on the chloridation reaction rate of PCC-CaO. (HCl concentration: 1500 ppm).
Figure 3.7. Effect of multi-cyclic CCR on the chloridation reactivities for PCC-CaO and limestone-CaO as well as enhancing effect on the deactivated limestone-CaO by two hydration strategies. (Particle size: below 180 μm; Calcination condition: 700 °C, 100 % N₂; Carbonation condition: 650 °C, 10% CO₂ + 90 % N₂; Chloridation condition: 550 °C, 500 ppm HCl; Hydration condition: 400 °C, 100 % H₂O).
Figure 3.8. Effect of calcination temperature on the chloridation reactivity for PCC-CaO and limestone-CaO as well as effect of hydration on the deactivated limestone-CaO. (Particle size: below 180 μm; Chloridation condition: 550 °C, 1500 ppm HCl (N₂ as balance); Hydration condition: 400 °C, 100 % H₂O).
Figure 3.9. Effect of chloridation temperature on the chloridation reaction rate of limestone-CaO. (HCl concentration: 3000 ppm; Particle size: below 180 μm; Space velocity: 3000 h⁻¹).
Figure 3.10. Effect of space velocity on the chloridation conversion of limestone-CaO. (HCl concentration: 3000 ppm; Particle size: below 180 μm; Chloridation temperature: 550 °C).
Figure 3.11. HCl capture capacity comparison of CaO sorbents from limestone, activation, deactivation, and reactivation. (HCl concentration: 3000 ppm; Particle size: below 180 μm; Chloridation temperature: 550 °C; Space velocity: 3000 h⁻¹).
Figure 3.12. XRD diffractograms of CaO sorbents obtained from various precursors.
Figure 3.13. Principle of inert marker experiment. (a) Original sorbent with inert marker (platinum in this study); (b) “Outward Growth Mode” where reactants move from solid-solid interface to gas-solid interface; (c) “Mixed Growth Mode” where inward reactants diffusion is comparable with outward reactants diffusion; (d) “Inward Growth Mode” where reactants move from gas-solid interface to solid-solid interface.
Figure 3.14. SEM micrograph of cross-section of the partially-chlorided CaO tablet.
Figure 3.15. (a) SEM micrograph of EDS analyzed cross-section; (b) Platinum mapping of the cross-section; (c) Chlorine mapping of the cross-section; (d) Calcium mapping of the cross-section.
CHAPTER 4

Ionic Transfer Mechanism of COS Reaction with CaO: Inert Marker Experiment and Density Functional Theory (DFT) Calculation

4.1 Introduction

High-temperature dry removal of carbonyl sulfide (COS) from coal-derived synthesis gas (syngas) using CaO sorbent is a promising technique due to the sorbent’s low cost, high sulfur capture capacity, versatility in capture of multiple acidic gases from syngas, and potentially high process efficiency.\(^1\) The direct reaction of CaO and COS is shown in Equation 4-1.

\[
\text{CaO (g) + COS (s)} \rightarrow \text{CaS (s) + CO}_2 (g) \quad \Delta H^\circ (298 \text{ K}) = -93.2 \text{ kJ mol}^{-1} \quad (4-1)
\]

Due to the larger molar volume of CaS compared with CaO, the formed CaS product layer tends to cover the fresh CaO surface area and plug the internal pores. Therefore, direct COS-CaO contact is subsequently hindered and further CaO conversion is most likely controlled by the ionic diffusion through the CaS product layer. Hence, clear understanding to ionic transfer mechanism can help illustrate ways to improve the sorbent performance. In most solid-phase ionic transport processes, ions diffuse via crystal defects which are imperfection of the crystal structure.\(^{15}\) Generally, such ionic diffusion process needs to maintain local and global electro-neutrality. For this specific reaction scheme, the overall ionic transfer in the CaS layer can be dominated by 1)
counter-current diffusion of inward $S^{2-}$ anions and outward $O^{2-}$ anions; or 2) outward co-current diffusion of $Ca^{2+}$ cations and $O^{2-}$ anions; or a combination of both processes (see Figure 4.1). Hence, in this study, inert marker experiment and DFT calculation were used to identify and explain the dominating ionic transfer mechanism.

4.2 Methods

4.2.1 Inert Marker Experiment

In this study, inert marker experiment was conducted to identify the dominating ionic transfer mechanism and product layer growth mode in the CaO-COS reaction system. 99.95 % pure CaO powder (Aldrich Chem) was pelletized into tablets of 6 mm diameter and 3 mm thickness. The tablets were sintered at 1200 °C under N$_2$ for 48 hours in a horizontal tubular furnace. Purpose of sintering these tablets at such condition is to eliminate the internal pore structure in order to avoid gas diffusion into the center of the tablet during sulfidation reaction. After the CaO tablets were well sintered and cooled down to room temperature, a strip of Pt paint (SPI supplies) was applied to one side of each tablet.

CaO tablets were then put into a Thermogravimetric Analyzer (TGA) (Perkin Elmer Pyris 1) and heated to 400 °C for 15 days under a reactant gas mixture consisting of 5000 ppm COS and balance N$_2$ at a total flow rate of 120 ml min$^{-1}$. After that, the tablets were cooled down to room temperature and prepared for the followed analyses. A sample was prepared for X-ray Diffraction (XRD) analysis. A tablet was mounted in epoxy resin, diagonally cut, and polished on its cross-section. This polished cross-section
was then examined by a Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS).

### 4.2.2 Density Functional Theory (DFT) Calculation

The CaS crystal structure used in this study came from the American Mineralogist Crystal Structure Database (AMCSD). Density Functional Theory (DFT) calculations were employed to estimate the energy barriers for the ionic diffusion. These calculations were carried out using Vienna ab-initio Simulation Package (VASP). Projector Augmented Wave (PAW) approach of Generalized Gradient Approximation in the Perdew-Burke-Ernzerhof (GGA-PBE) form was applied for the calculations. A 2×2×1 super-cell was constructed to represent the CaS bulk phase. For the ionic diffusion, the transition states between the initial configurations and the final configurations were determined by the Climbing Image Nudged Elastic Band (CI-NEB) method. Four configurations in-between were generated. The spring force constant was set to be -5.0 eV Å². A kinetic energy cutoff of 350 eV was used, and 2×2×3 Monkhorst-Pack scheme was used for bulk CaS structures. Ions were relaxed by a conjugate-gradient algorithm until the forces on unconstrained ions decreased to below 0.01 eV Å⁻¹. The energy barrier for ionic diffusion is defined as the energy difference between the system energy at the transition state and that of the initial configuration before diffusion.

### 4.3 Results and Discussion

#### 4.3.1 Inert Marker Experiment

As an effective method in identifying dominating ionic transfer mechanism of solid-state reactions, inert marker experiment is often performed. This experiment
involves attachment of small inert particles to the original COS-CaO interface as a marker (see Figure 4.2a). When the COS-CaO reaction takes place, there forms a CaS layer on the solid CaO surface. And the CaS layer thickens as the reaction and ionic transfer proceed. When the reaction goes to some extent, the relative location of the inert marker is determined by the overall diffusion direction of ionic species through the product layer. If the outward co-current diffusion of \( \text{Ca}^{2+} \) cations and \( \text{O}^{2-} \) anions dominants the ionic transfer process, the inert marker’s relative location would change from original COS-CaO interface to CaS-CaO interface. If the ionic diffusion through the product layer is dominated by the counter-current movement of inward \( \text{S}^{2-} \) anions and outward \( \text{O}^{2-} \) anions, the CaS product layer would grow at CaS-CaO interface. The resulting inert marker is still at gas-solid interface (see Figure 4.2c). If the “co-current diffusion” and “counter-current movement” are comparable, the CaS layer would grow both at the COS-CaS interface and CaS-CaO interface, leaving the marker buried in the CaS layer.(see Figure 4.2d)

The X-Ray pattern of the partially reacted powder is shown in Figure 4.3, which shows that the partially reacted sample is composed of CaO and CaS. Therefore, reaction represented by Equation 1 is valid in this study, and no other unexpected solid product was produced.

Figure 4.4a shows the scanning electron micrograph of the cross-section of a partially reacted tablet. As shown in that figure, the final position of Pt marker is at the gas-solid interface, which indicates that the Pt marker remains unaltered from its original location. To identify the solid phases, Energy Dispersive Spectroscopy (EDS) was performed to obtain elemental mappings of the sample. The mappings of platinum, sulfur,
and calcium are presented in Figure 4.4(b-d). From the three mappings, relative locations of Pt marker, CaS layer, and CaO bulk phase can be clearly identified: the CaS layer is “sandwiched” between the Pt layer and CaO bulk phase with the Pt layer located at the gas-solid interface. This layout corresponds to the case of “inward growth mode”. That is, the dominating ionic transfer mechanism is that the S$^{2-}$ anions derived from COS diffuse inward through the CaS layer to react with CaO at CaS-CaO interface, counter-currently with outward diffusion of O$^{2-}$ anions from CaO to COS-CaS interface to form CO$_2$.

4.3.2 DFT Calculation

It was suggested in the previous literature that Schottky disorder and related vacancy (ionic) migration predominate in CaS and other alkaline earth sulfides. Therefore, the concentrations of cation vacancies and anion vacancies in CaS are assumed to be comparable, and the competition in ionic transfer is determined by the energy barrier of ionic diffusion via vacancies.

Figure 4.5 illustrates the diffusion energy barriers of Ca$^{2+}$ cation, O$^{2-}$ anion, and S$^{2-}$ anion during their migration from one site to an adjacent corresponding vacant site in CaS crystal structure, respectively. As shown in this figure, the Ca$^{2+}$ cation diffusion is the most difficult, and the diffusion energy barrier of O$^{2-}$ anion is lower than that of S$^{2-}$ anion. The high energy barrier for Ca$^{2+}$ cation migration can be interpreted based on the CaS crystal structure. Since the CaS is of Face-Centered Cubic (FCC) structure, all the S$^{2-}$ anions form close-packed structure with Ca$^{2+}$ cations being loosely located in the octahedral interstices. In order to penetrate a S$^{2-}$ anion layer and migrate to a neighboring Ca$^{2+}$ vacancy, a Ca$^{2+}$ cation has to “push away” close-packed S$^{2-}$ anions. Therefore, even
though Ca$^{2+}$ cation has advantage in terms of smaller size, diffusing through a close-packed anion layer is relatively difficult. In contrast, since S$^{2-}$ anion or O$^{2-}$ anion only needs to diffuse through a loosely located Ca$^{2+}$ cation layer, the corresponding diffusion energy barriers can be significantly lower than that of the close-packed case. Due to the smaller size, the diffusion of O$^{2-}$ anion is easier than that of S$^{2-}$ anion. Given the highest diffusion energy barrier for Ca$^{2+}$ cations, the outward co-current diffusion of Ca$^{2+}$ cation and O$^{2-}$ anion is a less favorable transport pattern, which is consistent with the result from the inert marker experiment.

### 4.4 Concluding Remarks

Through inert marker experiment, the ionic transfer process in CaO reaction with COS is found to be dominated by the counter-current movement of inward S$^{2-}$ anions and outward O$^{2-}$ anions. This result is further confirmed by the DFT calculation result that such counter-current movement has the lowest diffusion energy barrier.
Figure 4.1. Illustration of the ionic transfer processes in the reaction of COS and CaO.
Figure 4.2. Principle of inert marker experiment. (a) Original CaO with Pt marker; (b) outward growth mode; (c) inward growth mode; (d) mixed growth mode.
Figure 4.3. X-ray diffraction pattern on partially reacted CaO sample.
Figure 4.4. (a) SEM micrograph of the cross sectional area; (b) platinum mapping; (c) sulfur mapping; (d) calcium mapping.
Figure 4.5. The DFT-calculated diffusion energy barriers of three key processes.
CHAPTER 5

Ionic Diffusion through Calcite Layer during the Reaction of CaO and CO₂

5.1 Introduction

Calcite is the most commonly existing form of CaCO₃ in naturally-occurring minerals and industrial products.¹¹ CaCO₃ of calcite structure can be formed by the reaction of CaO and CO₂ at a wide range of conditions, as shown in Equation 5-1. Understanding this material and its formation mechanism is of great interest in geology, materials science, chemistry, chemical engineering, etc. For example in geology, it helps researchers understand and analyze the rock formation and evolution.⁷⁷ In the chemical engineering, there is intensive ongoing research of using CaO as sorbent to capture CO₂ for sequestration.¹,⁹,⁵⁰

\[ \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \]  

(5-1)

During the calcite formation via reaction of CaO and CO₂, there first forms a thin layer of CaCO₃ on the CaO solid-grain surface. Because CaCO₃ has higher molar volume (36.9 cm³/g) than CaO (16.7 cm³/g), this formed product layer would cover the solid surface and hinder the direct contact of CaO and CO₂. Further solid conversion has to proceed through solid-phase ionic diffusion. This ionic diffusion process can be dominated by: 1) inward diffusion mode: counter-current diffusion of inward CO₃²⁻ anion groups and outward O²⁻ anions, 2) outward diffusion mode: outward co-current diffusion
of $\text{Ca}^{2+}$ cations and $\text{O}^{2-}$ anions, or 3) mixed diffusion mode: the combination of both processes 1 & 2 (see Figure 5.1).

Previously, Anderson\textsuperscript{78} used a C\textsuperscript{14}O\textsubscript{2} isotopic exchange experiment to measure the surface area of a CaCO\textsubscript{3} (calcite) sample and found some residual C\textsuperscript{14}O\textsubscript{2} in the remaining calcite sample, from which it was claimed that carbon is a self-diffusing species in CaCO\textsubscript{3}. In a later study, Anderson\textsuperscript{79} studied the self-diffusion coefficients of carbon and oxygen in calcite. Based on these experimental results, Bhatia and Perlmutter\textsuperscript{80} proposed a mechanism for the reaction of CaO and CO\textsubscript{2}, which follows the inward diffusion mode and is widely accepted by the following works. However, the ionic diffusion process in a stable calcite structure is different from that in the calcite formation process. In a stable calcite structure, the self-diffusion of one single carbon cation through vacancies is possible. While in the reaction of CaO and CO\textsubscript{2}, self-diffusion of carbon cations without corresponding oxygen anions is unlikely for the product layer growth. This implies that the previously measured self-diffusion coefficients may not apply to this dynamic reaction process. In addition, even if Anderson’s result\textsuperscript{78} can prove that carbon or CO\textsubscript{3}$^{2-}$ anion group is a diffusing species in calcite, it cannot exclude the possibility of a mixed diffusion mode. Hence, in this study, inert marker experiment is performed to identify the dominating ionic transfer mechanism in the reaction of CaO and CO\textsubscript{2} and elucidate the ambiguity in the previous works.

### 5.2 Theory of Inert Marker Experiment

As a simple and effective method, inert marker experiment is often performed to identify the solid-phase ionic transfer mechanism in gas-solid reactions. This method uses
a piece of inert material as a marker on the surface of solid reactant. This inert material
does not dissolve into either gas or solid phase, thereby marking the initial gas-solid
interface throughout the entire reaction process. As illustrated in Figure 5.2a, a piece of
Pt layer is placed on the top of a dense CaO solid. After partial carbonation, the final
location of this inert material is determined by the dominating solid-phase ionic transfer
mechanism. If the outward co-diffusion of Ca\(^{2+}\) cations and O\(^{2-}\) anions is much faster, the
CaCO\(_3\) product layer grows outward at the gas-solid interface and the inert marker is
“sandwiched” between the CaCO\(_3\) layer and the unreacted CaO bulk solid (see Figure
5.2b). If the counter-current diffusion of inward CO\(_3^{2-}\) anion groups and corresponding
outward diffusion of O\(^{2-}\) anions is much faster than the outward co-diffusion of
Ca\(^{2+}\) cations and O\(^{2-}\) anions, the product layer grows inward into the CaO solid, which is
characterized by the final Pt location at the gas-solid interface (see Figure 5.2d). If both
processes proceed at comparable rates, the product layer grows both at the gas-solid and
solid-solid interfaces, which buries the inert marker in the product layer (see Figure 5.2c).
Hence, by finding the final location of the inert marker in the solid, the dominating solid-
phase ionic transfer mechanism during the CaO + CO\(_2\) reaction can be identified.

5.3 Experimental Details

Similar to the previous studies,\(^9,10\) CaO powder (99.95 % pure, Aldrich Chem)
was pelletized into cylindrical tablets (D = 6 mm, H = 4 mm) by a 5 MPa pressure, which
were then sintered at 1200 \(^\circ\)C under N\(_2\) environment for 3000 minutes. Purpose of this
high-temperature sintering is to remove the internal voids, so that no gas would diffuse
into the pellet during the carbonation reaction. After the CaO tablets were sintered dense
and cooled down to the ambient temperature, they were put into a horizontal tubular
furnace and heated to 650 °C at 100 % CO₂ for about 4 months. Then, the tablets were mounted into epoxy resin and diagonally cut, as illustrated in Figure 5.3. The tablet’s cross-sectional area was polished for Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS) analyses. A partially reacted CaO sample was analyzed by X-ray Diffraction (XRD).

5.4 Results and Discussion

From the SEM graph in Figure 5.4 a, it can be seen that the Pt layer is on the top of the CaO/CaCO₃ solid phase. To better identify the solid phases, mappings of Pt, Ca, and C are obtained from an EDS analysis (see Figure 5.4 b to d). It further confirms that the Pt layer is above the partially reacted CaO tablet. This layout corresponds to the inward diffusion mode, in which the CO₃²⁻ anion groups diffuse inward into the solid center and the O²⁻ anions diffuse outward to the solid surface. The inward diffusing CO₃²⁻ anion groups form new CaCO₃ at the CaCO₃/CaO interface. Meanwhile, the outward diffusing O²⁻ anions react with gaseous CO₂ and form CO₃²⁻ anions on the solid surface. In order to maintain local and global charge balance, the ratio of inward CO₃²⁻ anion groups to outward O²⁻ anions should be 1:1. This result experimentally proves the mechanism proposed by Bhatia and Perlmutter⁸⁰ and excludes the possibility of a mixed diffusion mode, which was omitted in Anderson’s work.⁷⁸

To explain the experimental result, a partially reacted CaO sample was first analyzed by X-ray Diffraction to identify the formed solid product. As shown in Figure 5, the partially reacted solid sample consists of unreacted CaO and formed CaCO₃, and the formed CaCO₃ is of the calcite structure.
In all the three possible CaCO$_3$ crystal structures: calcite, aragonite, and vaterite, the CO$_3^{2-}$ anion group has a significantly larger size than Ca$^{2+}$ cation and O$^{2-}$ anion. Generally, a larger ionic species has a higher diffusion energy barrier, which adversely affects its diffusion in a crystal structure.$^{17}$ However, it has been previously reported that, in the crystal structure of CaX (X = e.g. Cl$_2$ and S), co-diffusion of a Ca$^{2+}$ cation and an O$^{2-}$ anion requires a cation vacancy and a neighboring anion vacancy to satisfy local charge/mass balance. Generally, the possibility of such neighboring vacancy pairs in a crystal structure is very low, which makes this co-diffusion a less favorable pattern in most CaX solids.$^9$ An exception is the formation of CaSO$_4$, where the pyramid-shaped SO$_4^{2-}$ anion group is extremely large and creates more free space for this co-diffusion process. Because the CO$_3^{2-}$ anion group is of a plane-shaped structure, the calcite structure should be theoretically more packed than CaSO$_4$. In addition, the CO$_3^{2-}$ has one less anion than SO$_4^{2-}$. Hence, it is possible that the extremely low concentration of Ca$^{2+}$/O$^{2-}$ vacancy pairs outweighs the advantage in diffusion energy barriers of Ca$^{2+}$ cation and O$^{2-}$ anion, thereby making the co-diffusion of Ca$^{2+}$ cations and O$^{2-}$ anions a less favorable diffusion pattern. Future work can use theoretical simulation to verify this theory. Even though CO$_3^{2-}$ anion group is the dominating diffusing species, its high diffusion energy barrier determines its low diffusivity in the CaCO$_3$ crystal structure, which explains the fact that the ionic-diffusion-controlled step in the overall CaO + CO$_2$ reaction is very slow.$^{22}$

5.5 Concluding Remarks

In this study, an inert marker experiment is performed to study the dominating solid-phase ionic transfer mechanism during the formation of calcite (CaCO$_3$) by CaO
and CO₂. It was found that the CaCO₃ product layer grows inward into the solid center, which corresponds to the counter-current diffusion of inward CO₃²⁻ anion groups and outward O²⁻ anions. That is, after the initial CaCO₃ layer is formed on the solid surface, the gaseous CO₂ reacts with the O²⁻ anions on the solid surface and forms CO₃²⁻ anion groups, which diffuse inward through the CaCO₃ layer to the CaCO₃/CaO interface to form new CaCO₃. Meanwhile, the O²⁻ anions diffuse outward from the CaCO₃/CaO interface through the CaCO₃ layer to the solid surface to react with gaseous CO₂. To satisfy local and global charge balance, the ratio of inward CO₃²⁻ anion groups to outward O²⁻ anions should be 1:1. Even though the co-diffusion of Ca²⁺ cations and O²⁻ anions is advantageous in smaller ion sizes, the low possibility of co-occurrence of a cation vacancy and a neighboring anion vacancy in CaCO₃ crystal structure hinders this diffusion process, thereby making the counter-current diffusion a more favorable process.
Figure 5.1. Illustration of the two competing ionic diffusion processes in the reaction of CaO and CO₂.
Figure 5.2. Principle of inert marker experiment. (a) the original CaO solid with an inert marker (platinum in this study); (b) outward diffusion mode; (c) mixed diffusion mode; (d) inward diffusion mode.
Figure 5.3. (a) illustration of the layout of Pt layer on the CaO tablet; (b) illustration of the half tablet after the diagonal cutting.
Figure 5.4. (a) SEM micrograph of the cross-sectional area; (b) Pt mapping; (c) Ca mapping; (d) C mapping.
Figure 5.5. X-ray diffraction pattern of the partially reacted CaO solid sample.
CHAPTER 6

Experimental Study of the Mechanism of Increases of Surface Area and Pore Volume of CaO by Hydration: Effects of Physical and Chemical Sub-Steps in a Typical Water-Hydration

6.1 Introduction

The increase of surface area and pore volume of CaO by hydration was discovered during the early 20th century or even earlier, when the hydrated lime became a commercial product for modern society.\textsuperscript{11,81} Although the apparent reactions involved in this process are very simple, as shown in Equation 6-1 and 6-2, the surface area and pore volume of the solid CaO can be significantly increased after a hydration step and a subsequent dehydration step.\textsuperscript{1,27,82-87}

\begin{align*}
\text{Hydration: } \text{CaO (s)} + \text{H}_2\text{O (g or l)} & \rightarrow \text{Ca(OH)}_2 (s) \quad (6-1) \\
\text{Dehydration: } \text{Ca(OH)}_2 (s) & \rightarrow \text{CaO (s)} + \text{H}_2\text{O (g)} \quad (6-2)
\end{align*}

Because of this unique property of CaO, both water-hydration and steam-hydration are widely applied as an activation/reactivation strategy of CaO sorbents for capture of SO\textsubscript{2}, CO\textsubscript{2}, and other acidic gases in syngas and coal-combustion gas.\textsuperscript{9,82-88} Application of hydration to CaO-based sorbents for SO\textsubscript{2} capture in Fluidized Bed Combustion (FBC) and from coal-combustion flue gas started probably around 1980s,\textsuperscript{88} while it received wide attention for CO\textsubscript{2} capture during the past decade with the arising
global warming concern. In the past decades, this sorbent activation/reactivation approach has been successfully demonstrated in many experimental setups and reaction schemes, which shows promising prospects in large-scale commercialization.\textsuperscript{83-87} To study the mechanism of this phenomenon and related optimization works, a number of experimental and theoretical works were performed, and several theories were proposed, which were summarized in various works.\textsuperscript{1,89} However, most of these theories tried to explain this phenomenon by varying one single reaction parameter in the overall hydration process, \textit{e.g.} water-to-CaO ratio, temperature, pressure, additives \textit{etc}. However, a hydration process, especially a water-hydration process, is a process of multi-phase interaction, which involves multiple physical and chemical sub-steps. Change of one reaction condition can generally affect more than one sub-steps in the hydration process. For example, temperature of water-hydration can possibly affect the hydration reaction rate, \(\text{Ca(OH)}_2\) solubility, physical liquid-solid interaction by vibration of water molecules, formation of \(\text{Ca(OH)}_2\cdot n\text{H}_2\text{O}\), \textit{etc}., which could all possibly affect the resulting solid properties and complicate the understanding of this mechanism. Hence, conclusions based on such methodology are often discrete and sometimes inconsistent.\textsuperscript{81,89}

In this chapter, a well-believed “single-factor” mechanism: “physical attrition theory” is first tested to demonstrate its limitation in explaining the hydration mechanism.\textsuperscript{11,81} And, a typical water-hydration is divided into several chemical and physical sub-steps, which are then independently investigated. The effect of each sub-step on the solid morphological properties (surface area and pore volume) is individually studied with Brunauer-Emmett-Teller (BET) analysis.
6.2 Experimental Details

Materials

CaO powder (99.95% pure, < 50 µm, named “raw CaO powder”, used to make CaO pellet in this study), Ca(OH)\textsubscript{2} powder (99% pure, < 50 µm, named “raw Ca(OH)\textsubscript{2} powder”), and naturally-occurring limestone (~ 97% pure CaCO\textsubscript{3}, < 50 µm) were obtained from Aldrich Chemicals, MP Biomedicals, and Graymont, respectively. Ethanol (100% pure) was from Decon labs. 99.99% pure N\textsubscript{2} was used for calcining Ca(OH)\textsubscript{2} and limestone to CaO for BET tests.

Morphological Property Test

The morphological properties of Ca(OH)\textsubscript{2} and CaO solids were tested in a NOVA 4200e analyzer (Quantachrome Company). The BET surface area and pore volume were measured at -193 °C using liquid N\textsubscript{2} as adsorbent. For each Ca(OH)\textsubscript{2} sample, its derived CaO sample was prepared on a Perkin-Elmer (Pyris 1) Thermogravimetric Analyzer (TGA) apparatus by calcining Ca(OH)\textsubscript{2} at 700 °C for 5 minutes. This fixed calcination condition is to exclude the effect of calcination condition on the resulting CaO sorbents. To ensure accuracy, the surface area and pore volume presented in this study are averaged values. In addition, key experiments were repeated using other CaO precursors, which are not presented here to avoid data redundancy.

Examination of “Physical Attrition” Theory (Hydration with Controlled Heat Release)
A batch of limestone was calcined at 700 °C for 30 minutes as the un-sintered CaO, which is referred to as the “limestone-CaO”. A batch of sintered CaO sample was prepared by calcining limestone at 900 °C for 2 hours (named “sintered-CaO”). The regular hydration was carried out by gradually adding ~15 ml de-ionized water directly onto the “sintered-CaO” sample (~ 4.5 g). This solid sample was dried and calcined to a CaO sample (named “water-hydration-CaO”) for BET test. The hydration with controlled heat release, as shown in Figure 1, was performed with same amount of “sintered-CaO” sample put into the container 1. Bottom of this container was submerged into liquid N₂ (~ -193 °C). After stabilization, de-ionized water was slowly added into the container 1. As soon as the water droplet contacted the CaO solid and container, it immediately froze into super-cold ice (~ -193 °C) and covered the CaO solid. After the same amount of water was added, the container 1 was slowly moved out of the liquid N₂ and placed into the ambient condition. After the ice fully melted into liquid and the liquid-solid mixture stabilized for a while, the solid sample was dried and calcined into a CaO sample (named “LN-hydration-CaO”) for BET test.

**Effect of Chemical Conversion of CaO to Ca(OH)₂ (Moisture Hydration of a CaO Pellet)**

“Raw CaO powder” was pressed into a cylindrical pellet (d = 6 mm, h = 3 mm) at 5 MPa pressure. The pressed CaO pellet was sintered at 1200 °C for 3000 min to simulate a CaO particle. This sintered CaO pellet is named “sintered CaO pellet” in the following sections. As shown in Figure 2, this well sintered CaO pellet was put on a support stage
and placed into a sealed container, with some water at the bottom. The CaO pellet reacted with the moisture, while it is isolated from the ambient CO$_2$ by the sealed container. The morphological change of this CaO pellet during the moisture-hydration was photographed by a digital optical camera (Nikon D5000) on the first three days. The surface area and pore volume of the “raw CaO powder”, the “sintered CaO pellet”, and the CaO derived from moisture-hydration of the CaO pellet (named “moisture-hydration-CaO”) were measured. A similar moisture hydration experiment was repeated by using calcined lime as the starting material.

**Effects of Physical and Chemical Interactions between Ca(OH)$_2$ and Water**

The physical interaction of Ca(OH)$_2$ and water was studied by putting 2 g “raw Ca(OH)$_2$ powder” in 40 ml and 140 ml ethanol, respectively. The liquid-solid mixtures were heated at about 100 °C to vaporize the ethanol, producing “Ca(OH)$_2$-40ml-ethanol” and “Ca(OH)$_2$-140ml-ethanol” samples, respectively. Their calcined CaO samples are named “Ca(OH)$_2$-40ml-ethanol-CaO” and “Ca(OH)$_2$-140ml-ethanol-CaO”, respectively. To study the effect of chemical interaction between Ca(OH)$_2$ with water, 2 g “raw Ca(OH)$_2$ powder” was first mixed with 40 ml de-ionized water. From this mixture, the undissolved solid was filtered out and dried at $\sim$ 100 °C, which is named “Ca(OH)$_2$-40ml-undissolved”. Its calcined CaO sample is named “Ca(OH)$_2$-40ml-undissolved-CaO”. The surface area and pore volume of these Ca(OH)$_2$ samples and their derived CaO samples were measured by BET. This experiment was repeated by using calcined lime as the starting material.
Effect of Precipitation of Dissolved Ca(OH)$_2$

The effect of precipitation of dissolved Ca(OH)$_2$ was studied by drying whole mixtures of 2 g “raw Ca(OH)$_2$ powder” with 40 ml and 140 ml de-ionized water, respectively. Surface area and pore volume of the dried Ca(OH)$_2$ samples (named “Ca(OH)$_2$-40ml-water” and “Ca(OH)$_2$-140ml-water”, respectively) and their calcined CaO samples (named “Ca(OH)$_2$-40ml-water-CaO” and “Ca(OH)$_2$-140ml-water-CaO”, respectively) were tested by BET. This experiment was repeated by using calcined lime as the starting material.
6.3 Results and Discussion

6.3.1 Examination of the “Physical Attrition Effect” Theory (Hydration with Controlled Heat Release)

It is common knowledge that the CaO hydration process is usually coupled with rapid/strong heat release, which led the previous researchers to believe that the inner pore expansion and inter-particle attrition due to this violent reaction break the bigger particles into smaller ones. Other “evidence” used to support this theory was that a smaller average particle size was found after hydration. Hence, this theory is widely used to explain the mechanism of increases of surface area and pore volume of CaO sorbent after hydration, and many experimental results about hydration were explained based on this theory, e.g. “dead burn” and “drowning of the quicklime.” In this study, this theory was first examined by comparing a regular water-hydrated sample (“water-hydration-CaO”) with a sample hydrated at a controlled heat release (“LN-hydration-CaO”). As shown in Figure 6.1, at about -196 °C, the hydration reaction rate would be close to zero. This means that there was no quick heat release by reaction at the moment the water (or ice) contacts the CaO solid. After the CaO solid was frozen into a big ice shell and slowly moved out of liquid nitrogen, the hydration reaction gradually started, from which the reaction heat was slowly released and quickly absorbed by the surrounding water (or ice). In this manner, any effect due to quick heat release was minimized. During this process, no bubble or sharp sound, which often occurs during regular water hydration, was observed, implying minimal level of violent reaction.

As shown in Table 6.1, CaO samples from both hydration processes demonstrate noticeable increases in surface area and pore volume. If such increases are caused by the
physical attrition or pore cracking due to violent reaction-heat release, as many researchers would believe, there should be an obvious difference between these two samples. However, by comparing the “LN-hydration-CaO” and “water-hydration-CaO”, the surface area and pore volume of both samples are at the same level, indicating that the prevention of quick heat release does not reduce the overall increases in surface area and pore volume. This experimental result suggests that the widely believed “physical attrition effect” theory cannot explain the increases of surface area and pore volume of CaO after hydration.

6.3.2 Sub-Steps in a Typical Water-Hydration

A typical hydration process can be illustrated as in Figure 6.3, regardless of whether in a water-to-CaO mode or a CaO-to-water mode. Upon contact between solid CaO and water, the chemical conversion from CaO to Ca(OH)$_2$ occurs instantly. This chemical conversion induces solid volume expansion due to the higher molar volume of Ca(OH)$_2$ and a consequently increase in internal stress. Whether this formed product layer can hold this increased stress is mainly dependent on its mechanical strength and other intrinsic material properties. In case of CaO hydration in moisture/steam, this intrinsic conversion denotes the entire process, which involves no further interaction with liquid water after the initial reaction. After step 1, the formed Ca(OH)$_2$ further interacts with water both physically (step 2) and chemically (step 3). The weakly bonded particles physically disperse in water and re-integrate after drying. Meanwhile, the Ca(OH)$_2$ may further chemically react with water. In the fourth step, a small portion of solid dissolves into water and precipitates out during drying.
6.3.3 Effect of Chemical Conversion from CaO to Ca(OH)$_2$ (Moisture Hydration of a CaO Pellet)

To observe the morphological change during the chemical conversion from CaO to Ca(OH)$_2$, a well sintered CaO pellet (“sintered CaO pellet”, d = 6 mm) was used to simulate a calcined CaO particle (d < 100 μm). Using a sintered CaO pellet can facilitate visual observation of the entire moisture-hydration process by avoiding complicated preparation, transportation, isolation from ambient CO$_2$, and particle locating in multiple microscopic analyses. Similar approaches have been widely applied in the studies of solid-phase product layer growth in gas-solid reactions.$^{10,17,68,69}$ The CaO pellet was then put into a moist environment. Images of the changing pellet were photographed on the first, second, and third days. As shown in Figure 6.4, the CaO pellet gradually swelled and broke into powders and smaller pieces. It has been reported in literature that CaO pellets prepared by an identical method can still maintain pellet integrity after chloridation, sulfation, or sulfidation, although these three reactions also induce pellet volume expansion. This comparison indicates that the powder formation and pellet breaking are not necessarily the result of molar volume increase from CaO (17 cm$^3$/mol) to Ca(OH)$_2$ (33 cm$^3$/mol). The increases of surface area and pore volume during the moisture-hydration (also the step 1 in water hydration) should be explained by the unique particle breaking during the hydration process, and this particle breaking is not a result of violent heat-release as proved above. In the previous studies about cement and dental materials,$^{91,92}$ Ca(OH)$_2$ has been reported to have extremely low crack resistance and weak tensile strength. For most volume-increasing gas-solid or liquid-solid reactions, the overall reaction has two steps: 1) the surface chemical reaction step and 2) the solid-
phase ionic diffusion step. Given the low ionic diffusivity in solids, the solid-phase ionic diffusion step is usually the rate-controlling step. But in the hydration of CaO, its weak mechanical strength cracks the swelling Ca(OH)$_2$ product layer as the reaction proceeds, which circumvents the slow solid-phase ionic diffusion and opens pathways for direct water (or steam) penetration onto the unreacted CaO. Without the diffusion resistance of the product layer, the CaO can react with water (or steam) at a very high rate, resulting in concentrated reaction-heat release within a short time. This property can also explain why hydration of CaO is a violent exothermic reaction, even though its reaction heat ($\Delta H = -109$ kJ/mol) is not significantly high compared with most gas-solid and liquid-solid reactions. Therefore, the rapid heat release is the result of particle breaking, rather than the reason for that which is believed by many researchers.

To qualitatively confirm the increases of morphological properties after this moisture-hydration reaction, the surface areas and pore volumes of raw CaO powder, sintered CaO pellet, and moisture-hydration-derived CaO sample were measured and shown in Table 6.2. As can be seen, the “moisture-hydration-CaO” has significant increases in surface area and pore volume as compared with the “sintered CaO pellet” and “raw CaO powder”. These increases qualitatively confirm the morphological change by particle breaking and cracking described above. This trend was also qualitatively confirmed with calcined lime powder as the starting material.

Even though steam/moisture hydration at different reaction conditions (e.g. temperature, pressure) can produce CaO sorbents with different resulting morphological properties, the major increase can all be attributed to this particle breaking. And different reaction conditions would affect the mechanical cracking process, thereby resulting in the
difference in morphological properties. Future work can focus on the mechanical change during product layer expansion, which is a widely studied topic in materials science and engineering.\textsuperscript{93-95}

\textbf{6.3.4 Effects of Physical Interaction and Chemical Reaction of Ca(OH)\textsubscript{2} with Water}

Simultaneously or after the first conversion from CaO to Ca(OH)\textsubscript{2}, the solid cluster would physically interact with water. And some weakly bonded particles might be disintegrated by multi-phase interaction and re-integrated after drying. Given the fact that Ca(OH)\textsubscript{2} has no solubility in ethanol, the mixing in ethanol (40 ml and 140 ml) can simulate the physical dispersion in water. To ensure consistent and uniform morphology of the starting material and avoid accumulated experimental errors, commercially available Ca(OH)\textsubscript{2} was used as the starting material where the surface-area-relative-standard-deviation was below 3\%. As shown in Table 6.3, the physical interaction slightly decreases the surface area and pore volume of the raw Ca(OH)\textsubscript{2} and its derived CaO, and the 140 ml ethanol samples have similar decreases as the 40 ml ones. After the Ca(OH)\textsubscript{2} solid is well mixed with ethanol, the micro-particles may settle down slower than the macro-ones and are also relatively more mobile in the liquid phase. It is possible that some micro-particles may be trapped in the surface pores of the macro-particles. Another possible reason for this decrease is that the agglomeration of solid particles would be stronger after a wetting process.\textsuperscript{96} Because of these two possible factors by physical interaction, some surface pores are blocked and the overall surface area is reduced.

To study the effect of chemical reaction of Ca(OH)\textsubscript{2} with water, 2 g Ca(OH)\textsubscript{2} powder was mixed with 40ml water. This mixing process involves a process of physical
interaction and a process of chemical reaction. To minimize the effect of solution drying, the undissolved solid was filtered out and dried. By comparing the “Ca(OH)$_2$-40ml-undissolved” samples with the “Ca(OH)$_2$-40ml-alcohol” and “raw Ca(OH)$_2$ powder” samples, it can be found that the chemical reaction step has an obvious increasing effect on the solid morphological properties. It was reported that Ca(OH)$_2$ can chemically bond water molecules in water$^1$ and forms Ca(OH)$_2$$\cdot$$n$H$_2$O ($n = $ e.g., 1, 2, and 4), which theoretically has a significantly larger molar volume than Ca(OH)$_2$. Formation of Ca(OH)$_2$$\cdot$$n$H$_2$O would further enlarge the crack in particle, and a more porous structure would be generated after the chemically bonded water molecules are dried out of the chemical structure. Similar approaches are widely applied in pharmaceutical and some other related research in the synthesis of amorphous and high-surface-area materials.$^{97,98}$ This result indicates that, in addition to the apparent reaction 6-1 and 6-2, the chemical reaction of Ca(OH)$_2$ and water should also be considered as an important step in the study of CaO hydration. This trend was also qualitatively confirmed with calcined lime powder as the starting material.

**6.3.5 Effect of Precipitation of Dissolved Ca(OH)$_2$**

During the final drying step, the dissolved Ca(OH)$_2$ would precipitate out and deposit onto the solid surface. Even though the Ca(OH)$_2$ has very low solubility in water, the precipitated solid may alter the surface porous structure and change the morphological properties. To study the effect of solution drying and precipitation of the dissolved Ca(OH)$_2$, 2 g Ca(OH)$_2$ was first mixed with 40 ml and 140 ml water, respectively. These two mixtures were dried at the same temperature. It was observed that, during the drying process, the transparent upper solution gradually became blurry.
and tiny solids were formed. From Table 6.4, it can be found that the Ca(OH)$_2$ dried from a higher water-to-Ca(OH)$_2$ ratio mixture tends to have lower surface area and pore volume. This trend is similar to the result from a previous study, which showed that a higher water-to-CaO ratio produced Ca(OH)$_2$ with less surface area.

To further study this process, 2 g Ca(OH)$_2$ and 40 ml water were mixed and dried in two manners: drying of the entire liquid-solid mixture and drying of the undissolved solid. It is shown in Table 6.4 that the “Ca(OH)$_2$-40ml-water” has lower surface area and pore volume than the “Ca(OH)$_2$-40ml-undissolved”, which suggests that the solution drying and solute precipitation process has a decreasing effect on the solid’s surface area and pore volume. This trend was also qualitatively confirmed with calcined lime powder as the starting material.

During the solution drying, the dissolved solute would precipitate out and form micro-particles, which settle on the bottom macro-particle and plug some of the existing pores. This trend is not as obvious for the derived CaO samples, since calcination from Ca(OH)$_2$ to CaO may open some of the plugged pores. This mechanism also explains a previous experimental result that higher hydration temperature favors the morphological enhancement,\(^\text{81}\) given that the solubility of Ca(OH)$_2$ in water is lower at higher temperatures. In addition, it has been reported that an ethanol/water solution has better regenerating/activating effect than pure water towards SO$_2$ and CO$_2$ capture, the reason of which was hypothesized to be the enhanced water affiliation, penetration to CaO, and lower Ca(OH)$_2$ solubility.\(^\text{81,99-100}\) According to this study, it is possible that the ethanol/water solution dissolves less Ca(OH)$_2$ than in pure water, thereby having a lower loss by pore plugging during the drying step. It is suggested that, in the future work of
using water solution as hydrating agent, the Ca(OH)$_2$ solubility and precipitation process should be considered.

6.4 Concluding Remarks

This chapter describes the mechanism of increases of surface area and pore volume of CaO by hydration. The overall hydration process is divided into four individual sub-steps, and the changes of surface area and pore volume by each step are examined. During the first step, the formed Ca(OH)$_2$ product layer would crack into smaller pieces as the CaO is converted to Ca(OH)$_2$. The Ca(OH)$_2$ may further chemically bind water molecules and generate more pores after these water molecules are dried out from the Ca(OH)$_2$ structure. Because of the physical interaction with water, some micro-particles would fall into the pores of the bigger ones and the wetting process induces stronger particle agglomeration, thereby slightly reducing the overall surface area and pore volume. When the solution dries, some solute may precipitate out and form micro-particles, which plug the pores of macro-particles and draw back some of the overall increases of surface area and pore volume by hydration. Study of the effect of each individual sub-step in an overall hydration process can provide new explanations/insights to the previous experimental results and help understand the intrinsic hydration mechanism from a different angle.
<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>limestone-CaO</td>
<td>19.600</td>
<td>0.099</td>
</tr>
<tr>
<td>sintered-CaO</td>
<td>5.194</td>
<td>0.038</td>
</tr>
<tr>
<td>LN-hydration-CaO</td>
<td>37.736</td>
<td>0.227</td>
</tr>
<tr>
<td>water-hydration-CaO</td>
<td>37.001</td>
<td>0.225</td>
</tr>
</tbody>
</table>

Table 6.1. Morphological information of CaO samples in the study of “physical attrition effect” theory.
Table 6.2. Morphological information of CaO samples in the study of effect of chemical conversion from CaO to Ca(OH)$_2$. 

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw CaO powder</td>
<td>19.504</td>
<td>0.150</td>
</tr>
<tr>
<td>sintered CaO pellet</td>
<td>3.347</td>
<td>0.029</td>
</tr>
<tr>
<td>moisture-hydration-CaO</td>
<td>23.392</td>
<td>0.176</td>
</tr>
<tr>
<td>Sample I.D.</td>
<td>Surface Area (m$^2$/g)</td>
<td>Pore Volume (cc/g)</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>raw Ca(OH)$_2$ powder</td>
<td>14.980</td>
<td>0.084</td>
</tr>
<tr>
<td>Ca(OH)$_2$-40ml-alcohol</td>
<td>12.045</td>
<td>0.078</td>
</tr>
<tr>
<td>Ca(OH)$_2$-140ml-alcohol</td>
<td>11.472</td>
<td>0.086</td>
</tr>
<tr>
<td>Ca(OH)$_2$-40ml-undissolved</td>
<td>30.648</td>
<td>0.143</td>
</tr>
<tr>
<td>raw Ca(OH)$_2$ powder-CaO</td>
<td>30.524</td>
<td>0.230</td>
</tr>
<tr>
<td>Ca(OH)$_2$-40ml-alcohol-CaO</td>
<td>29.380</td>
<td>0.225</td>
</tr>
<tr>
<td>Ca(OH)$_2$-140ml-alcohol-CaO</td>
<td>28.997</td>
<td>0.216</td>
</tr>
<tr>
<td>Ca(OH)$_2$-40ml-undissolved-CaO</td>
<td>37.178</td>
<td>0.287</td>
</tr>
</tbody>
</table>

Table 6.3. Morphological information of Ca(OH)$_2$ and derived CaO samples in the study of effects of physical and chemical interactions with water.
<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Volume (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw Ca(OH)$_2$ powder</td>
<td>14.980</td>
<td>0.084</td>
</tr>
<tr>
<td>Ca(OH)$_2$-40ml-undissolved</td>
<td>30.648</td>
<td>0.143</td>
</tr>
<tr>
<td>Ca(OH)$_2$-40ml-water</td>
<td>26.749</td>
<td>0.143</td>
</tr>
<tr>
<td>Ca(OH)$_2$-140ml-water</td>
<td>19.341</td>
<td>0.136</td>
</tr>
<tr>
<td>raw Ca(OH)$_2$ powder-CaO</td>
<td>30.524</td>
<td>0.230</td>
</tr>
<tr>
<td>Ca(OH)$_2$-40ml-undissolved-CaO</td>
<td>37.178</td>
<td>0.287</td>
</tr>
<tr>
<td>Ca(OH)$_2$-40ml-water-CaO</td>
<td>36.424</td>
<td>0.292</td>
</tr>
<tr>
<td>Ca(OH)$_2$-140ml-water-CaO</td>
<td>31.797</td>
<td>0.293</td>
</tr>
</tbody>
</table>

Table 6.4. Morphological information of Ca(OH)$_2$ and derived CaO samples in the study of effect of solution drying and solute precipitation.
Figure 6.1. Experimental setup of hydration of sintered CaO at controlled heat release rate.
Figure 6.2. Experimental setup of moisture-hydration of a well-sintered CaO pellet, which simulates a CaO particle.
Figure 6.3. Illustration of a typical water-hydration process of CaO. (step 1: chemical conversion from CaO to Ca(OH)$_2$, step 2: physical interaction of Ca(OH)$_2$ with water, step 3: chemical reaction of Ca(OH)$_2$ and water, step 4: precipitation of dissolved Ca(OH)$_2$).
Figure 6.4. Images of morphological change of a sintered CaO pellet during moisture-hydration. (a: sintered CaO pellet on the first day, b: the second day, c: the third day, d: after a gentle touch on the third day)
CHAPTER 7

Reactive Solid Surface Morphology Variation via Ionic Diffusion

7.1 Introduction

Gas-solid reaction is a ubiquitous chemical process in modern industries and natural environment. In a gas-solid reaction, the solid reactant(s) chemically absorbs/exchanges component(s) from/with the gaseous reactant(s), respectively. One of the most important factors that characterize a gas-solid reaction is the solid surface structure that significantly affects the reaction rate and resulting solid properties. A solid surface can be generally regarded as a combination of smooth, convex, and concave structures. It is known that such surface structures vary in the course of reactions by three major mechanisms: 1) mechanical interaction; 2) molar volume change; and 3) heat-induced sintering. In some reactions like hydration of CaO, the reaction-induced physical stress would mechanically affect the surface structure, leading to surface cracking in most cases. Additionally, if the molar volume of the solid product is larger than that of the solid reactant, the expansion of solid “molecules” narrows the inter-solid distance, thereby closing surface concave structures. If the solid product has a smaller molar volume than the solid reactant, the surface concave structure would be enlarged. When the gas-solid reaction occurs at a high temperature, the sintering effect tends to smooth the solid surface by “transporting” solid species from surface convex structures to concave structures under the driving force of surface-energy gradient. These three
major mechanisms dominate people’s understandings towards solid surface structure variation during gas-solid reactions to date. However, a large number of gas-solid reactions incur outward ionic diffusion of solid species, *e.g.*, oxidation of most pure metals and sulfation of lime.\textsuperscript{17,103} The role of solid-phase ionic diffusion in solid surface structure variation is still not clearly understood. It is shown in this chapter that, if a gas-solid reaction involves outward ionic diffusion of solid species, the solid surface tends to smooth by this reaction-induced diffusion process. Specifically, the surface concave structure is buried and the surface convex structure is flattened. This phenomenon should occur and only occur in the gas-solid reactions involving outward ionic diffusion of solid species. The surface smoothing effect unraveled in this chapter can serve to provide a possible fourth mechanism that supplements the three traditionally acknowledged surface structure variation mechanisms.

### 7.2 Methods

#### 7.2.1 Experimental Details

Dense pure iron tablets are used to simulate micro-scaled iron grains. A dent ($W = 3 \text{ mm}, D = 3 \text{ mm}$) is engraved on one tablet surface to simulate a 2-D micro-concave, and an equilateral triangular structure ($L = 3 \text{ mm}$) is fabricated on one tablet surface to simulate a 2-D micro-convex. Using a bulk dense solid to simulate a solid grain is widely applied in the studies of solid-phase ionic transfer mechanism during gas-solid reactions.\textsuperscript{9,10,17,71} For the concave structure, a thin layer of platinum is applied on both the outer surface of the engraved dent to mark the initial gas-solid interface. The iron tablets are then put into a box furnace and heated to 1000 °C at air condition. After a period of
oxidation, the tablets are cooled down to the room temperature and removed from the
furnace. They are diagonally cut, and the cross-sectional area is polished for SEM and
EDX analyses.

7.2.2 Simulation

The effect of outward iron cation diffusion on the surface structure was simulated
using the classic diffusion model:

\[
\frac{\partial C_{Fe}}{\partial t} = \nabla \cdot (D \nabla C_{Fe})
\]  

(7-1)

Where, \(C_{Fe}\) is the concentration of iron cation. \(C_{Fe}\) is set to be 1 for dense iron. It is
assumed that the outermost solid surface is always \(Fe_2O_3\), where \(C_{Fe}\) equals to \(7.1/(30.5/2)\) = 0.47, given that the molar volumes of dense Fe and \(Fe_2O_3\) are 7.1 cm\(^3\)/mol and 30.5
\(cm^3/mol\), respectively. \(D\) is the diffusion coefficient, which is assumed to be constant in
calculation. Only a two-dimensional version of this equation is considered.

To define the solid outer surface growth, it is assumed that the outward diffusive
flux of iron cations through the solid outer surface is first collected by the next mesh
layer (mesh size = \(dx^2\)). As shown in Equation 7-2, when the cumulative outward
diffusive flux of iron cations in the next mesh layer reaches to 0.47\(dx^2\), the next mesh
layer is designated as the new solid outer surface, where \(C_{Fe} = 0.47\). Then, iron cations
start to diffuse from this new mesh layer to the next mesh layer.

\[
\sum j \cdot n dx dt \geq 0.47 dx^2
\]  

(7-2)
7.3 Results and Discussion

To study the effect of outward ionic diffusion of solid species to the solid surface structure, oxidation reaction of pure-iron tablets with a micro-concave structure and a micro-convex structure is examined. To better understand the following results, a typical pure iron oxidation process at the dense grain level is shown in Figure 7.1. It can be seen that iron diffuses from the pure iron phase through the initial gas-solid interface onto the new gas-solid interface to react with oxygen gas. As a result, the iron oxides layer grows outward at the gas-solid interface. Because of the outward diffusion of iron, the lattice vacancies would form in the iron phase, which then agglomerate into a porous-iron layer. As the reaction continues, the interface of porous-iron and dense-iron migrates inward into the solid interior. Most gas-solid reactions involving outward ionic diffusion of solid species proceed in a similar manner.

It can be seen from Figure 7.2 that, as the oxidation reaction starts, the iron oxide solid product gradually grows into the valley area through the initial gas-solid interface (interface of iron-oxide and porous-iron during the reaction), which is marked by a layer of inert platinum marker during the course of oxidation reaction. As the oxidation time increases, the surface concave is gradually buried by the outward growth of iron oxides product, and the concave depth gradually decreases. This concave burial and depth decrease can be attributed to the difference in accumulation of the solid product into the valley of the concave structure and onto the top of the concave structure.

To better understand the surface concave burial by the outward ionic diffusion, it is helpful to review the basic diffusion process on the solid surface. On a flat surface, the
outward ionic diffusion rate should be equal everywhere and its direction is perpendicular to the gas-solid interface. In a concave structure, regardless of the specific shape, there is a larger diffusing surface pointing to the concave valley, which would accumulate more product solid in the concave than on the top of the concave, as illustrated in Figure 7.3. This uneven solid product accumulation between the valley and the top of a concave results in the decreasing concave volume and depth. Even though the molar volume increase per se has a concave burying effect, different ionic diffusion mechanisms would yield different extents of concave burial. If a molar-volume-increasing reaction proceeds through inward diffusion of gas-derived ionic species, the concave burial is only the result of molar volume increase when the sintering effect is not considered (see Figure 7.4a). In contrast, the concave tends to bury to a greater extent by the outward ionic diffusion of solid-phase reactant (see Figure 7.4b), because the outward ionic diffusion of solid-phase reactant generally transports the solid-phase reactant from the interior to the surface and generates internal vacancies. Such vacancies would agglomerate and form “trapped” pores inside the solid phase, which generally do not directly contribute to the gas-solid interaction. Therefore, the concave burying effects by the molar volume increase and this outward diffusion of iron cations are different.

In a gas-solid reaction, a concave structure can be enlarged when the solid product has a smaller molar volume than the solid reactant and the reaction proceeds through inward diffusion of gas-derived ionic species (see Figure 7.5a). However, if this reaction involves outward ionic diffusion of solid-phase reactant, there still exists possibility that the overall concave structure is buried (see Figure 7.5b), which indicates that the concave burying effect of the outward ionic diffusion of solid-phase reactant does not depend on
the molar volume change. Hence, the concave burying effects by the molar volume increase and the outward ionic diffusion of solid-phase reactant should be differentiated.

Figure 7.6 shows the SEM graphs of the pure iron oxidized after different oxidation time lengths. As can be seen, the boundary line of dense-iron in the surface convex area quickly draws back to the bulk pure iron tablet as the reaction proceeds, which results in a longer vertical distance from the outer product layer surface to the boundary of dense-iron in the convex area compared to the bulk flat area. However, the overall vertical height of the surface convex on the bulk tablet decreases. Thus, it can be found that this iron oxidation reaction tends to flatten the surface convex structure.

In order to explain this convex flattening effect in the iron oxidation process, it is helpful to review the ionic diffusion process in the convex structure. As illustrated in Figure 7.7a, as the oxidation starts, a thin layer of iron-oxides product is formed on the iron surface. Because the iron oxidation proceeds through outward diffusion of iron cations, a thin layer of iron with vacancies (porous iron) is also present between the iron-oxides layer and the dense-iron phase. The dense-iron phase can be regarded as $C_{Fe} = 1$, while the iron concentration in the oxide layer and the porous iron is less than 1 ($C_{Fe} < 1$). Under this iron concentration gradient, iron cations diffuse outward from the dense-iron boundary to the gas/iron-oxide interface. On a flat dense-iron surface, the possible diffusing angle of iron cations is 180°. Hence, the outward iron diffusion rate on a flat surface should be equal and the overall product layer grows vertically. While in the surface convex with an angle of $\alpha$ ($\alpha < 180^\circ$), the diffusion angle is $360^\circ - \alpha$, which is larger than 180° (see Figure 7.7a). Thus, the outward diffusion rate of dense-iron in the convex area is faster than that on the flat surface. Therefore, as illustrated in Figure 7.7b,
the relative height \((L_2)\) of the dense-iron in the surface convex gradually decreases, which makes the vertical distance from the dense-iron boundary (where \(C_{Fe} = 1\)) to the gas/solid interface (\(\text{Fe}_2\text{O}_3\), where \(C_{Fe} = 0.47\)) in the convex area \((L_1)\) larger than on the flat surface \((L_4)\). The longer vertical diffusing distance for the same iron cation concentration drop (from \(C_{Fe} = 1\) to \(C_{Fe} = 0.47\)) has a lower diffusion driving force, which results in a lower vertical outward flux of iron cations in the convex area. Hence, the vertical product layer growth in the convex area is slower than that on the bulk flat surface. This slower vertical product growth in the convex area does not conflict with the overall faster outward diffusion of iron cations in the same area. It is because that the overall outward diffusion in the convex goes to a wider angle, while the bulk flat surface can only grow up vertically. This is why the overall height of the surface convex \((L_3)\) gradually decreases as the oxidation reaction proceeds.

It is noted that this convex flattening effect by the outward ionic diffusion of solid-phase reactant does not depend on the molar volume change, as illustrated in Figure 7.8a. In contrast, if the reaction proceeds through inward diffusion of gas-derived ionic species, e.g., \(\text{CaO (s)} + \text{CO}_2 (g) \rightarrow \text{CaCO}_3 (s)\), the structural ions (\(\text{Ca}^{2+}\) cations) do not participate in the solid-phase ionic diffusion. Theoretically, each \(\text{CaO}\) “molecule” just locally expands to a bigger \(\text{CaCO}_3\) “molecule” without altering the arrangement of crystal layers. Consequently, the height of the surface convex expands or shrinks proportionally to the molar volume change (see Figure 7.8b), while the inward diffusion of gas-derived ionic species (e.g., \(\text{CO}_3^{2-}\) anion group) per se should have a negligible effect on the convex structure. This comparison illustrates that the convex flattening effect is not the
necessary result of a gas-solid reaction. It is directly related to the dominating ionic diffusion mechanism.

To simulate this concave burial and convex flattening by the outward diffusion of iron cations during oxidation, a 2-D continuum diffusion model was established. As shown in Figure 7.9 a-b, as the diffusion process proceeds, the surface concave structure is gradually filled and the height of surface convex structure gradually decreases. These simulation results show the same trends of surface variation as the experimental results. The iron diffusivity used in this simulation is $1.3 \times 10^{-7}$ cm$^2$/s, which is in good agreement with the experimentally measured iron cation diffusivities in iron oxides from the previous studies.$^{106,107}$

It can be generally concluded that the four independent factors i.e., mechanical interaction, sintering effect, molar volume change, and solid-phase ionic diffusion can all affect the morphology variation in a gas-solid reaction: 1) mechanical interaction can either increase or decrease solid surface roughness, mainly depending on the materials properties and the specific reaction conditions; 2) the surface smoothing effect by sintering is mostly unconditional; 3) the molar volume decrease tends to enlarge a concave structure and reduce a convex structure, while molar volume increase yields an opposite effect; 4) when a gas-solid reaction proceeds through inward diffusion of gas-derived ionic species, the inward ionic diffusion of gas-derived ionic species per se has a negligible effect on the surface morphology. However, when a gas-solid reaction involves outward ionic diffusion of solid-phase reactant, the outward ionic diffusion tends to fill a concave structure and flatten a convex structure. Hence, when
describing/predicting the solid morphology variation in a gas-solid reaction, the four independent factors described above should be all considered.

7.4 Concluding Remarks

As shown in this chapter, the outward ionic diffusion of solid species during gas-solid reactions tends to smooth a solid surface by filling concave structures and flattening convex structures. It is speculated that this surface smoothing effect should occur in any gas-solid reactions that involve outward ionic diffusion of solid species (e.g., oxidation of most pure metals and sulfation of lime). Hence, a big rough plate surface tends to become perfectly flat, while a small solid particle of irregular shape tends to become spherical. Even though this effect is similar to the sintering effect, their mechanisms are different. Sintering is induced by heat, which is a physical factor. While the surface smoothing effect via outward ionic diffusion is driven by the chemical-reaction-induced ionic concentration gradient. The mechanism revealed in this chapter can serve to provide a possible fourth mechanism that supplements the traditionally acknowledged surface variation mechanisms associated with the 1) mechanical interaction, 2) molar volume change, and 3) heat-induced sintering.
Figure 7.1. Illustration of solid-layer distribution and solid-phase ionic diffusion in oxidation of pure iron. (a) before oxidation; (b) after partial oxidation.
Figure 7.2. Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray (EDX) graphs of the cross-sectional area of the concave structure at different oxidation time lengths. (a) before oxidation; (b) 3-day oxidation; (c) 6-day oxidation. (the Pt marker is identified by EDX and outlined by the red dots).
Figure 7.3. Schematic illustration of the concave burial and concave depth decrease by the outward diffusion of iron cations for concaves of three representative shapes. (a) a rectangular concave; (b) a semi-spherical concave; (c) a triangular concave.
When the solid product has a larger molar volume than the solid reactant.

(a): if the reaction proceeds through inward diffusion of gas-derived ionic species.

(b): if the reaction involves outward ionic diffusion of solid-phase reactant.

Figure 7.4. Illustration of the theoretical concave variation in a gas-solid reaction, where the solid product has a larger molar volume than the solid reactant. (a) Inward diffusion of gas-derived ionic species, (b) outward ionic diffusion of solid-phase reactant.
Figure 7.5. Illustration of the theoretical concave variation in a gas-solid reaction, where the solid product has a smaller molar volume than the solid reactant. (a) inward diffusion of gas-derived ionic species, (b) outward ionic diffusion of solid-phase reactant.
Figure 7.6. Scanning Electron Microscopy (SEM) graphs of the cross-sectional area of the convex structure at different oxidation time lengths. (a) before oxidation; (b) 8-hour oxidation; (c) 12-hour oxidation. (the gas-solid interface and the interface of porous-iron and dense-iron are outlined by the blue dots and yellow dots, respectively).
Figure 7.7. Illustration of (a) the ionic diffusing angle when the oxidation initially starts and the product layer growth in the convex structure after oxidation time lengths (b) $T_1$ and (c) $T_2$ ($T_1 < T_2$).
Figure 7.8. Illustration of the theoretical surface convex variation by (a) outward ionic diffusion of solid-phase reactant and (b) inward diffusion of gas-derived ionic species.
Figure 7.9. Simulation of variation of the (a) concave and (b) convex structures by the iron oxides product layer growth as oxidation reaction proceeds. (the background colour is removed for better illustration).
CHAPTER 8

Conclusions and Future Research and Prospects for Chemical Looping Particle

The concept of chemical looping was proposed at early $20^{th}$ century, but only got world-wide attention during the past two decades. After years of intensive study, this basic concept has been proved viable and economic analyses show very promising process efficiencies for this novel process compared to conventional fossil fuel conversion technologies, especially when CO$_2$ capture is considered.\(^1\) As one of the most important factors to its future commercial success, the chemical looping particles have to maintain stable and satisfactory reactivity and recyclability. Different from the well-established catalysts and “one-time” consumable solid reactants, the chemical looping particles go through cyclic gas-solid reactions, which feature in the cyclic capture-and-release of the component from the gas reactants. During the cyclic reactions, the solid reactants undergo cyclic changes of morphological properties and crystal structures, which poses unprecedented and unrealized difficulties to understanding of the solid behavior and seeking optimization strategies.

First of all, it have been widely reported that chemical looping particles, no matter in a pure form or an optimized form, tend to have deteriorating morphological properties as the cyclic reaction proceeds, which decreases the solid reactivity and recyclability.\(^1\) Most previous works attribute this loss to high-temperature sintering, which leads numerous research efforts to the optimization of initial solid morphological properties and anti-sintering.\(^4\) These are typical perspectives and solutions in catalysis reactions
where the catalysts are not converted as well as “one-time” gas-solid reaction where only the initial solid morphology matters. As pointed out in a previous chapter. The cyclic reaction per se is a universal independent deactivating factor to the solid morphology, which means that the deterioration of initial solid morphology is unavoidable. That is, the surface area and pore volume of the fresh particles decrease rapidly in the first cycles and gradually stabilize at an equilibrium level. Even though the initial solid surface and pore volume can be significantly increased by some sophisticated techniques and stabilize at a higher level, the effectiveness is much less pronounced when considering the cost of such techniques. Hence, there seems to be no need for further improvement of solid morphology at unreasonable costs. A decent equilibrium morphological property should be sufficient for a particle with outstanding ionic conductive capability. It was also reported that the negative effect of a higher temperature is conditional, which is against most researchers’ perception and shows the complexity of the particle deactivation mechanism. It is very important to understand the exact deactivation process/mechanism for a given particle in order to find an effective optimization strategy.

Another aspect that requires intensive attention and research efforts is the solid ionic conductive capability. For a particle with a reasonable level of surface area and pore volume, a good ionic conductive rate can sustain the chemical-reaction-controlled step, thereby compensating the reactivity loss due to morphological properties. However, most naturally-occurring materials and physically-supported particles have low intrinsic ionic conductivity, which thus requires advanced artificial modification or selection of better candidates from natural/industrial sources. Given that this ionic diffusive property is much less susceptible to sintering and morphological deterioration, effective
enhancement on this aspect should be an important research focus. Because the study of solid-phase ionic diffusion behavior in chemical engineering and energy-related fields only started a few decades ago, its importance has not been widely acknowledged or realized by the chemical looping researchers. Compared to the morphological optimization, the previous efforts on the ionic conductive enhancement are not only discrete, but also lack in-depth theoretical support. For a given type of chemical looping particles (e.g. Co-based), it is suggested to first systematically study the effects of various factors in the crystal lattice on the overall ionic diffusion process, with the focuses on the diffusion energy barrier and diffusion pathway. A good example is the mechanism studies of the reactions of CaO with acidic gases in syngas (i.e., H₂S, COS, HCl) and coal-combustion flue gas (i.e., SO₂ + O₂, CO₂). Such mechanism information can both provide theoretical guidance to artificial synthesis of novel particles and explain the performance of materials from trial-and-error screening. However, due to the lack of research attention, theoretical preparation, and characterization facility, the trial-and-error screening strategy would still dominate the ionic conductivity optimization in the predictable future.

After years of intensive R&D at many research institutes all over the world, the chemical looping processes have arisen from bench-scale reactors to sub-pilot and even pilot-scale units. Compared to the successful reactor scaling-up, most development of chemical looping particles is still at the stage of quantitative accumulation, while qualitative breakthrough is scarce to date. To avoid the embarrassment that the particle performance eventually becomes the “weak point” for commercial implementation, the
current optimization strategies need to be re-evaluated and more high-quality research efforts should be devoted for the particle development.
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