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Multi-Scale Simulation of Carbon Capture Processes Based on Mesoporous Silica-Supported, Polyethyleneimine-Impregnated Sorbents

Kuijun Li

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Multi-Scale Simulation of Carbon Capture Processes Based on Mesoporous Silica-Supported, Polyethyleneimine-Impregnated Sorbents

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Dissertation submitted
to the Benjamin M. Statler College of Engineering and Mineral Resources
at West Virginia University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Mechanical Engineering

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2016

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ABSTRACT

Multi-Scale Simulation of Carbon Capture Processes Based on Mesoporous Silica-Supported, Polyethyleneimine-Impregnated Sorbents

Kuijun Li

The mechanism of CO₂ uptake in silica-supported, polyethylenimine (PEI)-impregnated sorbents under dry and humid conditions has been investigated in a new chemical model based on quantum chemical calculations and a comparison of reaction-diffusion models with experimental data. First-principles quantum chemical calculations showed that the zwitterion, which is not stable in the gas phase even when considering a polar environment similar to water, can be stabilized by nearby water and amine molecules. Stabilized zwitterions serve as diffusive intermediates to transport adsorbed CO₂ into the PEI bulk. Compared to amine-stabilized zwitterions, water-stabilized zwitterions are more numerous and have a lower activation energy for deprotonation. The formation of bicarbonate is not favored because of the high energy of formation and activation energy.

A reaction-diffusion model based on this new chemistry has been developed and implemented using a finite volume method. The model treats transport only in the bulk phase of PEI, as this is much slower than gas-phase diffusion. The simulation results were compared with a set of experimental data from thermogravimetric analysis (TGA). This model reproduced the experimental adsorption behaviors both qualitatively and quantitatively under both dry and humid conditions.

Bayesian calibration using quantum chemistry calculated priors for physical parameters was employed to connect the model with experimental data. Uncertainties from both the model parameters and model form discrepancy from the adsorption model were quantified in the form of a joint sample-based distribution obtained through Markov Chain Monte Carlo (MCMC) sampling. Dynamic discrepancy functions in the Bayesian Smoothing Splines Analysis of Variance (BSS-ANOVA) framework were included in the equilibrium constants and diffusion coefficients. Results of calibration showed that the proposed approach is capable

of replicating the experimental behavior, both qualitatively and quantitatively: The TGA data was well covered by the calibration results. The calibration results were then incorporated within a process-scale model (of a bubbling fluidized bed adsorber) by propagating the posterior distribution.

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CHAPTER 1

INTRODUCTION

With the global mean temperature continuously increasing since 1850,[1, 2, 3] global warming and climate change due to greenhouse gases (GHGs) emissions is drawing concerns. Carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydro-fluorocarbons (HFCs), perfluorocarbons (PFCs) and sulfur hexafluoride (SF_6) have been listed as greenhouse gases that contribute to global warming.[4] CO_2 is the most important contributor among these GHGs and is responsible for about 64% of the total enhanced greenhouse effect.[5] The concentration of CO_2 in the atmosphere has increased from 280 ppm to 395 ppm in the last 50 years and may increase up to 570 ppm by the year 2100, causing around a 1.9 °C rise of the global mean temperature.[6, 7] The burning of fossil fuels, which provide more than 80% of the world's energy requirement, is the largest single source of global GHGs emissions. The application of renewable energy, such as solar energy, wind energy, bioenergy, and hydrogen as fuel may reduce the dependence on fossil fuels. However, considering the slow pace of the scale-up of renewable energy, fossil fuels will continue to be the major energy source for many decades. The emission of CO_2 will continue to increase as the energy consumption increases along with industrialization, and the increase of the world population.

Carbon capture and storage (CCS) technology, as an efficient method to reduce the CO_2 emission and stabilize the CO_2 concentration in the atmosphere, is currently drawing more and more attention, both for the pre- and post-combustion emissions from coal, oil and nature gas-fired power plants[8, 9, 10, 11, 12, 13] and for direct capture of CO_2 from the atmosphere.[14, 15, 16, 17, 18, 19, 20] CCS contains many technologies including CO_2 capture, transportation and storage. CO_2 is compressed into liquid and supercritical fluid to be transported to the storage place, for example in geological or ocean reservoirs, after it

is captured at the point of generation.

The CO₂ capture process is a significant part of the CCS project and accounts for 70-80% of the total cost of CCS technologies.[21] CO₂ capture technologies in fossil fuel power plants can be categorized as three kinds, pre-combustion capture, oxy-fuel combustion capture and post-combustion capture. Pre-combustion capture is a process of capture CO₂ in fossil fuels before they are used for power generation. The primary fuel (coal, natural gas, crude oil, etc.) is gasified to produce a syngas consisting primarily of carbon monoxide (CO) and hydrogen (H₂) in the integrated gasification combined cycle (IGCC). Then CO in the gas stream is converted to CO₂ for separation. Oxy-combustion capture is using high purity oxygen (>95%) instead of ambient air to combust with fuels. The production of this process mainly contains CO₂ and H₂O, and CO₂ can be easily separated out.[22] The main disadvantage of Oxy-combustion is that a large amount of oxygen is needed, which is expensive, both in terms of capital cost and energy consumption. Post-combustion capture is the process that removes CO₂ from the flue gas after combustion. Post-combustion capture is the most applied technology in CO₂ capture because it can be embedded into the existing plants without much modification. Various carbon capture technologies including cryogenic distillation, membrane separation, absorption, and adsorption have been developed and even commercialized on small scale but not for power plants or direct air capture. Among these technologies, chemical adsorption using aqueous alkanolamine solutions is proposed to be the most feasible technology for point source (*i.e.*, power plant) capture before the year 2030.[23, 24] However, scaling up amine scrubbing could increase the cost of electricity by as much as 80% in new pulverized coal power plants, while reducing the power plant's net efficiency by approximately 30%.[25, 26] Solid sorbent adsorption can potentially decrease these numbers but is lacking proof at industrial scales.

A fundamental understanding of the adsorption chemistry in SSA sorbents will facilitate technological development. CO₂ adsorption using silica supported amine sorbents has been studied by many groups. The zwitterion mechanism is frequently used for explain-

ing the adsorption chemistry. However, the existence of zwitterion intermediates and the stability of the zwitterion are under debate. Water dramatically improves the adsorption capacity of SSA sorbents, but no one has clarified the role of water in the adsorption process. Understanding the adsorption mechanism and the effect of water are critical to the material development and process design.

Computer models are frequently used to investigate real complex problems. Many real world problems are too difficult or too expensive to experiment at real scales, for example, the weather forecasting, subsurface hydrology, nuclear reactor performance, combustion in power plants and carbon capture systems. Computer models are normally established first to represent models of systems at small scale, for example, the movement of small solid particles, nuclear reaction, combustion mechanism and chemical kinetics. Then the small models are applied to large-scale systems for making predictions. Because computer models are developed based on assumptions and simplifications, ineluctably, there will be some uncertainties in predicting the physical processes.

No prediction is complete without a description of its uncertainty.[27] Many of these uncertainties arise during upscaling to larger models. Two main uncertainties are from the model parameter and model discrepancy. These uncertainties from the small-scale model have a significant impact on the accuracy and reliability of the predictions of large-scale systems. Improper representation of these uncertainties may result in inaccurate or even wrong predictions. Therefore, it is important to quantify the effect of the propagation of these uncertainties during upscaling.

In this present study, first-principle quantum chemistry calculation has been used to study the stability of zwitterions. New mechanisms and chemistry of CO_2 reaction and diffusion in the SSA sorbents were proposed and implemented through mathematical modeling. Simulation results were compared against the experimental data. Bayesian calibration was used to calibrate the model to the experiment data. An uncertainty quantification approach includes dynamic discrepancy functions has been developed and applied in the calibration.

The joint posterior distribution of uncertainties from model parameters and model discrepancy has been propagated to a process model for predictions.

CHAPTER 2

STATE-OF-THE-ART

2.1 Post-combustion CO₂ Capture Technologies

Various post-combustion carbon dioxide capture technologies were developed and under development for commercialization. Each kind of technology has its own advantages and disadvantages. Widely applied post-combustion CO₂ capture technologies including absorption, cryogenics, membrane, and adsorption are reviewed in this section.

2.1.1 Absorption

Chemical absorption is the method of using alkaline solvents to neutralize the CO₂ that is absorbed from the gas phase into the liquid phase after contact with the solution. A concentrated CO₂ stream is released to be further compressed for transport and storage after breaking down the intermediate compounds in the solution by reheating in a stripping column. The solvent can be recycled back to the absorber. The operation pressure is around 1.0 bar and the temperatures in the absorber and stripper are generally in the ranges of 40-60°C and 120-140°C, respectively.[24] CO₂ recovery rates of 98% can be achieved, and product purity can be in excess of 99%.[28] The flow diagram of chemical absorption of CO₂ is shown in Figure 2.1(a). This process requires large equipment and intensive energy input, therefore is not economy.

Chemical absorption processes differ in the solvents used for CO₂ capture. The four major processes are amine absorption, aqua-ammonia absorption, dual-alkali absorption and sodium carbonate slurry absorption.[29] Amine-based solvents are the major chemical solvents that have been used to remove CO₂ from natural gas to produce food level CO₂ for over 60 years by the natural gas industry.[30] Amine can be classified as primary, secondary or

Figure 2.1: Flow diagram of chemical absorption and adsorption. Figure taken from ref. [29]

tertiary based on the degree of substitution of the nitrogen atom. Monoethanolamine (MEA) is the most commonly used amine due to its relatively low cost and good thermal stability. MEA consists of one alkanol chain and two hydrogen atoms bonded to a nitrogen atom and thus it is a primary amine with the molecular formula $(C_2H_4OH)NH_2$. Besides MEA, diethanolamine (DEA) and methyl diethanolamine (MDEA) are often used as absorbents. DEA consists of two alkanol chains and one hydrogen atom bonded to the nitrogen atom and is a secondary amine with the molecular formula $(C_2H_4OH)_2NH$. MDEA is a tertiary amine which has the molecular formula $(C_2H_4OH)_2N(CH_3)$. Primary and secondary alkanolamines can react directly with CO_2 to form carbamates. Carbamates cannot be formed through a direct reaction between tertiary alkanolamines and CO_2 because of the lack of hydrogen atoms attached to the nitrogen atom. However, bicarbonate can be formed through the hydrolysis reaction. The proposed mechanisms of CO_2 absorption in the amine-based solvents (MEA) are shown in Figure 2.2.[31]

Mixed amines of primary amines, secondary amines, and tertiary amines also have been used for different purposes,[30] for example, to reduce the solvent regeneration energy. Puxty and coworkers investigated the absorption performance of 76 amines as shown in Figure 2.3.

Figure 2.2: Proposed reaction sequence for CO₂ capture by amine-based solvents (MEA). Figure taken from [31]

Figure 2.3: CO₂ absorption capacity versus amine group pK_a. Figure taken from ref. [32]

Chemical absorption using amine-based solvents is capable of capturing low concentrations of CO₂ in the flue gas. This process is the most mature technology for CO₂ capture and it has been commercialized for many decades for chemical and food industries. Fluor Enterprises Inc., Randall Gas Technologies, and ABB Lummus Global Inc. all have commercialized flue gas plants for salable CO₂ products to chemical and food industries based on amine solvents.[33] Based on their recently developed amine solvents, Mitsubishi Heavy

Industries Ltd. has commercialized a flue gas CO_2 recovery process and licensed it to a fertilizer company in India for CO_2 capture.[33] It seems that they are the only company marketing flue gas CO_2 recovery technology, but not for CO_2 capture from power plants. However, the solvent has disadvantages like high energy consumption for solvent regeneration, low amine loading capacity, partially regeneration, solvent degradation and upscaling difficulty. These disadvantages limit the efficiency of chemical absorption of CO_2 from power plants.

Organic solvents can physically absorb CO_2 rather than reacting chemically. The relatively weak interaction between CO_2 and the absorbent decreases the energy requirement for regeneration. The solubility of CO_2 in the solvent depends on the partial pressure of CO_2 and the gas temperature. Based on Henry's Law, physical absorption takes place in the solvent at high CO_2 concentration and low temperature. Desorption takes place at reduced concentration and increased temperature during the regeneration of solvent. Physical absorption has been applied to many industrial processes to remove acid gas at high concentration.[34] Some physical absorption processes for CO_2 absorption such as Selexol (dimethylether or propylene glycol), Rectisol (methanol), Purisol (N-methylpyrrolidone), Morphysorb (morpholine), and Fluor (propylene carbonate) are commercially available. The Selexol process has the advantages of low vapor pressure, low toxicity, and less corrosive solvents and can be used to remove both CO_2 and H_2S at low temperature.[34] The Rectisol process uses stable absorbent and is less corrosive. It is capable of handling gases containing sulfur. Low energy consumption is the advantage of a Purisol or Morphysorb process.[35] The solubility of CO_2 in the Fluor process is high and it is suitable for high CO_2 partial pressures.[36]

Table 2.1 lists the commercial CO_2 absorption solvents used in industry for physical and chemical absorptions.

Table 2.1: Commercial CO₂ Scrubbing Solvents Used in Industry. Table taken from ref. [37]

Absorption process	Solvent	Process conditions	Developer/ licensor
Physical Solvent			
Rectisol	Methanol	-10/-70°C, >2 MPa	Lurgi and Linde, Germany; Lotepro Corporation, USA
Puisol	n-methyl-2-pyrrolidone (NMP)	-20/+40°C, >2 MPa	Lurgi, Germany
Selexol	dimethyl ethers of polyethylene glycol (DMPEG)	-40°C, 2-3 MPa	Union Carbide, USA
Fluor Solvent	Propylene carbonate	Below ambient temperatures, 3.1-6.9 MPa	Fluor, El Paso, USA
Chemical Solvent			
<i>Organic (Amine Based)</i>			
MEA	2.5 n monoethanolamine and chemical inhibitors	~40°C, ambient-intermediate pressures	Dow Chemical, USA
Amine Guard (MEA)	5 n monoethanolamine and chemical inhibitors	~40°C, ambient-intermediate pressures	Union Carbide, USA
Econamine (DGA)	6 n diglycolamine	80-120°C 6.3 MPa	SNEA version by Societe National Elf Aquitaine, France
ADIP (DIPA & MDEA)	2-4n diisopropanolamine 2 n methyldiethanolamine	35-40°C, >0.1 MPa	Shell, Netherlands
MDEA	2 n methyldiethanolamine		
Flexsorb/ KS-1, KS-2, KS-3	Hindered amine		Exxon, USA; M.H.I.
<i>Inorganic</i>			
Benfield and versions	Potassium carbonate & catalysts Lurgi and Catacarb with arsenic trioxide	70-120°C, 2.2-7 MPa	Lurgi, Germany; Eickmeyer and Associates, USA; Giammarco Vetrocoke, Italy
Physical/ Chemical Solvents			
Sulfinol-D and Sulfinol-M	Mixture of DIPA or MDEA, water and tetrahydrothiophene (DIPAM) or diethylamine	>0.5 MPa	Shell, Netherlands
Amisol	Mixture of methanol and MEA, DEA, diisopropylamine (DIPAM) or diethylamine	5/40°C, >1 MPa	Lurgi, Germany

2.1.2 Cryogenic Separation

Cryogenic separation is a process that physically separates CO₂ from flue gas by condensation. The impurities of the flue gas including NO_x, SO_x and H₂O, etc need to be removed before it can be cooled for CO₂ de-sublimation. Only CO₂ and N₂ are left in the flue gas. Under the right conditions, CO₂ will condense while N₂ remains as a gas. Highly concentrated liquid CO₂ can be collected after gaseous N₂ is separated. Two cryogenic separation technologies for the post-combustion CO₂ capture have been proposed: (1) Clodic and his coworkers have proposed a process that gaseous CO₂ is first de-sublimated onto the surface of heat exchanger fins and then recovered as liquid CO₂ at elevated pressures;[38] (2) Tuinier and his coworkers have proposed a process using packed beds where the CO₂ is first

de-sublimated onto the packing material and then released to produce gaseous CO_2 . [39] The following Figure 2.4 is the process flow diagram for cryogenic separation of CO_2 as proposed by Clodic and Younes.

Figure 2.4: Cryogenic separation process proposed by Clodic and Younes. Figure taken from ref. [29]

One important advantage of cryogenic separation over other processes is: its product is liquid CO_2 which does not need further compression for transport by pipeline or ship. The CO_2 recovery rate is very high but limited to streams that contain high concentrations of CO_2 . Cryogenic separation is most promising for separation of CO_2 from high pressure gases which contain a high concentration of CO_2 . However, the capital cost of equipment and refrigerant is extremely high. The energy requirement for cooling the system makes this process inefficient. Besides, other processes for removing impurities need to be included before the flue gas enters this process.

2.1.3 Membrane Separation

A membrane acts as a filter to selectively remove the intended gas or gases from a mixture as shown in Figure 2.5. The pressure gradient between two sides of the membrane is the driving force of separation dominated by Fick's law. Therefore, a proper pressure difference across the membrane needs to be created for efficient separation. Permeability

and selectivity are the two characteristics controlling the performance of the membrane. They are dependent on the flue gas component and the membrane material properties. The small molecule of CO_2 gas results in fast diffusion in many membrane materials. The relatively high molecular weight impels its strong adsorption and easy dissolution at higher concentrations in membranes.

Figure 2.5: Schematic of the gas separation membrane. Figure taken from ref. [34]

Membrane separation construction is simple because there is no phase change, no need to add chemicals to the membrane, or heat to regenerate a solvent or sorbent within the membrane. Therefore, it requires significantly less energy than other technologies when high purity is not vital. Silica, zeolite[40], inorganic, carbon, alumina, cellulose acetate, polymeric[41, 42, 43], hydrogen-selective[44, 45, 46] and facilitated transport membranes[47] have been investigated for CO_2 separation from mixtures. Membrane separation technology has been developed for CO_2 removal in natural gas (mainly CO_2 and CH_4) production, H_2 and syngas production and NH_3 production.[48, 49, 50, 51, 52] Cellulose acetate membranes, selective polyimides, polyaramides have been commercialized to remove unwanted CO_2 from the desired product in succession since the 1980s. Air Products and Chemicals and Ube Industries are marketing membrane systems that collect CO_2 for enhanced oil recovery and landfill gas upgrading, respectively.[33]

The impurities from the post-combustion emissions such as NO_x and SO_x may have adverse effects on the efficiency of the membrane, so the membranes need to be chemically resistant to these chemicals or they have to be removed prior to the membrane separation. The flue gases need to be cooled prior to membrane separation because many membranes have an operating temperature below 100°C and do not perform well at high temperatures, although some membranes operating at higher temperature have also been developed.[51, 53, 54] Membrane separators do suffer because they are either not selective enough or they are not very permeable to CO₂. The low removal efficiency and low purity of CO₂ make this process ineffective.[7]

2.1.4 Adsorption

Adsorption can be used to separate CO₂ from industry process streams generated by fossil fuel burning. It is a process that involves the intermolecular forces between gases and the surface of certain solid materials. Depending on the sorbents, CO₂ can be adsorbed either by weak physical interactions (physisorption) or strong chemical interactions (chemisorption). The adsorption of the gases depends on temperature, CO₂ partial pressure, surface area, surface forces and adsorbent pore size.[54, 55] The capacity of most sorbents drastically decreases when the temperature is above 100°C. CO₂ is adsorbed by a bed of sorbents while other gases pass through during adsorption. During the desorption process, CO₂ is driven through the adsorbent which can be regenerated. Both pressure swing adsorption (PSA) which regenerates the adsorbents by reducing pressure and temperature swing adsorption (TSA) which regenerates the adsorbents by increasing temperature are widely investigated and commercialized for H₂, N₂, CO₂, and CH₄ production. Electrical swing adsorption which regenerates adsorbents by passing a low-voltage electric current is another promising method. The desorption process of physisorption is less energy intensive because it is a low heat release reaction compared to chemisorption. Therefore, physisorption is reversed at a lower temperature than chemisorption. The adsorption performance, cost,

reliability, and cycling of the adsorbent are the key factors to successful commercial applications. A variety of solid sorbents for physical adsorption and chemical adsorption using mesoporous adsorbents impregnated and grafted with amines have been proposed.

2.1.4.1 Physical Adsorption

The physical adsorption using porous solid adsorbents such as activated carbon, ordered mesoporous silica, zeolites and metal-organic frameworks (MOFs) will be discussed in this section.

The pore structure, pore size distribution, active surface structure, and other factors are controlling the adsorptive nature of activated carbon.[56, 57] The preparation processes of activated carbon are introduced by Rodriguez-Reinoso[56] and Davini.[58] The advantages such as low cost, high thermal stability, simple regeneration and wide availability make it one of the most promising adsorbents for capturing CO₂ in the processes for energy generation and hydrogen production. They can be produced from coal, wood, biomass and industry byproducts.[57] High CO₂ adsorption capacity can be observed at high CO₂ concentration.[57] However, as shown in Figure 2.6, its CO₂ adsorption capacity decreases rapidly as temperature increases and the adsorption efficiency is low at low CO₂ pressure conditions. Experimental data from Na and his coworkers showed good agreement with predictions from the Langmuir-Freundlich model and illustrated that CO₂ uptake on this activated carbon decreased from ca. 3.2 to 1.5 mmol g⁻¹ as temperature increases from 15 to 55°C. Gases smaller than CO₂ can also fill up the pore space in activated carbons. The amount of N₂ adsorbed at the same time is shown in Figure 2.7. The CO₂ adsorption capacity of activated carbon at temperatures above 55°C is weak and highly sensitive to temperature. The surface area and pore structure of activated carbon materials have been modified by using different precursor and fabricating methods to improve the CO₂ adsorption capacity and decrease the sensitivity to temperature. Activated carbon adsorbents showed good reversibility of adsorption and low sensitivity to moisture.[60] The regeneration is less

Figure 2.6: Adsorption isotherm of CO_2 on activated carbon. Figure taken from ref. [59]

Figure 2.7: Adsorption isotherm of N_2 on activated carbon. Figure taken from ref. [59]

energy intense because of the weak physical interaction with CO_2 . [57]

The properties of high surface area, high pore volume, tunable pore size, and good thermal stability make ordered mesoporous silica (OMS) a candidate for CO_2 adsorption.

Different families of mesoporous silica materials including M41S, folded sheet mesoporous material-16 (FSM-16), Santa Barbara Amorphous type material (SBA-n), MCM41 and anionic-surfactant-templated mesoporous silica (AMS) *et al.* have been reported.[61, 62, 63, 64, 65, 66] Experiment showed that the smaller the pore channel of OMS, the higher CO₂ adsorption capacity can be obtained.[67] However, the CO₂ adsorption capacities are not high enough, especially at low pressure. Functionalized OMS, especially amine-functionalized OMS has been widely investigated and used as chemical adsorbents because of the chemical interaction between CO₂ and amine groups. They are less sensitive to temperature and have higher adsorption capacity under low CO₂ concentration.[68, 69, 70]

Zeolites, a type of porous crystalline aluminosilicates, consist of interlocking tetrahedrons of SiO₄ and AlO₄ joined together by shared oxygen atoms in various arrangements. Molecules can penetrate the pores contained in the open crystal lattices. The exchangeable cations such as Na⁺, K⁺, Ca²⁺, and Mg²⁺ are located in the channels and cavities throughout the structure to balance the negative charge created by the substitution of an AlO₄ for a SiO₄. Zeolites are good materials for post-combustion adsorption due to their favorable kinetics and capacities at mild operating conditions. Various zeolites have been synthesized for CO₂ adsorption, mainly zeolite 13X and zeolite 5A.[71, 72, 73, 74, 75] The performance of zeolites is largely affected by their size, charge density, the chemical composition of cations and operating conditions.[19] Full regeneration is hard to achieve by pressure swing, but can be achieved by temperature swing. This process is energy intense because zeolites are typically used at high pressure and require very high regeneration temperatures for full regeneration, often above 200°C.[72, 76] Their CO₂ adsorption capacities are so sensitive to temperature change that the uptake of CO₂ decreases significantly even with a small increase of the operating temperature.[73] The CO₂ capacity rapidly decreases when the temperature is increased above 30°C.[77, 78] The CO₂ and N₂ adsorption equilibrium on zeolite 13X at different temperatures have been investigated by Rodrigues's group [73], as shown in Figure 2.8 and Figure 2.9. Their experiments fit with the Toth and multisite Langmuir

models and concluded that zeolite 13X is very selective to carbon dioxide, which makes it a very good candidate for methane purification or carbon dioxide sequestration. The flue gas must be cooled and cleaned of impurities such as SO_x, NO_x, and H₂O prior to contact with adsorbents for adsorption.

Figure 2.8: CO₂ adsorption equilibrium on zeolite 13X. ■ T=298K; ♦ T=308K; ● T=323K; solid lines, Toth model; dotted lines, multisite Langmuir. Figure taken from ref. [73]

MOFs have a very high surface area, high thermal stability, controllable pore structures and tunable pore surface properties that enable them to be good adsorbents.[79, 80, 81] After it was first used for CO₂ capture at room temperature by Yaghi's group[82], new types of MOFs have been developed for achieving high CO₂ capacity and stability by many other groups.[83, 84, 85, 86, 87, 88] The performance of MOFs are excellent at high CO₂ pressure and dramatically reduced when they are exposed to gas mixtures.[24, 88] However, most MOFs have poor CO₂ capture performances at a low CO₂ partial pressure and it is energy cost to compress flue gases to high pressure. These facts are displayed in Figure 2.10 which is the CO₂ capacities of several MOFs at room temperature conducted by Millward and Yaghi.[82] A comparison of CO₂ capacity between MOFs, zeolite, and carbon also have been

Figure 2.9: N_2 adsorption equilibrium on zeolite 13X. ■ $T=298K$; ♦ $T=308K$; • $T=323K$; solid lines, Toth model; dotted lines, multisite Langmuir. Figure taken from ref. [73]

Figure 2.10: Gravimetric CO_2 capacities for several MOFs at room temperature. Figure taken from ref. [82]

conducted by Millward and Yaghi as shown in Figure 2.11. The uptake of CO_2 increases as pressure increases for all three adsorbents. MOFs have better performance when CO_2

pressure is above 15 bars.

Figure 2.11: Comparison of volumetric CO₂ capacity for MOFs, zeolite 13X pellets, and MAXSORB carbon powder. Figure taken from ref. [82]

Low CO₂ selectivity is the major drawback for most physical adsorbents. Although activated carbon and MOF materials achieving relatively higher CO₂ adsorption capacity seem to be promising CO₂ adsorbents, they operate at high pressures and low temperatures which are not economically feasible. Silica materials are facing the problems of lower adsorption capacity and low selectivity toward CO₂.

2.1.4.2 Chemical Adsorption

Chemical adsorption uses supported amine sorbents to adsorb CO₂ from the gas phase onto the solid surface. In contrast to amine solutions, degradation due to evaporation and vessel corrosion are not serious issues any more. Silica supported amines were first used for CO₂ capture by Tsuda in 1992.[89] Amine groups immobilized onto a mesoporous silica substrate with either ordered porosity (such as SBA-15) or disordered porosity (silica xerogel) were used for CO₂ capture under dry conditions. The disordered structures are hard to characterize and therefore it is difficult to clearly understand the molecular structure of

the adsorbent. By contrast, ordered mesoporous silica are excellent candidates for scientific study because they are easy to synthesize, easy to characterize and many aspects of their structures are tunable.[90]

The amines may be covalently bonded to the substrate through the reaction of an aminosilane with silanol groups on the silica surface[31, 91, 92, 93, 94, 95] or physically impregnated into the silica support pore space.[68, 96, 70, 97, 98, 99, 100, 101, 102] The amine within these sorbents behaves similarly to a liquid alkanolamine and thus takes up appreciable amounts of CO_2 and H_2O . [103, 104, 105, 106] The first reported amine-impregnated silica for CO_2 capture is MCM-41 by Song.[68] It has a high surface area with cylindrical pores of relatively small diameter, with low molecular weight polyethyleneimine (PEI) to create an adsorbent they termed a “molecular basket”. After that, several groups have reported their experiment and simulation results using different amine-impregnated silica like MCM-41, MCM-48, SBA-15, SBA-16, and KIT-6 as CO_2 adsorbents.[107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119]

In order to achieve the maximum capture capacity per weight of adsorbents, a lot of amines from monoamines to aminopolymers have been investigated for impregnation into silica supports. The most commonly used amine is PEI. PEI contains a linear or branched mixture of primary, secondary and tertiary amines and the repeat structure is shown in Figure 2.12. The nitrogen percentage in PEI varies as the proportions of primary, secondary and tertiary amines change. Changing their proportions will change the CO_2 capture kinetics as well as the capacity (equilibrium capture capacity). Different PEI-impregnated silica has been synthesized to investigate the CO_2 capture capability by several groups.[98, 99, 120] Other amines, tetraethylenepentamine (TEPA) and diethanolamine (DEA) as shown in Figure 2.12 were impregnated into silica supports to prepare CO_2 adsorbents.[70, 97, 121] The low-molecular-weight PEI is preferred because it has less possibility to block pores.

The equilibrium adsorption capacity under dry conditions depends on the PEI loading, pore size, surface area, CO_2 partial pressure and operating temperature. As shown in Figure

Figure 2.12: Amines, silanes, monomers, and polymers used in the synthesis of solid supported amine adsorbents. Figure taken from ref. [90]

2.13,[97] the capacity and amine efficiency of DEA-impregnated silica reached the maximum at 7.26 mmol of DEA/g-adsorbent and decreased at higher loadings. The DEA will deposit on the external surface of adsorbents after filling all the internal pores. In the case of excessive DEA, film diffusional resistance becomes a limiting factor for the kinetics of CO₂ uptake, resulting in the decrease of adsorption. Song's group also found that the adsorption capacity increased as PEI loadings increased from 0 to 30 wt %, reached a plateau from 30 to 50 wt %, and then decreased to the capacity of pure PEI at 100%.[68, 69, 122]

Figure 2.13: CO₂ adsorption capacity and adsorption rate as a function of DEA content on PE-MCM-41 under 5% dry CO₂ in N₂. Figure taken from ref. [97]

Ahn and his coworkers investigated the textural and adsorption properties of 5 different mesoporous silica supports.[98] After PEI is loaded into the mesoporous pores of silica support materials, the corresponding textural properties such as the surface area, pore volume, and average pore diameter are changed as shown in Table 2.2. The density of amine

Table 2.2: Textural Properties of Mesoporous Silica Materials Before and After PEI Loading. Data from ref. [98]

	Surface area (BET) (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (BJH) (nm)
MCM-41	1042	0.85	2.8
MCM-41-PEI 50	4	0.01	—
MCM-48	1162	1.17	3.1
MCM-48-PEI 50	26	0.10	—
SBA-15	753	0.94	5.5
SBA-15-PEI 50	13	0.04	—
SBA-16	736	0.75	4.1
SBA-16-PEI 50	23	0.02	—
KIT-6	895	1.22	6.0
KIT-6-PEI 10	430	0.68	5.9
KIT-6-PEI 30	251	0.49	5.4
KIT-6-PEI 50	86	0.18	5.3
KIT-6-PEI 60	—	—	—
KIT-6-PEI 70	—	—	—

groups has an important role in the efficient adsorption of CO₂. Large surface area, pore

volume, and pore diameter allow higher loading into the silica particles. The surface area, pore volume, and pore size decrease as PEI loading increases. There is almost no pore volume remaining in the silica support with small pore volumes and pore diameters after 50 wt% PEI loading. They found that under the same 50 wt% PEI loading, the equilibrium adsorption capacities increased in the order $\text{MCM-41} < \text{MCM-48} < \text{SB-16} \approx \text{SBA-15} < \text{KIT-6}$, which is same as the order of average pore diameter of the base support (2.8, 3.1, 4.1, 5.5, and 6.0 nm, respectively).[98] It is also same as the order of the internal surface area after 50 wt% PEI loading: $\text{MCM-41} (4) < \text{SB-15} (13) < \text{SBA-16} (23) < \text{KIT-6} (86)$. It seems to be more suitable to use supports with large pore volume, pore diameter, and surface area to impregnate amine.

As measured by Song in Figure 2.14, at a given temperature, the adsorption capacity increases as the CO_2 concentration increases from 0 to 30% of atmospheric pressure and remains at a plateau afterward.[68] Unlike zeolites and activated carbons, the CO_2 partial pressure was shown to have a small impact on adsorption capacity. Zhu observed that there is only about 5% loss in the adsorption capacity when the CO_2 partial pressure was reduced from 100 to 5%.[70]

Although a temperature swing approach is needed for desorption and the sorbents may degrade during the temperature swing cycles, CO_2 capture using amine functionalized adsorbents is considered one of the most promising technologies for CCS.[123] High surface area, high stability, high CO_2 selectivity and fast kinetics provide the SSA sorbents the capability of capturing CO_2 at any CO_2 partial pressure. Adsorption capacities for silica support amine adsorbents at mild operating conditions (0.05 – 1.0 bar CO_2 and 25-75°C) range from 0.089 to 0.22 g CO_2 /g adsorbent.[90]

According to thermodynamics, equilibrium CO_2 capacity should increase as temperature decreases because CO_2 adsorption is an exothermic process. However, it has been widely observed that when starting from a low temperature and zero CO_2 loading, capacity first increases with increasing temperature in dry CO_2 before passing through a maximum

Figure 2.14: The influence of CO₂ concentration in the CO₂/N₂ mixture on the adsorption performance of MCM-41 with 50 wt% PEI at 75°C. Concentration is given as percentage of 1 bar. Figure taken from ref. [68]

and decreasing again.[68, 70, 98, 124, 102] The temperature with the highest capacity is different for different materials and synthesis methods. For KIT-6 with 50 wt% PEI loading, it is 75°C as shown in Figure 2.15. This indicates the existence of a diffusive limitation in highly loaded sorbents, leading to meta-stable states. This hypothesis has been confirmed by attenuated total reflectance spectroscopy experiments.[125] Diffusive intermediates are critical for transporting CO₂ into the amine bulk because the diffusion coefficient of CO₂ in amine-impregnated sorbents is low.

2.1.5 Summary

Among these technologies, chemical absorption using aqueous alkanolamine solutions is proposed to be the most practicable technology for CO₂ capture in the next few decades.[23, 24] However, scaling up amine scrubbing could largely increase the cost of electricity and reduce the power plant's net efficiency.[25, 26] The low contact area between gas and liquid, low CO₂ loading and absorbent corrosion are the drawbacks to being overcome for aqueous

Figure 2.15: The effect of temperature on the CO₂ adsorption-desorption performance of KIT-6 with 50 wt% PEI loading. Figure taken from ref. [98]

amine absorption. Although less energy is needed for regeneration, physical absorption and physical adsorption are sensitive to the flue gas temperature. Most emissions from fossil fuel power plants need to be cooled to a low temperature prior to being physically absorbed or adsorbed. The performance of physical absorption and physical adsorption is easily affected by the moisture, which is a normal component of fossil fuel power plant emissions. Cryogenic separation is not a practical means to separate CO₂ from flue gases because of the high energy cost. Membranes also need to cool the flue gas first and their efficiency is low when the CO₂ concentration in flue gas is low. For post-combustion emissions, the largest component of the flue gases is nitrogen and CO₂ is only a minor component. There is no need to compress CO₂ to high pressure to separate it from N₂ for chemical adsorption because it is efficient even at low CO₂ partial pressures. The advantages of fast kinetics, thermal stability, high CO₂ selectivity, efficient even at both low and high CO₂ partial pressures, and high CO₂ adsorption capacity make solid sorbent adsorption a good alternative to decrease the energy penalty and achieve the CO₂ capture purpose but still needs to be proven at large scales. It

is also potential to use solid sorbents to capture CO_2 directly from air.

2.2 Water Effect on CO_2 Capture Capacity

For CO_2 chemical or physical absorption in aqueous solutions, water acts as a base. Therefore, the existence of water vapor will not have much influence on CO_2 absorption. However, water vapor is a serious problem for cryogenic separation, membrane separation, and physical adsorption. The water content of the flue gas will form ice and damage the equipment during cryogenic separation. The impact of water vapor on the CO_2 adsorption capacity of activated carbons is adverse because of the competitive adsorption from H_2O . The performance of zeolites and MOFs are good under dry flue gas but decline in the presence of moisture. Zeolites tend to be more sensitive to H_2O than acid gases due to their hydrophilic nature. Polar H_2O molecules will preferentially adsorb to the exchangeable cations, effectively eliminating adsorption sites for CO_2 molecules.[126] Water molecules can displace the ligands and create structural defects in the crystal lattice of the MOFs, decreasing the lifetime and capacity of the membranes. Figure 2.16 shows the equilibrium isotherms for CO_2 on NaLSX at 35°C . [76] It can be seen that the CO_2 capacity of NaLSX dramatically decreases as the water concentration increases.

On the contrary, moisture can improve the performance of silica supported amine sorbents for CO_2 adsorption. Many experiments have shown that water dramatically improves the stability of the amine-loaded materials by preventing from forming urea groups as well as increases the capacity of SSA sorbents.[105, 103, 127] Song's group showed that the CO_2 adsorption capacity of PEI/MCM-41 at 75°C was increased from 2.05 mmol/g-PEI under 15% of anhydrous CO_2 to 2.95 mmol/g-PEI under 13% of CO_2 with 10% of moisture.[120] Jones's group also observed that the CO_2 adsorption capacity increased about 50% under prehydrated condition compared to non-prehydrated condition using silica supported PEI hollow fiber sorbents.[128] Figure 2.17 shows the breakthrough curves of the PEI-modified glass (PG) fiber for CO_2 under simulated dry and moist flue gas by Chen's group.[129] Its

Figure 2.16: H₂O effect on NaLSX at 35°C under equilibrium isotherms. Figure taken from ref. [76]

CO₂ adsorption capacity under humidified conditions (3.98 mmol CO₂/g) is much higher than that under dry conditions (0.26 mmol CO₂/g).[129] Therefore, understanding the role of water in the adsorption process is critical for the optimal design of sorbents and capture processes.

Cooperating with the amine group and CO₂, water can act as a free base for deprotonation of zwitterions and can enable the formation of products such as carbonic acid and bicarbonate.[97, 120, 122, 130, 108, 131] Bacsik *et al.* and Gebald *et al.* detected additional free amine groups in the presence of water vapor using FTIR.[127, 132] Water is known to change the semi-crystalline structure of aminopolymers, substituting amine-amine hydrogen bonds with amine-water bonds, thus significantly opening up the structure. However, water is also likely to affect the diffusion mechanism of CO₂. The diffusion limitation under dry conditions disappears under humidified conditions. A quantum chemical study on the stability of zwitterions conducted by Mebane *et al.* suggested that water may be involved in forming a more stable diffusive intermediate.[96] This kind of stable diffusive intermediate

Figure 2.17: Comparison of CO₂ breakthrough curves from simulated dry and moist flue gas. Figure taken from ref. [129]

can decrease the energy barrier of diffusion.

In summary, the existence of moisture in flue gas has a very small influence on absorption; negative effect on cryogenic, membrane and physical adsorption; positive effect on chemical adsorption. This behavior indicates the potential of using amine-modified sorbents to capture CO₂ from humid flue gases. However, the mechanism of how H₂O improves the CO₂ adsorption capacity is still in dispute.

2.3 Reaction Kinetics

The two-step zwitterion mechanism and single-step termolecular mechanism were proposed as the mechanism of CO₂ reacting with primary and secondary alkanolamines. Although they were proposed and developed from the reactions between CO₂ and aqueous solutions, they can also be considered as the mechanism of CO₂ reaction with non-aqueous solvents and solid sorbents. The following reviews the theories of these two mechanisms.

The earliest mechanism for the formation of carbamate in aqueous alkanolamines is a two-step zwitterion mechanism first proposed by Caplow and later reintroduced by Danckwerts.[133, 134, 135, 136] It suggested that the reaction between CO_2 and primary and secondary alkanolamines proceeds through the formation of a zwitterion which is a short-lived intermediate. The zwitterion then forms carbamate by the deprotonation by a free base B:

Applying quasi steady-state assumption to the zwitterion concentration, the overall rate of reaction of CO_2 can be written as:

$$r = \frac{k_{2.1}[\text{CO}_2][\text{R}_2\text{NH}]}{1 + \frac{k_{-2.1}}{k_B[\text{B}]}} \quad (2.3)$$

where $k_{2.1}$ and $k_{-2.1}$ are the forward and backward rates of reaction of 2.1, and $k_B[\text{B}]$ represents the deprotonation of zwitterion intermediate by any base in the solution.

The CO_2 -amine zwitterion is formed through reaction (2.1) and followed by base-catalyzed deprotonation of zwitterion by any base existing in the solution. Therefore, the concentrations of free amine, H_2O , and OH^- in an aqueous solution will contribute to the zwitterion deprotonation. In lean aqueous solutions the species free amine, H_2O , and OH^- can act as bases:[137]

The concentration of OH^- is relatively low in the reaction of amine with CO_2 . Therefore, its contribution normally is negligible.[138] For non-aqueous solvents or sorbents, only the free amine can act as a base and hence the CO_2 capacity is limited to 0.5 mol CO_2 per mole of amine.[135]

When deprotonation is much faster than the decomposition of the zwitterion ($k_{-2.1} \ll k_B[\text{B}]$), the zwitterion formation is the rate-limiting factor. Eq. (2.3) goes to:

$$r = k_{2.1}[\text{CO}_2][\text{R}_2\text{NH}] \quad (2.7)$$

It suggests that the reaction is first order with respect to both CO_2 and amine. When zwitterion deprotonation is the rate-limiting factor ($k_{-2.1} \gg k_B[\text{B}]$), Eq. (2.3) becomes:

$$r = \frac{k_{2.1}k_B[\text{B}][\text{CO}_2][\text{R}_2\text{NH}]}{k_{-2.1}} \quad (2.8)$$

This suggests a fractional reaction order between one and two with respect to the amine concentration.

Although the zwitterion mechanism is capable of explaining the first, second and fractional order kinetics for a variety of amines in aqueous and non-aqueous solutions, there is no direct evidence of the existence of the zwitterion even in aqueous solution.[139] One possible explanation is that the zwitterion intermediate is a transient state during the formation of carbamates. It is produced and consumed so fast that it is difficult to detect by any analytical method.[140]

Another mechanism which includes a termolecular reaction between CO_2 , amine and a base has received extensive attention. The termolecular mechanism first proposed by Crooks and Donnellan assumed that an amine combined with one molecule of a base reacts simultaneously with one molecule of CO_2 in a single step.[141] This mechanism was reviewed and further developed by da Silva and Svendsen in their ab initio study of carbamate formation from CO_2 and alkanolamines.[140] This one-step process goes through a loosely-bound com-

plex as the intermediate to form carbamate rather than a zwitterion. This can be written as:

Amine and H_2O are the dominating bases in aqueous solutions, and only the amine is the dominant base in non-aqueous solvents or sorbents. The corresponding reactions with amine and water are:

The forward reaction rate of the termolecular mechanism is:

$$r = (k_{\text{Am}}[\text{R}_2\text{NH}] + k_{\text{H}_2\text{O}}[\text{H}_2\text{O}])[\text{CO}_2][\text{R}_2\text{NH}] \quad (2.12)$$

When the water is the dominant base, the reaction is of first order with respect to the amine and the forward rate becomes:

$$r = k_{\text{H}_2\text{O}}[\text{H}_2\text{O}][\text{CO}_2][\text{R}_2\text{NH}] \quad (2.13)$$

When the amine is the dominant base, the reaction is of second order with respect to the amine and the forward rate becomes:

$$r = k_{\text{Am}}[\text{CO}_2][\text{R}_2\text{NH}]^2 \quad (2.14)$$

With a different concentration of amine and H_2O , the order of reaction can be broken to fractional and shift between one and two. Although the termolecular mechanism can describe the fractional reaction orders for aqueous alkanolamine solutions, it fails to explain the occurrence of changing reaction orders with the concentration of amine observed for nonaqueous

alkanolamine solutions,[142] as was experimentally observed by many investigators.[143, 144] Moreover, the termolecular mechanism does not provide a mobile intermediate for the diffusion of CO₂ through PEI which has been experimentally observed.

Bicarbonate is commonly cited as a possible explanation for the enhanced uptake of CO₂ on amine-modified silica in the presence of humidity.[97, 120, 122, 130, 108, 131] Bicarbonate is formed through

In the presence of moisture, 1 mol of amine can adsorb 1 mol of CO₂ to form a bicarbonate. In dry conditions, 2 mol of amine is consumed to adsorb 1 mol of CO₂, which will limit the CO₂ adsorption capacity. In this way, it is concluded that the CO₂ adsorption capacity in dry conditions is much lower than that in moist conditions.

Although Didas, *et al.* proposed that bicarbonate was formed based on the comparison of IR spectra,[145] the FTIR band assignment for bicarbonate in ethylamines remains controversial.[146, 127] Bicarbonate was only observed on materials with very low amine loadings and long time scale in their study. Indeed, the IR spectra of the same adsorption process can be understood very differently under a different assignment, and other groups concluded that there are no bicarbonates formed under dry and moist conditions in SSA sorbents.[147, 148, 115, 127, 149]

In summary, the zwitterion mechanism can explain the observed first, second, and fractional order kinetic reaction rates for many aqueous and nonaqueous CO₂-amine systems. However, the physical significance of the zwitterion is still unsettled. The termolecular mechanism can only explain the fractional order in aqueous CO₂-amine systems and does not provide diffusive intermediates. There is no evidence showing that bicarbonate is a dominant product of CO₂ adsorption in amine sorbents. Whether or not water leads to the formation of additional adsorbed states for CO₂, the vanishing metastability implies that

water must have an effect on the diffusion of CO_2 .

2.4 Quantum Chemistry Calculations

Quantum chemistry has been used to study the structural characteristics and the chemical reactivities of molecules, such as the energy gap between different orbitals, possible transition states and the enthalpy of reaction. Quantum chemical models are developed from the Schrödinger equation which was first proposed in late 1920's. However, it is not solvable for complex models but the one-electron system with approximations. Models were proposed based on the Hartree-Fock approximation. Because of the incomplete description of the correlation between electrons, Hartree-Fock models are lack accounting for the thermochemistry of reactions involving bond making and breaking. Several approaches have been proposed to address the electron correlation. Configuration interaction (CI), Møller-Plesset (MP) and density function models are commonly used. Configuration interaction and Møller-Plesset models, which use a combination of Hartree-Fock descriptions for ground and excited states to construct a more flexible description of electron motions, are capable of providing excellent descriptions of equilibrium geometries and conformations, as well as the thermochemistry of reactions where bonds are broken and formed. The theory and implementation of single-reference, multireference CI as well as full CI wave functions have been widely introduced.[150, 151, 152] The second-order Møller-Plesset model (MP2), as the simplest member of the class of Møller-Plesset models based on electron promotion, has been widely employed. Higher-order Møller-Plesset models (MP3, MP4, MP5, MP6, etc.) have been formulated, but in practice are limited to small systems and need a complete basis set.[153, 154, 155] Density function models, that include an explicit term to account for the effect of electron motions to other electrons based on Hartree-Fock models, have also been proven to be successful for determination of equilibrium geometries and conformations and for building the thermochemistry of reactions where bonds are broken or formed.[155] Density functional theory (DFT) with Becke's three-parameter hybrid exchange

functional, the Lee-Yang-Parr correlation functional (B3LYP), PBE0, BP86 and TPSS functional was adopted to obtain the geometries of reactants, intermediates, transition states, and products.[156, 157, 158, 159, 160]

The *Gaussian 09* program[161] is the most frequently used tool to perform the quantum chemistry calculations. Gaussian functions are used in the calculations of Hartree-Fock, density functional, Møller-Plesset and CI models. Several series of Gaussian basis sets has been widely used and are thoroughly documented. The basis sets including the CBS-QB3 (the complete basis set)[162], 6-31+G*, 6-31++G** and aug-cc-pVTZ (Dunning’s correlation-consistent polarized valence triplet-zeta basis set)[163] were broadly used. A summary of all-electron basis sets available in Spartan software (a molecular modeling and computational chemistry software developed by Wavefunction) is provided in Table 2.3.

Table 2.3: All-Electron Gaussian Basis Sets Available in Spartan. Table taken from ref. [155]

basis set	available elements
STO-3G	H-Xe
3-21G, 3-21G ^(*)	H-Xe
6-31G*, 6-31G** 6-31+G*, 6-31+G** 6-31++G*, 6-31++G**	H-Kr
6-311G*, 6-311G** 6-311+G*, 6-311+G** 6-311++G*, 6-311++G**	H-Ar
cc-pVDZ	H-Ar, Ga-Kr
cc-pVTZ	H-Ar, Ga-Kr
cc-pVQZ	H-Ar, Ga-Kr

Coupled-cluster method with single, double and triple excitations, CCSD(T), aug-cc-pVIZ basis set and with zero point energy (ZPE) correction has been used to calculate single-point energies. The formation of Enthalpies of reactions were calculated as $\Delta H =$

$\Delta E + P\Delta V$, where $\Delta E = \text{electronic energy} + \Delta \text{ZPE} + \Delta E_{trans} + \Delta E_{rot}$. [96]

Mebane and colleagues have reviewed the application of electronic structure calculations in the formation of carbamic acid in alkanol- and ethyleneamines in CO_2 adsorption in supported amine sorbents.[164] The accuracy of quantum chemical methods has been assessed based on recent studies.[165, 166, 164] In conjunction with an accurate basis set (like 6-311++G**), it was concluded that MP2 is expected to be the most accurate method, although the hybrid DFT approach of PBE0 was also within the “chemical accuracy” of 1 kcal/mol (4.2 kJ/mol). In the work of Mebane and his coworkers[96], quantum chemistry calculations investigated the zwitterion stability in ethylamines. Different quantum chemistry methods have been used as shown in Table 2.4. They concluded that ethylamine zwitterions

Table 2.4: Formation Energies (kJ/mol) for Zwitterion Species in Dielectric Media Representing the Gas Phase, DPA (as a Proxy for PEI), and Water. Table taken from ref. [96]

	$\epsilon_r = 1$		$\epsilon_r = 2.9$		$\epsilon_r = 78$		
method	MMA	DMA	MMA	DMA	MMA	DMA	DETA
B3LYP	50.1	45.1	25.1	37.6	9.2	2.9	10.5
PBE0	40.1	33.9	12.5	8.4	-8.4	-10.9	5.0
MP2	60.2	42.6			15.9	-0.4	13.8
CCSD	68.1	49.8			14.6	0.4	

may be barely stable in an aqueous environment ($\epsilon_r = 78$), but are not stable in a polar environment ($\epsilon_r = 2.9$) similar to that of anhydrous PEI. They called the stability of zwitterion diffusive intermediates in PEI into question, but suggested that physically bonded moieties involving amines, water and CO_2 may be better candidates for diffusive intermediates.

2.5 Uncertainty Quantification and Propagation

All models are the abstractions and simplifications of real complex problems. Many real problems, for example, the weather forecasting, seasonal or regional climate predictions, nuclear reactor performance, fluid dynamics, the combustion in a power plant and pharmaceutical treatment are too hard or expensive to experiment at their real scales. Computer models are normally established first to represent the models or systems at small scale, for example, the movement of solid particles, nuclear reaction, combustion mechanism and chemical kinetics. Then the results are applied to large-scale systems for making predictions and guidance for designs. Because computer models are developed based on scientific theories and assumptions, ineluctably, there will be some uncertainties in predicting the physical processes. No prediction is complete without a description of its uncertainty.[27] These uncertainties from the small-scale model have a significant impact on the accuracy and reliability of the predictions of large-scale systems. Improper representation of these uncertainties may result in inaccurate or even wrong predictions. Therefore, it is important to identify, quantify these uncertainties as well as the effect of uncertainty propagation during upscale.

2.5.1 Model Uncertainties

Uncertainty can be categorized as aleatory and epistemic uncertainties. Aleatory uncertainty is due to the inherent randomness in the system or its environment. It is irreducible because its fundamental nature is random.[167] Epistemic uncertainty is due to lack of knowledge of the modeler or observer. Its fundamental source is incomplete information or incomplete knowledge of the related system or model.[167] It can be eliminated with sufficient knowledge. Aleatory uncertainties are typically unbiased and can be characterized via a probabilistic framework such as probability density function (PDF) or cumulative distribution function (CDF), while epistemic uncertainties are less naturally defined

in a probabilistic framework because they are often biased.[168] The distinction between aleatoric and epistemic uncertainties are not always clear because the lack of knowledge is individualized. Many of these uncertainties have important effects the accuracy and stability of large-scale systems. It is critical to understand the sources of uncertainty in the model for model verification and validation.

The two main sources of model uncertainties are model inputs and model discrepancy. Model inputs include parameters used to describe the external environment such as boundary conditions, and parameters used in the model such as geometry, initial conditions, physical parameters. The model inputs are not always exactly known because of the difficulty of direct measurements, for example, the precise pore size or the exact surface area of the material. They may be determined in a bound or in a distribution based on measurement. Since the model parameters are impossible to define exactly, they are considered to be random input data in terms of a stochastic vector, θ , belonging to a probability space (Ω, σ, μ) . Model discrepancy exists in the abstractions, simplifications, approximations and assumptions made in the model development of physics, for example, the deviation from the ideal thermodynamics or the material homogeneous assumption. Model discrepancy is usually estimated through the comparison of simulation results with experiment data. Other uncertainties are observation errors and numerical errors. Observation errors are due to the imperfections of experimental systems and measurement errors. Numerical errors are due to roundoff, discretization, approximation errors, bugs and coding errors. If numerical errors are negligible, all epistemic uncertainties are from model discrepancies.

2.5.2 Uncertainty Quantification

The uncertainties analysis at small scale has been studied in many areas through various methods such as polynomial chaos expansion, high-dimensional model representation, intrusive methods and Monto Carlo integration. Model calibration is the process of estimating model inputs based on observations. Uncertainties from inputs are estimated

through the calibration of model results to experimental data. Frequentist and Bayesian techniques have been widely used to quantify the uncertainties associated with inputs based on experiment data. Gaussian Processes and a Bayesian Smoothing Splines Analysis of Variance (BSS-ANOVA) framework have been used to add the model discrepancy into model calibration.

2.5.2.1 Frequentist

Frequentist inference is based on a limiting case of repeated measurements and probability is fundamentally related to the frequency of a real or hypothetical event. Fisher advocated the p-value approach: the probability of observing a more extreme statistic if the null hypothesis were true.[169] Then it was refined to the α approach (The Neyman Pearson Lemma: Consider the test of two simple hypothesis $H_0 : \theta = \theta_0$ and $H_1 : \theta = \theta_1$. Suppose we have a random sample $X_1, X_2, \dots, X_n$ from a probability distribution with parameter θ . Then, if C is a critical region of size α and k is a constant such that: $\frac{L(\theta_0)}{L(\theta_1)} \leq k$ inside the critical region C and $\frac{L(\theta_0)}{L(\theta_1)} \geq k$ outside the critical region C . Then C is the best, that is, most powerful, critical region for testing the simple null hypothesis $H_0 : \theta = \theta_0$ against the simple alternative hypothesis $H_1 : \theta = \theta_1$.) by Neyman and Pearson[170] to test whether the differences in an experiment are sufficient to be unlikely to have happened by mere chance. The level of significance is tested against a null hypothesis. Frequentists used to assign probability to a repeatable event in which the uncertainty is due to randomness or sampling error instead of assigning probability to an event where uncertainty is also due to lack of knowledge.[171]

Maximum likelihood approaches are commonly used by frequentists to obtain the confidence intervals of parameters. Given a set of observation data $D = (x_1, x_2, \dots, x_N)$, the probability of observation i given the parameter θ is $p(x_i|\theta)$. Here, θ is the parameter that we want to estimate. Then the likelihood function can be constructed by computing the

product of the probabilities for each data point:

$$\mathcal{L}(\theta) = \prod_{i=1}^N p(x_i|\theta) \quad (2.16)$$

It is often more convenient to compute this on log scale.

$$\log \mathcal{L}(\theta) = \sum_{i=1}^N \log p(x_i|\theta) \quad (2.17)$$

θ can be determined by solving the equation $d \log \mathcal{L} / d\theta = 0$ so that the likelihood is maximized. It is the estimate of θ based on the observation data. This estimation of a quantity of interest usually is completed by putting a confidence interval (CI) around the value from the sample to infer the corresponding quantity in the population. In a frequentist approach, the parameters are considered to be fixed and probably unknown and the data is random. A frequentist 95% confidence interval for the mean μ means that if the same procedure to obtain confidence intervals was repeated many times, then in 95% of the cases would the mean lie in the 95% confidence interval.[171]. The confidence is in the procedure, not in the interval itself.[172, 173]

The main limitation of standard frequentist inference is that it does not condition on the observations. On the contrary, Bayesian inference does condition on the observations.

2.5.2.2 Bayesian

Bayesian calibration introduced by Kennedy and O'Hagan has been widely used for the calibration and validation of small-scale models as well as making predictions to the large-scale systems. Unlike frequentists in which the probability distribution is deduced from an infinite number of observations, for Bayesians, the probability is related to the knowledge about an event. Data is considered to be fixed and model parameters are random variables. Bayesian inference begins with a prior distribution which incorporates any knowledge about the parameters from previous experiments or analysis. Uncertainty from parameters

is quantified by a probability distribution. Inputs are formulated as random variables with an associated probability distribution. A posterior distribution can be obtained when a finite amount of data is taken into consideration. Bayes' theorem shows the mathematical relationship between the prior, the observations, and the posterior:

$$\mathcal{P}(A|B) = \frac{\mathcal{P}(B|A)\mathcal{P}(A)}{\int_A \mathcal{P}(B|A)\mathcal{P}(A)dA} \quad (2.18)$$

where $\mathcal{P}(A|B)$ is the posterior, the probability of A given information B; $\mathcal{P}(B|A)$ is the probability of observing B given A, called likelihood; $\mathcal{P}(A)$ is the prior probability of A; and the denominator integral is the probability of observing B over all possible values of A, called marginal likelihood or marginal density function of all possible observations.

A Bayesian approach to model calibration was introduced by Kennedy and O'Hagan. The main idea is Equation (2.19), along with the fact that δ is a GP. Posterior distributions of these model parameters that quantifies the uncertainty of θ can be derived using the observed data.[174] The difference between the model output and the data is considered to be the sum of model discrepancy and observation error. The relationship between observations z_i and model output y_i , model discrepancy δ_i and observation error ϵ_i is

$$z_i = y(x_i, \theta) + \delta_i + \epsilon_i \quad (2.19)$$

Bayesian techniques have many advantages over frequentist approaches for parameter estimation and hypothesis testing. They can be used in more complicated models (e.g. hierarchical nonlinear models) and provide practical results (credible region). It conditions on the observed data and does not depend on the data never observed.

2.5.2.3 Gaussian Processes

A Gaussian process is a generalization of Gaussian distribution whose mean function and covariance function is a vector and matrix, respectively. The difference is that Gaussian

process is over functions instead of over vectors. In a Gaussian distribution, every random variable is indexed by their position in the vector. In a Gaussian process (GP), for every input x there is an associated random variable $f(x)$ which is the value of function $f(x)$ at that location.[175] Let f be a GP with mean function m and covariance function c , mapping an input x into an output $y = f(x)$ in R . It can be written as:

$$f \sim GP(m, c) \quad (2.20)$$

f was regarded as an unknown function which becomes a random function in a Bayesian framework. The Gaussian process is a convenient class of distributions to represent prior knowledge about f . [174] f is considered to be a Gaussian process distribution if the joint distribution of $f(x_1), \dots, f(x_n)$ is multivariate normal distribution for all $x_1, \dots, x_n$, where $n = 1, 2, 3, \dots$. Gaussian process is capable of providing a tool to incorporate assumed or known distributions for δ and has been used for the realization of discrepancy function.[174, 164] For model evaluations at n input states $\zeta = [\zeta_1, \dots, \zeta_n]$, model discrepancy term:

$$\delta(\zeta, \mu, \sigma^2, \theta) = [\delta(\zeta_1, \mu, \sigma^2, \theta), \dots, \delta(\zeta_n, \mu, \sigma^2, \theta)]$$

is assumed to be from a multivariate normal distribution. If the δ function is stationary, for any two input states (ζ_i, ζ_j) , the corresponding (δ_i, δ_j) are correlated according to some function of $|\zeta_i - \zeta_j|$:

$$cov(\delta_i, \delta_j) = f(|\zeta_i - \zeta_j|) \quad (2.21)$$

The model discrepancy can be written as a multivariate normally distributed (MVN) random vector by splitting the state point vector ζ into its individual components of input parameters,

$$\delta \sim MVN(0, \Sigma) \quad (2.22)$$

where Σ is the symmetric positive definite covariance matrix with $\Sigma_{ij} = \sigma^2 \exp[-\frac{(\zeta_i - \zeta_j)^2}{\phi^2}]$. The range parameter ϕ controls the extent of the correlation between two points, and σ^2 controls the scale of the variance of the function from its mean.[164]

With the distributions of all the variables in the statistical model defined, the distribution for the experimental observations $\mathcal{Z}$ can be written:

$$\mathcal{Z} \sim MVN(Y(\theta), \Sigma(\beta), \psi I) \quad (2.23)$$

This distribution can be used to assign a probability density which is the likelihood $\mathcal{L}(\mathcal{Z}|\theta, \beta, \psi)$ to the experiment data $\mathcal{Z}$. The computational complexity of $\mathcal{O}(N^3)$ is required to obtain the inversion of the covariance matrix. Therefore, computational limitations will be an issue for the application of Gaussian process in a complex model.

2.5.2.4 The BSS-ANOVA Framework

A Bayesian Smoothing Spline (BSS) ANOVA framework has also been proposed and used to include a discrepancy term from the model to reality in the calibration by Reich *et al.*[176] The BSS-ANOVA framework has several advantages over the traditional Gaussian Process, including ease of handling categorical inputs and correlated outputs, and improved computational efficiency.[177] The discrepancy functions δ can be formulated using the BSS-ANOVA GP model.[176] A covariance function that uses the functional components from a functional ANOVA decomposition is applied.[178, 179] This approach provides a convenient parametric form to reduce the SDE equations to ODE equations, which are easier for calibration and uncertainty propagation. It also improves the computational efficiency by scaling linearly with the number of data points, as opposed to $\mathcal{O}(N^3)$ for a traditional GP [180, 181].

The inputs to the computer model are denoted as ζ with dimension P . The discrep-

ancy may be represented as:

$$\delta(\zeta) = \beta_0 + \sum_{r=1}^R \delta_r(\zeta_r) + \sum_{r < r'}^R \delta_{r,r'}(\zeta_r, \zeta_{r'}) + \dots \quad (2.24)$$

where $\beta_0 \sim N(0, \varsigma_0^2)$, each main effect functional component is $\delta_r \sim GP(0, \varsigma_r^2 K_1)$, $\varsigma_r^2 K_1$ is the covariance function for δ_r , $r = 0, \dots, R$, K_1 is the BSS-ANOVA covariance function described in the BSS-ANOVA covariance function as below [176]:

$$K_1(u, u') = B_1(u)B_1(u') + B_2(u)B_2(u') - \frac{1}{24}B_4(|u - u'|) \quad (2.25)$$

where B_l is the l^{th} Bernoulli polynomial. The parameters and inputs have to be normalized to $[0, 1]$ before they can be used in the analysis because covariance function operates in the domain $[0, 1]$. Two-way interaction functions are assumed to be $\delta_{r,r'} \sim GP(0, \varsigma_r^2 K_2)$, where

$$K_2((u, v), (u', v')) = K_1((u, u'), (v, v')) \quad (2.26)$$

They are just the products of the first-order kernels. In this way, three-way or higher order interaction functional components can be defined. According to ref. [177], the KL decomposition can be applied to each component of δ separately. The constant constant β_0 has one eigenfunction with eigenvalue ς_0^2 . The covariance functions are additive, for example:

$$\varsigma_r^2 K_1(s, t) = \varsigma_r^2 K_{1,1}(s, t) + \varsigma_r^2 K_{1,2}(s, t) + \varsigma_r^2 K_{1,3}(s, t) \quad (2.27)$$

with $K_{1,1}(s, t) = B_1(s)B_1(t)$, $K_{1,2}(s, t) = B_2(s)B_2(t)$, $K_{1,3}(s, t) = -B_4(s)(|s - t|)/4!$, such that

$$\delta_r(t) = X_1(t) + X_2(t) + X_3(t) \quad (2.28)$$

with $X_k(t) \stackrel{iid}{\sim} GP(0, \varsigma_r^2 K_{1,k})$, $k = 1, 2, 3$. The first two terms in Equation (2.27) have the one non-zero eigenvalue, eigenfunction pair (ς_r^2, B_1) and (ς_r^2, B_2) . The number of non-degenerate

eigenvalue, eigenfunction pairs is not finite, but can be approximated with a single eigen-decomposition of the matrix $K_{1,3}$. [177]

Reich, *et al.* have showed that each functional component in (2.24) can be further written as an orthogonal basis expansion [176] like

$$\delta_r(\zeta_r) = \sum_{l=1}^{\infty} \beta_{r,l} \phi_l(\zeta_r), \quad \beta_{r,l} \stackrel{iid}{\sim} \mathcal{N}(0, \tau_r^2) \quad (2.29)$$

τ_r is the typical prior standard deviation of δ_r corresponding to a particular ζ_r^2 . The ϕ_l

Figure 2.18: First nine eigenfunctions from the Karhunen-Loève expansion for a main effect function from the BSS-ANOVA covariance

terms in the expansion are the eigenfunctions in the Karhunen-Loève (KL) expansion. [182, 183] They have increasingly higher frequency and decreasingly less magnitude, as shown in

Figure.2.18.[180] The terms after some value L are less important and can be truncated. It was suggested by Storlie, *et al.* that $L \geq 25$ is more than sufficient for most problems.[177] The decomposition in Equation (2.29) can be used for two-way and higher interactions. The ϕ_l for two-way interactions are the products of the corresponding main effect basis functions and similarly for three-way and higher interactions.[177] In many problems, it is sufficient to include only main effects and two-way interactions. The three-way interactions can be included if any lack of fit is present. Therefore, the overall model in (2.24) becomes:

$$\delta(\zeta) = \sum_{j=1}^J \sum_{l=1}^{L_j^\delta} \beta_{j,l} \phi_{j,l}(\zeta) \quad (2.30)$$

$$\beta_{j,l} \stackrel{iid}{\sim} \mathcal{N}(0, \tau_j^2) \quad (2.31)$$

where j indexes over the J functional components included in the discrepancy realization, and l indexes over the number of basis function L_j^δ used for the j^{th} functional component of the discrepancy representation. The $\beta_{j,l}$, $\phi_{j,l}$, and τ_j would correspond to a particular term in the expansion of (2.29) for the j^{th} functional component.

2.5.3 Uncertainty Propagation

Intrusive, non-intrusive and hybrid are the main approaches used in uncertainty propagation. The propagation of both model inputs uncertainties and model discrepancies are critical to the construction of prediction intervals or pdf for the quantity of interest for large-scale systems. They can be quantified and propagated to a upscale model through a sample-based posterior distribution. A road map of the upscaling methodology presented by Bhat *et al.* is shown in Figure 2.19.[181] The prior distributions of model parameters are from experience or calculations and the prior distribution of model discrepancy is usually a Gaussian process prior. These prior distributions are used to calibrate the small-scale model to experimental data and estimate the unknown parameters and discrepancy. A posterior

Figure 2.19: The upscale methodology diagram. Figure taken from ref. [181].

distribution including model parameters and model discrepancy is produced to propagate to a large-scale process model. A model that quantifies and propagates the uncertainty in upscaling and extrapolation through a “model-plus-discrepancy” approach was proposed by Mebane *et al.*[164]. This approach predicted the experimental data to model simulations that includes the estimated observation error, the model discrepancy, and the growing uncertainty in between data points and unmeasurable conditions. This approach provided a useful metric of uncertainty in a multi-scale system. It also can shift the uncertainty from model parameters to model discrepancy based on the prior information.[164]

An efficient way to propagate forward the uncertainty was introduced and tested by Bhat *et al.*.[181] A dynamic discrepancy approach that includes the discrepancy function within the chemical rate expressions was employed in a small-scale sorbent model that de-

scribes the adsorption of CO₂ by an amine based sorbent. Full details about this model can be found in [164]. A Bayesian approach with prior model parameter distributions from quantum chemistry calculations and prior discrepancy distribution from Gaussian Process was applied to this small-scale model. The posterior distribution π is obtained through simulation using Markov Chain Monte Carlo (MCMC). A number of samples from the posterior distribution were drawn and forward propagated to the large-scale system model by solving a set of differential equations in which dynamic discrepancy $\delta(\beta)$ has been embedded into. The calibration and upscaling with dynamic discrepancy was applied to experimental data (TGA) to predict the capture fraction of CO₂ in a large-scale process model.

2.6 Summary

This chapter provided an overview of the CO₂ capture technologies under development. The development status, influencing factors, CO₂ capture capacity, water effect, advantages, and disadvantages have been analyzed. Two widely investigated mechanisms: the zwitterion mechanism and the termolecular mechanism are introduced as well as the disputes to be answered. Methods of quantum chemistry calculations and uncertainty quantification and propagation have also been introduced.

CHAPTER 3

STABILIZED ZWITTERION MECHANISM

Quantum chemical calculations conducted by Joel Kress at Los Alamos National Laboratory (LANL) revealed that the zwitterion was unstable in both gas phase and polar environment. However, it can be stabilized by water and amine molecules. Hydronium carbamate and ammonium carbamate are produced through water-stabilized and amine stabilized zwitterions, respectively. This chapter introduces the energy states and molecular structures of these chemical species. A new chemical reaction system based on these stabilized zwitterions will also be introduced.

3.1 Quantum Chemical Calculation Results

Gaussian 09[184] using a 6-311+G** basis set and the PBE0 hybrid DFT has been applied to calculate electronic structures. The effect of a slightly polar environment provided by anhydrous PEI, with $\epsilon_r = 2.9$ was introduced by employing the PCM. Vibrational frequencies and zero-point energies (ZPEs) were calculated from the analytical Hessian. The Synchronous Transit-Guided Quasi-Newton method[185, 186] (QST2 and QST3) was employed for searching for the transition state. As required by the QST3 procedure, an initial guess for the transition state structure was constructed from a linear combination of the Cartesian coordinates of the reactants (zwitterion) and products (carbamate) structures. The initial structure guess was visualized in order to ensure there were no issues with steric hindrance and/or overlapping moieties between molecules. Most times this initial guess failed to yield a suitable transition state. Upon failure, the coordinates of the initial guess were modified by slightly changing the bond distances involved in the proton transfer (especially those bonds involved in the ring structures). Upon success, the frequency spectrum

of each transition state was calculated and the structure of the normal mode motion of the imaginary frequency corresponding to the transition state was visualized to ensure that the motion did indeed correspond to the reaction path that was desired. For example, many times the imaginary frequency normal mode corresponded to the torsional barrier of the rotation of one of the methyl groups. In this case, this “transition state” was discarded and another QST calculation was started using a slightly different initial guess for the QST search. Enthalpies of reaction were calculated as $\Delta H = \Delta E + P\Delta V$, where ΔE = electronic energy + ΔZPE + ΔE_{trans} + ΔE_{rot} . The translational ΔE_{trans} and rotational ΔE_{rot} are calculated for the CO_2 gas phase molecule only. Ideal behavior was assumed in this work term, yielding $P\Delta V = \Delta nRT = -RT$. This strategy assumes that ΔE_{trans} and ΔE_{rot} and the non-ZPE contribution to the vibrational ΔE_{vib} are equivalent for reactants and products in the adsorption reactions considered. (This is a good approximation in the limit that each entity is a piece of a long-chain polymer.) The same strategy is also assumed for the contributions to the changes in entropy ΔS . Therefore, ΔS was estimated using only the contributions from the gas phase molecules (either H_2O or CO_2). S_{vib} is negligible relative to S_{trans} and S_{rot} for gas phase molecules.

In ref.[96], the zwitterion was found unstable in both the gas phase and in a slightly polar environment ($\epsilon_r = 2.9$) similar to that of anhydrous PEI for all chemistries investigated (MMA and DMA) at both MP2 and PBE0 levels of theory. For solvation in water ($\epsilon_r = 78$), PBE0 yielded a stable zwitterion for both MMA and DMA. When explicit water molecules were considered, CO_2 binds to either 1) H_2O bound directly to an amine (linear structure) or 2) in a ring structure consisting of CO_2 and H_2O and an amine. The energies of formation in the gas phase were found to be -28 and -47 kJ/mol for the linear and ring topologies, respectively, using the B3LYP hybrid DFT.[157, 162] However, the kinetic study showed that the corresponding activation energy barriers are as high as 300 kJ/mol for carbamate formation, which is not consistent with experimental results. Therefore, searching for alternative intermediates is necessary. Water is known to change the semi-crystalline structure

of aminopolymers, substituting amine-amine hydrogen bonds with amine-water bonds, thus significantly opening up the structure. However, water is also likely to affect the diffusion mechanism for CO₂. This led to the finding that stabilized zwitterion species (zwitterion stabilized by other molecules of amine or H₂O) are better candidates. Another kind of carbamate (hydronium carbamate) which has lower activation energy is formed through this water stabilized zwitterion.

Under anhydrous conditions, the zwitterion can be stabilized by another amine and forms ammonium carbamate as following:

Two amine molecules react with one CO₂ molecule to form an amine zwitterion at the gas-amine interface. It will be consumed to form ammonium carbamate at the surface and after diffusion into the amine bulk. The chemical reaction process and molecular structures are shown in Figure 3.1. The energy of formation of amine-zwitterion is 5 kJ/mol. This positive formation energy implies that it is unstable relative to reactants. The barrier for deprotonation is high because the transition state consists of a four-membered ring where the proton is intermediate between the amine nitrogen and the carbamate oxygen.

Under humid conditions, the zwitterion can be stabilized by water molecules. This water-zwitterion is formed through

Hydronium-carbamate is formed through proton transfer as following:

Figure 3.1: Formation of ammonium carbamate through an amine stabilized zwitterion

The process and molecular structures of hydronium carbamate formation through a water stabilized zwitterions are shown in Figure 3.2. Compared to the anhydrous zwitterion, it has a much lower formation energy (-16 kJ/mol) which means that it is more energetic favorable. Meanwhile, the barrier for deprotonation is much lower than in anhydrous conditions because the transition state consists of a water molecule that actively participates in a six-membered ring in the bond breaking and making for proton transfer.

Figure 3.3 depicts the formation process of bicarbonate in reaction (2.15). The concentration of bicarbonate will be much smaller than hydronium carbamate and ammonium carbamate due to the weak energy of formation (-1 kJ/mol). The activation energy barrier in the formation of bicarbonate is also higher than hydronium carbamate. It indicates that it is appropriate to take bicarbonate as a minor product.

Figure 3.4 depicts the energy states of species in all three reactions. The formation reaction of ammonium carbamate, hydronium carbamate and bicarbonate are marked as 1, 2 and 3, respectively, and indicated by different colors.

Figure 3.2: Formation of ammonium carbamate through a water stabilized zwitterion.

Figure 3.3: Formation of bicarbonate through a water stabilized zwitterion.

Figure 3.4: Energetic diagram of ammonium carbamate (1, blue), hydronium carbamate (2, red) and bicarbonate (3, magenta) reactions. Figure taken from [187]

From the results of quantum chemistry calculations, we know that the zwitterion can be stabilized by water molecules as well as other amines in the sorbents. And the formation of hydronium carbamate is more favorable than ammonium carbamate under humid conditions. The concentration of bicarbonate formed is so small compared to the carbamates that we can ignore it. Then, we can build a chemistry model in which the formation of ammonium carbamate and hydronium carbamate are included.

3.2 Chemical Reaction System

A quantitative reaction-diffusion model was built based on the quantum chemistry results. Flue gases will contact and react with the free amines at the gas-amine interface,

form the diffusive intermediates that can be transported into the amine bulk and finally form carbamates. According to above analysis, the reaction system can be written as following:

Reaction (3.1) is the formation of a zwitterion under anhydrous conditions. It turns to an ammonium-carbamate pair as shown in reaction (3.2) at the surface or after diffusing into the amine bulk. When water exists in the flue gas, it can react with free amine sites at the surface to form bonded amine-water species (physically bonded), which can diffuse into the bulk. At the interface, this amine-water species will react with gas-phase CO_2 to form the new zwitterion stabilized by water as shown in reaction (3.4). This zwitterion turns to hydronium-carbamate at the surface or after diffusing into the bulk as the reaction (3.5). These three kinds of diffusive intermediates are denoted as z_1 , z_2 , z_3 , respectively. These variables are a part of the model derivation. Reactions (3.1), (3.3) and (3.4) are only occurring at the amine-gas interface and reach equilibrium fast. Reactions (3.2) and (3.5) can occur both at the surface and in the bulk.

CHAPTER 4

MODEL DEVELOPMENT

The mathematical implementation, calibration methods, uncertainty quantification approach, reduced-order model, process model and experimental method used in this study will be introduced in this chapter. A multi-scale microstructure model that splits the pores into three scales was adopted to the implementation of the mathematical model. Bayesian calibration with a dynamic discrepancy approach in the BSS-ANOVA framework was used to calibrate this reaction-diffusion model to experimental data. A reduced-order model was built to decrease the computation time of calibration. Markov Chain Monte Carlo sampling was used to obtain a joint sample-based posterior distribution of model parameters and discrepancy. Samples from the posterior distribution were incorporated into a process model which was developed based on Aspen Custom Modeler. Experimental data was obtained from a set of experiments conducted by National Energy Technology Laboratory (NETL) using branched PEI-impregnated silica.

4.1 Multiscale Microstructure Model

In the silica xerogels, a hierarchical pore structure with bimodal pore size distribution has been recognized through SEM images, nitrogen adsorption analyses, and porosimetry experiments.[188, 189, 190, 191]. A two-layer model has been proposed by Wang and Song, in which the PEI domain is separated into an exposed PEI layer that is accessible to gas and an inner bulky PEI layer that accessible through diffusion.[192] A multi-scale model that separates the sorbent into three length scales has been developed by Mebane and colleagues.[193] The illustration of the three length scales can be seen in Figure 4.1. It is convenient to study the reaction and diffusion process in these three different scale regions. CO_2 can move

Figure 4.1: Illustration of the three length scales of the microstructural model: (1) macroporosity (2) mesoporous particles and (3) silica-PEI composite. Figure taken from [193]

very fast in the largest scale region via gas-phase. Gas movement is limited by Knudsen diffusion in the intermediate length scale – mesoporous regions. Within the mesoporous regions, CO_2 can diffuse in the gas phase or be adsorbed at the amine surface. The intermediate scale can be viewed as quasi-spherical [189, 190] and spheres are commonly used for modeling. The smallest length scale is the smaller regions within the mesoporous areas that are completely filled with PEI and silica. The length scale of these regions depends on the remaining mesoporosity after polymer impregnation. Compared to the gas-phase diffusion, Knudsen diffusion is a slower process. However, it is still much faster than the solid-state diffusion process which is considered as the rate-limiting process. The reactions of CO_2 with free amine sites at the surface will achieve equilibrium after several minutes along with the continuous inflowing of CO_2 . [128, 194, 98] Therefore, the transport of CO_2 into the amine bulk at the smallest length scale is the key limiting factor for the sorbent capacity. In this study, the focus will be put on the diffusion and reaction in the amine bulk.

4.2 Reaction - Diffusion Model

Assuming a homogeneous environment of active amine for the adsorption of CO_2 and H_2O , the entire system follows ideal gas thermodynamics. We will take the reactions along the streamline as homogenous because the gases flow in at constant rates, although the gas concentrations will drop along the streamline as the gases flowing through and reacting with the amine sites at the interface under intermediate length scale. Equations (3.1), (3.3) and

(3.4) remain equilibrium. The surface site fractions of these three diffusive intermediates are:

$$z_{1_s} = \kappa_{3.1} P_{\text{CO}_2} S_s^2 \quad (4.1)$$

$$z_{2_s} = \kappa_{3.3} P_{\text{H}_2\text{O}} S_s \quad (4.2)$$

$$z_{3_s} = \kappa_{3.4} P_{\text{CO}_2} z_{2_s} \quad (4.3)$$

where P_{CO_2} and $P_{\text{H}_2\text{O}}$ are the partial pressures of CO_2 and H_2O in the flue gases; $\kappa_{3.1}$, $\kappa_{3.3}$, $\kappa_{3.4}$ are the equilibrium constants of Equations (3.1), (3.3) and (3.4), respectively. S is the free amine site fraction. The subscript “s” denotes the value at the gas-amine interface.

The formation rates of ammonium carbamates and hydronium carbamates are:

$$\frac{\partial x}{\partial t} = k_{3.2} z_1 - k_{-3.2} x^2 \quad (4.4)$$

$$\frac{\partial y}{\partial t} = k_{3.5} z_3 - k_{-3.5} y \quad (4.5)$$

where x and y represent the ammonium carbamate and hydronium carbamate, respectively. $k_{3.2}$, $k_{3.5}$, $k_{-3.2}$, $k_{-3.5}$ are the forward and backward reaction rates of (3.2), and (3.5) and $\kappa = k_f/k_r$. Equilibrium and rate constants are calculated as:

$$\kappa_i = \exp\left(\frac{\Delta S_i}{R}\right) \exp\left(\frac{-\Delta H_i}{RT}\right) / P \quad (4.6)$$

$$k_i = \gamma \exp\left(\frac{-\Delta E_i}{RT}\right) \quad (4.7)$$

where γ is a model parameter that depends on the temperature.

Based on the assumption of ideality, the mechanism for diffusion of CO_2 in immobilized amine bulk phase leads to the motion of these diffusive intermediates. The CO_2 group in z_1 and the H_2O group in z_2 can hop from one amine to the next and the CO_2 group in z_3

can hop from one z_2 to the next. Their diffusive fluxes are:

$$\bar{N}_{b_1} = -\frac{\epsilon_3}{\tau_3} n_v z_1 (1 - 2x_1 - y - z_1 - z_2 - z_3) u_{b_1}^* \nabla_3 \mu_{z_1} \quad (4.8)$$

$$\bar{N}_{b_2} = -\frac{\epsilon_3}{\tau_3} n_v z_2 (1 - 2x_1 - y - z_1 - z_2 - z_3) u_{b_2}^* \nabla_3 \mu_{z_2} \quad (4.9)$$

$$\bar{N}_{b_3} = -\frac{\epsilon_3}{\tau_3} n_v z_3 z_2 u_{b_3}^* \nabla_3 \mu_{z_3} \quad (4.10)$$

where $u_b^* = \zeta_b \exp\left(\frac{-\Delta H_b^\ddagger}{RT}\right)/T$, ζ_b is a factor depending on the average geometry surrounding the diffusing species and the frequency of collisions with other amine sites, and $\Delta H_b^\ddagger$ is the free energy barrier for the hopping of a CO_2 group from one amine site to the next. μ_{z_1} , μ_{z_2} , μ_{z_3} are the chemical potential of diffusive intermediates:

$$\mu_{z_1} = \mu_{z_1}^0 + RT \log \left(\frac{z_1}{1 - 2x - y - z_1 - z_2 - z_3} \right) \quad (4.11)$$

$$\mu_{z_2} = \mu_{z_2}^0 + RT \log \left(\frac{z_2}{1 - 2x - y - z_1 - z_2 - z_3} \right) \quad (4.12)$$

$$\mu_{z_3} = \mu_{z_3}^0 + RT \log \left(\frac{z_3}{1 - 2x - y - z_1 - z_2 - z_3} \right) \quad (4.13)$$

This leads to

$$\begin{aligned} \bar{N}_{b_1} = & -\frac{\epsilon_3}{\tau_3} RT n_v u_{b_1}^* \left[(1 - 2x - y - z_2 - z_3) \nabla_3 z_1 \right. \\ & \left. + z_1 \nabla_3 (2x + y + z_2 + z_3) \right] \end{aligned} \quad (4.14)$$

$$\begin{aligned} \bar{N}_{b_2} = & -\frac{\epsilon_3}{\tau_3} RT n_v u_{b_2}^* \left[(1 - 2x - y - z_1 - z_3) \nabla_3 z_2 \right. \\ & \left. + z_2 \nabla_3 (2x + y + z_1 + z_3) \right] \end{aligned} \quad (4.15)$$

$$\begin{aligned} \bar{N}_{b_3} = & -\frac{\epsilon_3}{\tau_3} RT n_v u_{b_3}^* \left[z_2 \nabla_3 z_3 \right. \\ & \left. + \frac{z_2 z_3}{1 - 2x - y - z_1 - z_2 - z_3} \nabla_3 (2x + y + z_1 + z_2) \right] \end{aligned} \quad (4.16)$$

According to the mass conservation, the change of intermediates in each control volume equals the influx minus the outflux and plus the source. This leads to the final mass balance

equations at the smallest length scale:

$$n_v \epsilon_3 \frac{\partial z_1}{\partial t} = \frac{\epsilon_3}{\tau_3} RT n_v u_{b_1}^* \nabla_3 \cdot \left[(1 - 2x - y - z_2 - z_3) \nabla_3 z_1 + z_1 \nabla_3 (2x + y + z_2 + z_3) \right] - n_v \frac{\partial x}{\partial t} \quad (4.17)$$

$$n_v \epsilon_3 \frac{\partial z_2}{\partial t} = \frac{\epsilon_3}{\tau_3} RT n_v u_{b_2}^* \nabla_3 \cdot \left[(1 - 2x - y - z_1 - z_3) \nabla_3 z_2 + z_2 \nabla_3 (2x + y + z_1 + z_3) \right] \quad (4.18)$$

$$n_v \epsilon_3 \frac{\partial z_3}{\partial t} = \frac{\epsilon_3}{\tau_3} RT n_v u_{b_3}^* \nabla_3 \cdot \left[z_2 \nabla_3 z_3 + \frac{z_2 z_3}{1 - 2x - y - z_1 - z_2 - z_3} \nabla_3 (2x + y + z_1 + z_2) \right] - n_v \frac{\partial y}{\partial t} \quad (4.19)$$

The model was solved numerically using a finite volume scheme in space and a Crank-Nicolson approach in time. n and $n+1$ are used to denote the old time level and the new time level. Iteration is used to get the converged solution at level $n+1$. l and $l+1$ are denoted as the last iteration and current iteration, respectively. The solution of $n+1$ iteration is calculated from the old time level and l iteration. Once solution at $l+1$ iteration converges, it will be used as the solution at time level $n+1$. The species concentrations of intermediates and products are calculated in control volumes at every time step. Subscript i denotes the i^{th} control volume. The difference equations of concentrations of ammonium carbamate and hydronium carbamate are as follows:

$$\frac{x_i^{l+1} - x_i^n}{\Delta t} = \frac{1}{2} [k_{3.2} z_{1,i}^n - k_{-3.2} x_i^{n2}] + \frac{1}{2} [k_{3.2} z_{1,i}^l - k_{-3.2} x_i^{l+12}] \quad (4.20)$$

$$\frac{y_i^{l+1} - y_i^n}{\Delta t} = \frac{1}{2} [k_{3.5} z_{3,i}^n - k_{-3.5} y_i^n] + \frac{1}{2} [k_{3.5} z_{3,i}^l - k_{-3.5} y_i^{l+1}] \quad (4.21)$$

The solutions of x and y in i^{th} control volume depend on the values of all other variables in that control volume, the information from the last time step and the last iteration. The difference equations of concentrations of three intermediates after amalgamation are as fol-

lowing:

$$\begin{aligned}
\frac{z_{1,i}^{l+1} - z_{1,i}^n}{\Delta t} &= \frac{3RTu_{b(1)}^*}{2\tau_3\Delta r_i(r_i^3 - r_{i+1}^3)} [r_i^2(1 - 2x_i^l - y_i^l - z_{2,i}^l - z_{3,i}^l)z_{1,i-1}^{l+1} \\
&\quad + (-r_i^2(1 - 2x_{i-1}^l - y_{i-1}^l - z_{2,i-1}^l - z_{3,i-1}^l) \\
&\quad - r_{i+1}^2(1 - 2x_{i+1}^l - y_{i+1}^l - z_{2,i+1}^l - z_{3,i+1}^l))z_{1,i}^{l+1} \\
&\quad + r_{i+1}^2(1 - 2x_i^l - y_i^l - z_{2,i}^l - z_{3,i}^l)z_{1,i+1}^{l+1}] \\
&\quad + \frac{3RTu_{b(1)}^*}{2\tau_3\Delta r_i(r_i^3 - r_{i+1}^3)} [r_i^2(1 - 2x_i^n - y_i^n - z_{2,i}^n - z_{3,i}^n)z_{1,i-1}^n \\
&\quad + (-r_i^2(1 - 2x_{i-1}^n - y_{i-1}^n - z_{2,i-1}^n - z_{3,i-1}^n) \\
&\quad - r_{i+1}^2(1 - 2x_{i+1}^n - y_{i+1}^n - z_{2,i+1}^n - z_{3,i+1}^n))z_{1,i}^n \\
&\quad + r_{i+1}^2(1 - 2x_i^n - y_i^n - z_{2,i}^n - z_{3,i}^n)z_{1,i+1}^n] \\
&\quad - \frac{1}{2}[k_{3.2}z_{1,i}^l - k_{-3.2}x_i^{l+1}] - \frac{1}{2}[k_{3.2}z_{1,i}^n - k_{-3.2}x_i^n]
\end{aligned} \tag{4.22}$$

$$\begin{aligned}
\frac{z_{2,i}^{l+1} - z_{2,i}^n}{\Delta t} &= \frac{3RTu_{b(2)}^*}{2\tau_3\Delta r_i(r_i^3 - r_{i+1}^3)} [r_i^2(1 - 2x_i^l - y_i^l - z_{1,i}^l - z_{3,i}^l)z_{2,i-1}^{l+1} \\
&\quad + (-r_i^2(1 - 2x_{i-1}^l - y_{i-1}^l - z_{1,i-1}^l - z_{3,i-1}^l) \\
&\quad - r_{i+1}^2(1 - 2x_{i+1}^l - y_{i+1}^l - z_{1,i+1}^l - z_{3,i+1}^l))z_{2,i}^{l+1} \\
&\quad + r_{i+1}^2(1 - 2x_i^l - y_i^l - z_{1,i}^l - z_{3,i}^l)z_{2,i+1}^{l+1}] \\
&\quad + \frac{3RTu_{b(2)}^*}{2\tau_3\Delta r_i(r_i^3 - r_{i+1}^3)} [r_i^2(1 - 2x_i^n - y_i^n - z_{1,i}^n - z_{3,i}^n)z_{2,i-1}^n \\
&\quad + (-r_i^2(1 - 2x_{i-1}^n - y_{i-1}^n - z_{1,i-1}^n - z_{3,i-1}^n) \\
&\quad - r_{i+1}^2(1 - 2x_{i+1}^n - y_{i+1}^n - z_{1,i+1}^n - z_{3,i+1}^n))z_{2,i}^n \\
&\quad + r_{i+1}^2(1 - 2x_i^n - y_i^n - z_{1,i}^n - z_{3,i}^n)z_{2,i+1}^n]
\end{aligned} \tag{4.23}$$

$$\begin{aligned}
\frac{z_{3,i}^{l+1} - z_{3,i}^n}{\Delta t} = & \frac{3RTu_{b(2)}^*}{2\tau_3\Delta r_i(r_i^3 - r_{i+1}^3)} [r_i^2 z_{2,i}^l z_{3,i-1}^{l+1} \\
& + (-r_i^2 z_{2,i-1}^l - r_{i+1}^2 z_{2,i+1}^l) z_{3,i}^{l+1} + r_{i+1}^2 z_{2,i}^l z_{3,i+1}^{l+1}] \\
& + \frac{3RTu_{b(2)}^*}{2\tau_3\Delta r_i(r_i^3 - r_{i+1}^3)} [r_i^2 z_{2,i}^n z_{3,i-1}^n \\
& + (-r_i^2 z_{2,i-1}^n - r_{i+1}^2 z_{2,i+1}^n) z_{3,i}^n + r_{i+1}^2 z_{2,i}^n z_{3,i+1}^n] \\
& - \frac{1}{2} [k_{3.5} z_{3,i}^l - k_{-3.5} y_i^{l+1}] - \frac{1}{2} [k_{3.5} z_{3,i}^n - k_{-3.5} y_i^n]
\end{aligned} \tag{4.24}$$

Except for the information on the last time step and the last iteration, the solution of z_1 , z_2 and z_3 in i^{th} control volume under the current iteration depends on the variables at $(i-1)^{th}$, i^{th} and $(i+1)^{th}$ control volumes. Therefore, they can be solved by a tri-diagonal matrix solver.

Simulated TGA curves were derived from the model solution using the formula

$$w_{CO_2} = M_{CO_2} n_v (\bar{x} + \bar{y} + \bar{z}_1 + \bar{z}_3) / \rho \tag{4.25}$$

$$w_{H_2O} = M_{H_2O} n_v (\bar{y} + \bar{z}_2) / \rho \tag{4.26}$$

where w is the weight fraction appearing in the normalized TGA output, M_{CO_2} is the molecular weight of CO_2 , M_{H_2O} is the molecular weight of H_2O , ρ is the density of the sorbent, and $\bar{x}$ and $\bar{y}$ are the average site fractions of carbamic acid and hydronium carbamate; $\bar{z}_1$, $\bar{z}_2$, $\bar{z}_3$ are amine stabilized zwitterions, water bonded amines and water stabilized zwitterions in the sorbent, respectively.

4.3 Model Parameters

In this chemistry model, there are 23 parameters related to the adsorption process including microstructural parameters, material properties, thermodynamic parameters, kinetic parameters and transport parameters. The solid fraction ϵ_3 can be estimated from residual porosity measurements. Here we use $\epsilon_3 = 0.5$ which is based on the loading of

sorbent substrate. The parameters τ_3 , polymer-phase tortuosity, on the other hand, characterize the relevant microstructure and the difference in transport modes between that of a sphere and the actual microstructure-averaged geometry. If the microstructure-averaged shape is spherical, then τ_3 is a constant. We use estimation value of $\tau_3 = 4$ in this model. The volumetric density n_v of adsorption sites in PEI is included in the study due to the uncertainty about the density of immobilized PEI as well as the extent of association between amine sites and the substrate. R_3 is the radius of pores at the smallest length scale. The number of sites per unit area of gas-PEI interface is $n_s = f(n_v)^{2/3}/N_a^{1/3}$, where f is an estimated parameter and N_a Avogadro's number. The thermodynamic parameters are the enthalpies $\Delta H_{3.1}$, $\Delta H_{3.2}$, $\Delta H_{3.3}$, $\Delta H_{3.4}$, $\Delta H_{3.5}$ and vibrational entropies $\Delta S_{3.1}$, $\Delta S_{3.2}$, $\Delta S_{3.3}$, $\Delta S_{3.4}$, $\Delta S_{3.5}$ associated with reactions (3.1), (3.2), (3.3), (3.4), and (3.5), respectively. The kinetic parameters are the activation enthalpies $\Delta H_{3.2}^\ddagger$ and $\Delta H_{3.5}^\ddagger$, and preexponential factors $\gamma_{3.2}$ and $\gamma_{3.5}$ (parameters which include the activation entropy) of the backward reaction rate constants $k_{-3.2}$ and $k_{-3.5}$. There are two transport parameters associated with the mobility of CO_2 and H_2O for each intermediate in bulk PEI: the preexponential factor and activation energy, $\zeta_{b_1}^*$ and $\Delta H_{b_1}^\ddagger$ for the mobility $u_{b_1}^*$; $\zeta_{b_2}^*$ and $\Delta H_{b_2}^\ddagger$ for the mobility $u_{b_2}^*$; $\zeta_{b_3}^*$ and $\Delta H_{b_3}^\ddagger$ for the mobility $u_{b_3}^*$.

The parameter values calculated by quantum chemistry by Joel Kress from LANL and the values used in the simulation are listed in Table 4.1. These values were used to validate this model against the data in literature and the data we have.

Table 4.1: Model Parameter Values Used in Simulation and Calculated from Quantum Chemistry by Joel Kress at LANL.

Parameters	Value used in model	Value calculated from QC
R_3 (nm)	70	—
n_s (* 10^{-7})	40	—
n_v (mol/m ³)	8000	—
$\Delta H_{3.1}$ (kJ/mol)	−4.5	+5
$\Delta S_{3.1}$ [J/(mol K)]	−167	−190
$\Delta H_{3.2}$ (kJ/mol)	−74	−75
$\Delta S_{3.2}$ [J/(mol K)]	−35	−10
$\Delta H_{3.2}^\ddagger$ (kJ/mol)	105	120
$\log_{10}(\gamma_{3.2})$	13.0	13.0
$\Delta H_{3.3}$ (kJ/mol)	−69	−35
$\Delta S_{3.3}$ [J/(mol K)]	−191	−195
$\Delta H_{3.4}$ (kJ/mol)	−29	−16
$\Delta S_{3.4}$ [J/(mol K)]	−218	−200
$\Delta H_{3.5}$ (kJ/mol)	−64	−42
$\Delta S_{3.5}$ [J/(mol K)]	−25	−10
$\Delta H_{3.5}^\ddagger$ (kJ/mol)	88	63
$\log_{10}(\gamma_{3.5})$	12.8	13
$\Delta H_{b_1}^\ddagger$ (kJ/mol)	36	—
$\log_{10}(\zeta_{b_1})$	−7.4	—
$\Delta H_{b_2}^\ddagger$ (kJ/mol)	30	—
$\log_{10}(\zeta_{b_2})$	−2.5	—
$\Delta H_{b_3}^\ddagger$ (kJ/mol)	45	—
$\log_{10}(\zeta_{b_3})$	−3.2	—

4.4 Bayesian Calibration

Bayesian calibration was used to calibrate the simulation results from this reaction-diffusion model to the experimental data based on the priors from quantum chemistry calculations. Set experimental data as $y = [y_1, y_2, \dots, y_N]$, model output as $\eta(\theta, \delta) = [\eta_1(\theta, \delta), \dots, \eta_N(\theta, \delta)]$, input vectors as $\zeta = [\zeta_1, \zeta_2, \dots, \zeta_P]$, model parameters as $\theta = [\theta_1, \theta_2, \dots, \theta_q]$, discrepancy as $\delta = [\delta_1(\zeta), \dots, \delta_M(\zeta)]$, and observation errors as $\epsilon = (\epsilon_1, \epsilon_2, \dots, \epsilon_N)^T$. A Bayesian calibration framework can be expressed as a stochastic model:

$$y = \eta(\theta, \delta; \zeta) + \epsilon(\psi) \quad (4.27)$$

where $\epsilon \sim N(0, \sigma^2 I_N)$, a normal distribution with variance σ^2 . BSS-ANOVA framework was used to represent the model discrepancy δ as a function of ζ and β as shown in Equation (2.29).

β - the parameters of the model discrepancy δ , and ψ - the parameters of the observation error were included in both the prior and the posterior distributions. According to [164], when the experimental data y is considered to be a realization of this stochastic process, to which a probability (or likelihood) can be assigned given the parameters θ , β and ψ , then the Equation (2.18) can be rewritten as:

$$\Omega(\theta, \beta, \psi|y) = \frac{1}{Q} \mathcal{L}(y|\theta, \beta, \psi) \pi(\theta, \beta, \psi) \quad (4.28)$$

$\Omega(\theta, \beta, \psi|y)$ is the posterior distribution we desire to obtain. $\pi(\theta, \beta, \psi)$ is the prior distribution that provides the initial probability of observing the given set of discrepancy and physical parameters. Prior distributions were assigned to all model parameters based on the information from quantum chemical calculations and previous scientific studies. The priors of discrepancy parameters are zero and have a unlimited range. They were not assigned based on science because of lacking information about the model discrepancy. However, they will be updated based on the accepted samples during the calibration. $\mathcal{L}$ is the likelihood that

provides the probability of observing the realistic data given the current set of parameters. It is normalized by integrating over all possible values, represented by Q .

$$Q = \int \mathcal{L}(y|\theta', \beta', \psi') \pi(\theta', \beta', \psi') d\theta' d\beta' d\psi' \quad (4.29)$$

Evaluating the integral Q is so difficult that a full posterior distribution is impossible to be expressed in closed form. Therefore, a numerical simulation must be applied to obtain samples from the posterior. Monte Carlo sampling is a good approach to obtain such samples. Model inputs are randomly drawn from their distributions in Monte Carlo routine and then the model is solved for each sample input. The resulting set of model outputs is a random sample from the overall output distribution and can be converted into an empirical probability density function.

θ , δ and σ^2 are the parameters that need to be estimated in order to obtain the full posterior distribution. Markov Chain Monte Carlo sampling was used to obtain the posterior distributions of model parameters and model discrepancy. In each iteration, a set of model parameters θ and model discrepancy parameters β was first proposed, the model was solved using these parameters, the likelihood was evaluated, and the proposal was either accepted or rejected. Then, the observation error σ^2 was proposed based on the difference between model output and experiment data.

Our MCMC routine specially equipped for calibration with BSS-ANOVA GPs is obtained from Sham Bhat from LANL. It is a hybrid sampling of scheme of Metropolis Hastings (MH) and Gibbs updates. Metropolis-Hastings sampling was used for the update of model parameters θ and β , and Gibbs sampling was used to update observation errors σ^2 and τ_r^2 . For θ , block updating were used to propose related parameters, for example, the enthalpy and entropy of formation. The number of model evaluation can be reduced in this way. For β , all the coefficients for each main effect and second order interaction coefficients were updated simultaneously. The covariance was computed every K steps and updated based

on the accept rate of each parameter. Gibbs updates were used to update τ_r^2 and σ^2 . A set of τ_r^2 (prior variance of δ_r) was then proposed based on the values of β . A new block proposal method and adaptive sampler has been added into this routine in order to improve the computational efficiency and convergence speed. After a sufficient number of iterations, the sample of θ and β will converge to a stationary distribution which is the posterior distribution. Eventually, a joint posterior distribution of the model parameters and discrepancy parameters can be acquired.

4.4.1 Markov Chain Monte Carlo (MCMC) Sampling

MCMC is essentially Monte Carlo integration using Markov chains to draw samples. It provides a Markov chain of values that contains a sample of draws from the posterior. According to Gilks, *et al.*, [195] Monte Carlo integration estimates the population means through sample mean by drawing samples $\{X_i, i = 1, \dots, N\}$ from distribution $\pi(\cdot)$ and then approximating

$$E[f(X)] \approx \frac{1}{N} \sum_{t=1}^N f(X_t) \quad (4.30)$$

X is usually a vector with fixed length p , for example $X = (x_1, x_2, \dots, x_q)$. The update of X includes the update of all the elements of vector X . This approximation can be accurate if X_i is independent and sample number N is sufficiently large. Samples $\{X_i\}$ can be generated by any process and do not have to be independent. A Markov chain is a method of drawing samples from a stationary distribution. Suppose a sequence of random variables, $\{X_0, X_1, \dots\}$ is generated so that at each time $t \geq 0$, the next state X_{t+1} is sampled from a distribution $P(X_{t+1}|X_t)$ that only depends on the current state of the chain X_t . In other words, given X_t , the next state X_{t+1} does not depend on the history of the chain $\{X_0, X_1, \dots, X_{t-1}\}$. This sequence is called a Markov chain and $P(\cdot|\cdot)$ is called the transition kernel of the chain. [195] The chain will finally converge to a unique stationary distribution $\phi(\cdot)$ that does not depend on time t or initial state X_0 . As time increases, the sampled points X_t will be very close to the

samples from this stationary distribution $\phi(\cdot)$. Therefore, after sufficient burn-in iterations, say m , points $\{X_t; t = m + 1, \dots, N\}$ will be samples approximately from $\phi(\cdot)$. [195] Then any desired expectation can be estimated by ergodic averages from Markov chain. For example, after discarding the burn-in samples, $E[f(X)]$ can be calculated from:

$$\overline{E[f(X)]} \approx \frac{1}{N - m} \sum_{t=m+1}^N f(X_t) \quad (4.31)$$

where X has the distribution $\phi(\cdot)$.

The length of burn-in m depends on the initial point, rate of convergence and other factors. There is no standard for the choice of m . Visual inspection by plotting the MCMC output is the most obvious and common way to determine m . Various convergence diagnostics methods have also been proposed and used to determine m . The posterior distribution obtained from MCMC output can be analyzed in terms of mean, standard deviation, correlations and credible regions of the quantity of interest.

Markov chain needs to be well constructed so that its stationary distribution is exactly the distribution of interest $\phi(\cdot)$. [195] The Metropolis-Hasting algorithm, which is proposed by Metropolis and then developed by Hastings, is a simple and efficient algorithm to construct the Markov chain.

4.4.2 Metropolis-Hastings Sampling

In Metropolis-Hasting algorithm, at each time t , the next state X_{t+1} is chosen by sampling a candidate point Y from a proposal distribution $q(\cdot|X_t)$. This proposed distribution can be any form and may depend on the current point X_t . [195] Thus, X_{t+1} will be also from $\phi(\cdot)$ if X_t is. The Metropolis-Hastings algorithm has transition kernel density as:

$$K(X, Y) = q(X, Y)\alpha(X, Y) \quad (4.32)$$

where $q(\cdot|X_t)$ may be a multivariate normal distribution with mean X and a fixed covariance matrix. And $\alpha(X_t, Y)$ is the probability for Y is accepted from X .

$$\alpha(X, Y) = \min\left(1, \frac{\pi(Y)q(X|Y)}{\pi(X)q(Y|X)}\right) \quad (4.33)$$

If the candidate point is accepted, the new state becomes Y ; if it is rejected, the chain does not move as X . [195] Thus the Metropolis-Hastings algorithm is as following:

Table 4.2: Metropolis-Hastings Algorithm

Initialize $t = 0, X_0 \sim q(\cdot)$ (prior distribution)
for $t = 1, 2, \dots$ do
Propose: X_{prop} from $q(\cdot X_t)$
Acceptance Probability:
$\alpha(X_{prop} X_t) = \min\left(1, \frac{\pi(X_{prop})q(X_t X_{prop})}{\pi(X_t)q(X_{prop} X_t)}\right)$
Propose: $u \sim Uniform(u; 0, 1)$
If $u \leq \alpha(X_{prop} X_t)$ then
Accept the proposal: $X_{t+1} \leftarrow X_{prop}$
else
Reject the proposal: $X_{t+1} \leftarrow X_t$
end if
end for

Although any form of proposal distribution $q(\cdot|\cdot)$ will ultimately propose samples from the population distribution $\pi(\cdot)$, the rate of convergence to the stationary distribution will strongly depend on how close they are. Therefore, the choice of proposal distribution must be made carefully. A proposal distribution that generates small steps will have a high acceptance rate but is a slow moving chain. One that generates large steps will propose new states from lower bound to upper bound, giving small values of $\pi(Y)/\pi(X_t)$ and a low

acceptance rate. Both cases will require much longer time to obtain reliable samples from a target distribution $\pi(\cdot)$ and need to be avoided.

X can be updated by block proposal (propose all the elements of X at the same time) or single proposal (one by one). Block updating the whole X using joint proposals requires only one judgment for accepting or rejecting the sample, which will reduce the number of model evaluations needed. It will significantly decrease the overall computational time for the MCMC procedure when the model is complex and model evaluation is time consuming. However, the acceptance rate will be low when the dimension of X is high. Single component Metropolis-Hastings which divides $\{X\}$ into components $\{X_1, X_2, \dots, X_s\}$ with possibly different dimensions and then updates these components one by one was originally proposed by Metropolis and has been used in many cases. This approach is very convenient and efficient when the model is simple and easy to solve.

In this study, Metropolis-Hastings was used for the update of model parameters θ_q and discrepancy term β . There are 23 “theta parameters” ($\theta_1, \theta_2, \dots, \theta_{23}$) in this reaction-diffusion model. Block proposal was used to update all the parameters at once. Multivariate normal distributions were used as the proposal distribution. A random vector was drawn from the multivariate normal distribution with a mean vector $\bar{\theta} = [\bar{\theta}_1, \dots, \bar{\theta}_{23}]$ and covariance matrix

$$V = \begin{bmatrix} \text{var}(\theta_1) & \text{cov}(\theta_1, \theta_2) & \dots & \text{cov}(\theta_1, \theta_{23}) \\ \text{cov}(\theta_2, \theta_1) & \text{var}(\theta_2) & \dots & \text{cov}(\theta_2, \theta_{23}) \\ \vdots & \vdots & \ddots & \vdots \\ \text{cov}(\theta_{23}, \theta_1) & \text{cov}(\theta_{23}, \theta_2) & \dots & \text{var}(\theta_{23}) \end{bmatrix}$$

Where $\text{var}(X) = \text{cov}(X) = E[(X - E[X])(X - E[X])^T]$ and $\text{cov}(X, Y) = \text{cov}(Y, X) = E[(X - E[X])(Y - E[Y])^T]$. An adaptive sampler was used to update the covariance matrix based on accepted proposals. The related covariance matrix was initialized and recalculated every 1000 thousand of MCMC steps based on last 2000 samples (except the first time). It then was used to be the proposal covariance matrix for the next 1000 proposals. The

number of steps for recalculating the covariance matrix can be adjusted according to the accept rate. After burn-in, the covariance matrix was fixed and used for the rest MCMC steps as the proposal. As implemented by Sham Bhat at LANL, the β parameters including all the main effect and second order interaction coefficients are updated simultaneously using a multivariate normal proposal. The basis functions are used to calculate a covariance for the block update for each discrepancy function.

4.4.3 Gibbs Sampling

After introduced by Geman and Geman in 1984,[196] Gibbs sampling has been used in Bayesian statistics as a basis MCMC method.[197, 198] It is a special case of Metropolis-Hastings algorithm that is useful when it is not convenient to sample from a multivariate posterior. Gibbs sampling is only possible when an analytical solution is available for the conditional posterior. We can get one of those for the observation error variance if we use a conjugate prior, which is Inverse Gamma. Gibbs sampling generates samples by sweeping through every variable (or block of variables) to sample from its conditional distribution with the rest of the variables unchanged. For instance, X contains random variables $\{x_1, x_2, \dots, x_P\}$, then the algorithms of Gibbs sampling is as following:

Table 4.3: Gibbs Sampling Algorithm

Initialize $t = 0, X_0\{x_1^0, x_2^0, x_1^0\} \sim q(\cdot)$ (prior distribution)	
for	$t = 1, 2, \dots$ do
x_1^{t+1}	$\sim p(x_1 x_2 = x_2^t, x_3 = x_3^t, \dots, x_P = x_P^t)$
x_2^{t+1}	$\sim p(x_2 x_1 = x_1^{t+1}, x_3 = x_3^t, \dots, x_P = x_P^t)$
$\vdots$	
x_P^{t+1}	$\sim p(x_P x_1 = x_1^{t+1}, x_2 = x_2^{t+1}, \dots, x_{P-1} = x_{P-1}^{t+1})$
end for	

The observation error, represented by ϵ , is assumed to be a white noise process with variance σ^2 . It was updated using Gibbs sampling starting from a diffuse Inverse Gamma prior.

$$P(\sigma^2|(y, \theta)) = IG\left(a + \frac{N}{2}, b + \frac{1}{2}(z - y)^T(z - y)\right) \quad (4.34)$$

τ_r^2 was also updated by Gibbs sampling using Inverse Gamma distribution:

$$P(\tau_r^2|(y, \beta)) = IG\left(a' + \frac{N}{2}, b' + \frac{1}{2}\beta^T\beta\right) \quad (4.35)$$

a, b, a', b' are the initial parameters defining an Inverse Gamma distribution.

4.5 Dynamic Discrepancy Model

A fully non-intrusive “block-box” approach is normally used to include the model form discrepancy for calibration. A joint distribution of model parameters and discrepancy can be obtained and propagated to large-scale model. However, the model discrepancy estimated from small-scale models may not be relevant to that at large-scale systems. Therefore, this approach is not always feasible in practice.[181] A dynamic discrepancy approach is preferred because it allows the dynamic system to change its path depending on the value of δ . A intrusive uncertainty quantification approach that includes the stochastic discrepancy function within the small-scale model equations has been used in the calibration. Each thermodynamic parameter and diffusive parameter has a unique discrepancy term based on the state variables ζ . Implementing the discrepancy in the equilibrium constants and diffusion coefficients allows us to naturally use a functional concurrent model.

$$\kappa_{new}^E = \exp\left(\frac{T\Delta S - \Delta H}{RT}\right) \exp(\delta^E(p, T)) = \kappa^E \exp(\delta^E(p, T)) \quad (4.36)$$

$$u_{b_i, new} = \frac{1}{T} \exp\left(-\frac{\Delta H_b^\ddagger}{RT}\right) \exp(\delta_i(\zeta)) = u_{b_i} \exp(\delta_i(\zeta)) \quad (4.37)$$

A set of stochastic differential equations (SDE) will be formed when a traditional GP prior is placed on δ . This SDE can be turned to an ODE when a BSS-ANOVA GP prior is applied to model parameters since it has the advantage of admitting a convenient and approximate parametric form that contains the entire stochasticity in its parameters. In a Bayesian calibration framework, the SDE can be easily integrated within the MCMC routine as follows: at each iteration, propose a set of model parameters and discrepancy parameters, obtain a solution of the state variable(s) from the ODE, evaluate the likelihood, and accept/reject the sample.[181] This framework provides an approach to estimate the joint posterior distribution, and allows for the forward propagation of uncertainty in the usual sample-based manner. An approach that includes the stochastic discrepancy function into the equilibrium constants and diffusion coefficients has been implemented in the calibration framework of our small-scale CO₂ adsorption model. Model form discrepancy was represented using a Gaussian process with a BBS-ANOVA covariance and the related differential equations are solved by MCMC.

This model is actually a one-dimension model because Knudsen diffusion is neglected and only the diffusion in the PEI bulk is considered. The main model discrepancy is from the diffusion process. Therefore, a model form dynamic discrepancy function that admits the possibility of model bias can be added to the diffusion coefficients. The equilibrium discrepancy was also included because most of the TGA data are considered to be collected at the equilibrium states. The diffusion coefficients of diffusive intermediates (z_1, z_2, z_3) control the concentrations of diffusive intermediates and the carbamates are the function of these intermediates. Therefore, the discrepancy in diffusion coefficients is a part of the functions of two products (x and y). The temperature (T), CO₂ partial pressure (p_{CO_2}) and H₂O partial pressure (p_{H_2O}) are the model inputs. They are functions of time and represent by $\zeta_i(t)$ for the i^{th} condition at time t . As has been discussed, we have the following chemical

reactions:

Then the equilibrium constants and kinetic constants and diffusion coefficients have the following form:

$$\kappa_{3.1}^E = \exp\left(\frac{T\Delta S_{3.1} - \Delta H_{3.1}}{RT}\right)/P \quad (4.38)$$

$$\kappa_{3.2}^E = \exp\left(\frac{T\Delta S_{3.2} - \Delta H_{3.2}}{RT}\right) \quad (4.39)$$

$$k_{-3.2}^K = \gamma_{3.2} \exp\left(-\frac{\Delta H_{3.2}^\ddagger}{RT}\right) \quad (4.40)$$

$$\kappa_{3.3}^E = \exp\left(\frac{T\Delta S_{3.3} - \Delta H_{3.3}}{RT}\right)/P \quad (4.41)$$

$$\kappa_{3.4}^E = \exp\left(\frac{T\Delta S_{3.4} - \Delta H_{3.4}}{RT}\right)/P \quad (4.42)$$

$$\kappa_{3.5}^E = \exp\left(\frac{T\Delta S_{3.5} - \Delta H_{3.5}}{RT}\right) \quad (4.43)$$

$$k_{-3.5}^K = \gamma_{3.5} \exp\left(-\frac{\Delta H_{3.5}^\ddagger}{RT}\right) \quad (4.44)$$

$$u_{b_1}^{*T} = \zeta_{b_1} \exp\left(\frac{-\Delta H_{b_1}^\ddagger}{RT}\right)/T \quad (4.45)$$

$$u_{b_2}^{*T} = \zeta_{b_2} \exp\left(\frac{-\Delta H_{b_2}^\ddagger}{RT}\right)/T \quad (4.46)$$

$$u_{b_3}^{*T} = \zeta_{b_3} \exp\left(\frac{-\Delta H_{b_3}^\ddagger}{RT}\right)/T \quad (4.47)$$

The forward reaction rates can be calculated through $k_f = \kappa \times k_r$.

The weight fractions of carbamates and water in the sorbent can be calculated using the following equations:

$$w_{CO_2} = M_{CO_2} n_v (\bar{x} + \bar{y} + \bar{z}_1 + \bar{z}_3) / \rho \quad (4.48)$$

$$w_{H_2O} = M_{H_2O} n_v (\bar{y} + \bar{z}_2) / \rho \quad (4.49)$$

The interested quantities are the concentrations of ammonium carbamate (x) and hydronium carbamate (y). Their reaction rates are:

$$\frac{\partial x}{\partial t} = k_{3,2}^K z_1 - k_{-3,2}^K x^2 \quad (4.50)$$

$$\frac{\partial y}{\partial t} = k_{3,5}^K z_3 - k_{-3,5}^K y \quad (4.51)$$

Therefore, the rate equation of x and y at the i^{th} control volume can be written as:

$$\frac{\partial x_i}{\partial t} = f_s(x_i, z_{1,i}, \zeta(t); \theta) \quad (4.52)$$

$$\frac{\partial y_i}{\partial t} = f_s(y_i, z_{3,i}, \zeta(t); \theta) \quad (4.53)$$

They depend on the values of all other species concentrations in that control volume.

When the dynamic discrepancy functions are added to the equilibrium constants and

diffusion coefficients, they have new forms:

$$\begin{aligned}\kappa_{3.1,new}^E &= \exp\left(\frac{T\Delta_{3.1} - \Delta H_{3.1}}{RT}\right) \exp(\delta_1^E(p_{\text{CO}_2}, T))/P \\ &= \kappa_{3.1}^E \exp[\delta_1^E(p_{\text{CO}_2}, T)]\end{aligned}\quad (4.54)$$

$$\begin{aligned}\kappa_{3.2,new}^E &= \exp\left(\frac{T\Delta S_{3.2} - \Delta H_{3.2}}{RT}\right) \exp(\delta_2^E(s, T)) \\ &= \kappa_{3.2}^E \exp[\delta_2^E(s, T)]\end{aligned}\quad (4.55)$$

$$\begin{aligned}\kappa_{3.3,new}^E &= \exp\left(\frac{T\Delta S_{3.3} - \Delta H_{3.3}}{RT}\right) \exp(\delta_3^E(p_{\text{H}_2\text{O}}, T))/P \\ &= \kappa_{3.3}^E \exp[\delta_3^E(p_{\text{H}_2\text{O}}, T)]\end{aligned}\quad (4.56)$$

$$\begin{aligned}\kappa_{3.4,new}^E &= \exp\left(\frac{T\Delta S_{3.4} - \Delta H_{3.4}}{RT}\right) \exp(\delta_4^E(p_{\text{CO}_2}, T))/P \\ &= \kappa_{3.4}^E \exp[\delta_4^E(p_{\text{CO}_2}, T)]\end{aligned}\quad (4.57)$$

$$\begin{aligned}\kappa_{3.5,new}^E &= \exp\left(\frac{T\Delta S_{3.5} - \Delta H_{3.5}}{RT}\right) \exp(\delta_5^E(z_3, T)) \\ &= \kappa_{3.5}^E \exp[\delta_5^E(z_3, T)]\end{aligned}\quad (4.58)$$

$$\begin{aligned}u_{b_1i,new}^{*T1} &= \zeta_{b_1} \exp\left(\frac{-\Delta H_{b_1}^\ddagger}{RT}\right) \exp\left[\delta^{T1}(z_{1,i-1}, z_{1,i}, z_{1,i+1}, \frac{1}{T})\right] / T \\ &= u_{b_1i}^{*T1} \exp\left[\delta^T(z_{1,i-1}, z_{1,i}, z_{1,i+1}, \frac{1}{T})\right]\end{aligned}\quad (4.59)$$

$$\begin{aligned}u_{b_2i,new}^{*T2} &= \zeta_{b_2} \exp\left(\frac{-\Delta H_{b_2}^\ddagger}{RT}\right) \exp\left[\delta^{T2}(z_{2,i-1}, z_{2,i}, z_{2,i+1}, \frac{1}{T})\right] / T \\ &= u_{b_2i}^{*T2} \exp\left[\delta^T(z_{2,i-1}, z_{2,i}, z_{2,i+1}, \frac{1}{T})\right]\end{aligned}\quad (4.60)$$

$$\begin{aligned}u_{b_3i,new}^{*T3} &= \zeta_{b_3} \exp\left(\frac{-\Delta H_{b_3}^\ddagger}{RT}\right) \exp\left[\delta^{T3}(z_{3,i-1}, z_{3,i}, z_{3,i+1}, \frac{1}{T})\right] / T \\ &= u_{b_3i}^{*T3} \exp\left[\delta^T(z_{3,i-1}, z_{3,i}, z_{3,i+1}, \frac{1}{T})\right]\end{aligned}\quad (4.61)$$

The discrepancy terms can be written as:

$$\delta^E[\zeta(t)] = \sum_{l=1}^{\infty} \beta_l \phi_l(\zeta_t) + \sum_{l=1}^{\infty} \sum_{l=j}^{\infty} \beta_{l,j} \phi_l(\zeta_t) \phi_j(\zeta_t) + \dots, \quad (4.62)$$

$$\delta^T[z_{j,i-1}(t), z_{j,i}(t), z_{j,i+1}(t), \zeta(t)] = \sum_{l=1}^{\infty} \beta_l \phi_l(z_{j,i-1}(t), z_{j,i}(t), z_{j,i+1}(t), \zeta_t) + \dots, \quad (4.63)$$

$$\beta_l \stackrel{iid}{\sim} \mathcal{N}(0, \tau_r^2) \quad j = 1, 2, 3$$

As shown in above equations, δ is comprised of a series of variable interactions (one-way, two-way, three-way, ...). Each interaction is comprised of a series of basis functions (ϕ_i) with a corresponding beta value (β_i or $\beta_{i,j}$). Determining the number of interaction and the number basis function per interaction is an attempt to find the balance between accuracy and complexity. Terms are added until it no longer makes a difference in the calibration. Including higher order interactions will increase the capabilities of the discrepancy at higher computational cost. It is usually decided by the data. Complex data curves will require a higher order of interaction. After the highest order of interaction is determined, optimizing the number of necessary basis functions per interaction is more of a fine tuning process. Technically, increasing the number of basis functions in each discrepancy term should allow for a more accurate quantification of the uncertainties between model output and experiment data. However, when the number of basis function is sufficient large, continuously increasing it will make little difference and largely increase the computation cost because of the decreasing amplitude of the basis functions.

In this model, the variables in δ_E are the temperature T and either partial pressure (p_{CO_2} or $p_{\text{H}_2\text{O}}$) or site fraction (s or z_3). The variables in δ_T are the temperature and site fractions of diffusive intermediate. The difference of the site fraction of diffusive intermediate ($z_i(j) - z_i(j+1)$) in two nearby control volumes can be used to present these site fraction terms. Therefore, there are only two variables in each δ meaning that only two-way

interaction between variables is needed.

$$\delta = \sum_{i=1}^L \beta_i \phi_i(\zeta) + \sum_{i=1}^{L'} \sum_{j=1}^{L'} \beta_{i,j} \phi_i(\zeta) \phi_j(\zeta') \quad (4.64)$$

where L and L' are the numbers of basis function for one-way and two-way interactions. It was demonstrated that using a total of 32 basis functions with corresponding beta values in the implementation of the BSS-ANOVA approach in our model is sufficient. It includes two one-way interactions each with eight basis functions and one two-way interaction with sixteen basis functions. Therefore, a total of 256 beta values is used for eight discrepancy terms (five equilibrium constants and three diffusion coefficient).

However, the computational cost of MCMC runs for a number of samples is usually large under traditional approach. It is critical to reduce the computational cost such that this approach can be more generally used. A reduced-order model aiming to decrease the computational cost through reducing the number of control volumes was developed and implemented.

4.6 Reduced Order Model

In a previous investigation conducted by Bhat, etc, MCMC coded in MATLAB was run to solve a simple model which had only two reactions and no diffusion for 200,000 samples using a 2.66 GhZ 6-Core Intel Xeon on a Mac Pro desktop with 16GB of RAM. Each evaluation of the sorbent model requires approximately six seconds and each iteration of MCMC requires 15 model evaluations. As a result to get the full posterior about 190 hours of computer time was needed.[181] By contrast, our current model including five reactions, three diffusive intermediates, and 23 parameters requires minutes for a single model estimation. The computational time is a huge limitation for obtaining the posterior distribution for both model parameters and model discrepancy, especially when a large number of samples are needed. Therefore, it is critical to find an approach to reduce the computation time such

that this method can be used in various applications.

To achieve the goal of reducing the computation time, a reduced order diffusion model as shown in Figure 4.3 based on the full diffusion model in Figure 4.2 has been embedded into the calibration. Control volumes are represented by the blocks in both figures. There

Figure 4.2: The diffusion model of CO₂ capture in sorbent.

are N control volumes (CVs) from the interface layer between CO₂ and sorbent. These five colored dots represent the five interested chemical species (x , y , z_1 , z_2 and z_3). Along the diffusion from the surface to deep bulk, the concentrations of diffusive intermediates will decrease and correspondingly, the concentrations of two carbamate products will decrease. The diminution of these dots represents the decrease of these concentrations. Normally, we have N CVs and the diffusion coefficients in each CV are different when the discrepancy is added into it. All diffusion coefficients and these species concentrations need to be calculated in every time step and every MCMC step during calibration. Because the governing equations of diffusion in each CV in the bulk are the same, the discrepancy in each CV will have the same format. Therefore, we can keep the surface layer and the last CV as the boundary conditions and merge all the CVs to three. In this way, we will only have five CVs. The

Figure 4.3: The reduced diffusion model of CO₂ capture in sorbent.

calculation time for solving a model with five CVs is much less than that for solving a model with 100 or 50 CVs. Considering the model always needs to be solved iteratively at every time step and the experimental data has a domain of at least several hundred seconds, the overall computational time can reduce by two orders of magnitude.

4.7 Process Model

Another goal of this study is to apply this small-scale model to large-scale models to make predictions for the quantity of interest and input conditions with uncertainty quantification. Once a joint sample-based posterior distribution was obtained by MCMC sampling. Samples were drawn from the posterior distribution and incorporated in a large-scale model. The large-scale model involves a fluidized-bed adsorber and is derived from a bubbling fluidized bed (BFB) model. The BFB model, which utilizes first generation particle-scale kinetics, was previously developed under the auspices of DOE's CCSI endeavor. It is capable of providing the profiles of temperature, concentration, and velocities along the axis.

It can predict the hydrodynamics of the bed and remain computationally fast and flexible such that it can be adapted to any adsorption and desorption reaction systems. A detailed description of this rigorous three-region process model is given in ref. [199]. The sketch of this process model was showed in Figure 4.4. Both solid sorbents and flue gas consisting of CO_2 , H_2O , and N_2 get injected at the bottom of the bed and flow upward through it to be mixed.

Figure 4.4: The sketch of Bubbling Fluidized Bed model. Data from [199]

The process model utilized in current study uses the reaction-diffusion-based second-generation particle model. Both the process model and particle model were modified by Priyadarshi Mahapatra from NETL. To reduce the computational complexity due to the introduction of a second spatial dimension, the original BFB model has been simplified. These simplifications and the process specifications are given below, do not undermine the significance of developing a true multi-scale model which could be utilized in demonstrating discrepancy during upscaling for this thesis. Both the gas and solid particles are introduced

at the bottom of the fluidized-bed vessel via a distributor plate. The particles are assumed to follow Geldart Group A class of material. The gas velocity is well above the minimum fluidization velocity and within the “bubbling fluidization regime”, however it is assumed that no bubbles are formed. The current model utilizes a single “emulsion” region/phase where gas is in direct contact with the solid particle. The particle length scale is radially discretized (spherical domain) into 30 control-volumes. The device length scale is axially discretized (cylindrical domain) into 25 control-volumes.

The model is implemented in Aspen Custom Modeler (ACM) (Aspen Technologies, Inc.). The particle length scale was solved using inbuilt partial differential equation (PDE) solver utilizing a 2nd order central finite difference method. At the device scale, a compartment-based approach, where axial differential terms were expressed as finite differences involving a first-order forward finite difference method was used. The physical property of the gas phase was calculated using commercial property packages (Aspen Properties in ACM) using the cubic equation of state. The physical properties of the solids were taken from experimental measurements. The process model involves 332890 equations and significantly larger number of non-zeroes, as reported by ACM. Computations have been conducted on a Windows-based Laptop Workstation utilizing 16-core Intel I7 Processor.

The discrepancy terms were evaluated using external procedure calls within ACM. These procedures coded in C were compiled into a dynamic link library using Intel Fortran Compiler, acted as an interface for fast evaluation of discrepancy terms and their residuals within the process models. The dynamic discrepancy evaluation framework was automated, with error handling capability, to read each posterior point from an excel spreadsheet and report the corresponding Lagrangian profiles for the solid particles. Due to large magnitudes of “step-changes” involved and the presence of external procedure calls, a homotopy-based approach was used to switch from one posterior point to another.

It must be emphasized that the process model involves a steady-state evaluation with process conditions varying spatially. However, to analyze the data corresponding to

the discrepancy evaluation at the simple particle scale a conversion to a temporal domain is required. This involves an interpretation of process conditions surrounding individual particle as they axially traverse through the adsorber bed. Hence, a Eulerian to Lagrangian transformation,[200] also known as “material” or “substantive” derivative, is utilized using flow-velocity of the solid particles in the emulsion region.

The output of this large-scale model has been converted to the carbon capture rate and operating conditions in the process.

4.8 Experiment

The amine-impregnated solid sorbent used in the experiment was created at NETL by MCMahan Gray. Thermogravimetric analysis was conducted to investigate the CO₂ adsorption behavior under different experimental conditions by Dan Fauth at NETL. In an experiment, an amount of sample was loaded in a microbalance quartz sample bowl and heated to 378K in a nitrogen environment to remove pre-adsorbed CO₂ and moisture, at a heating rate of 5 K/min, and held isothermally for 90 minutes before it was used for adsorption. Then the temperature was increased to 381K (Initial adsorption temperature) and the reactant gas was switched to either dry CO₂ (Mixture of 4%, 10%, 18.5% or 100% CO₂ balanced by nitrogen) or humid CO₂ (Mixture of 4%, 7.5%, 18.5% or 91% CO₂ and 9% H₂O balanced by nitrogen), maintaining a flow rate of 100 ml/min. Subsequent adsorption steps were conducted at 373, 365, 338, 330, 322K, followed by desorption steps at 338 and 381K. The hold time was approximately 90 minutes for each step. The CO₂ adsorption capacities were calculated on the basis of mass increase measured after incremental time exposure to the various gas mixtures and referenced to the initial sample mass after nitrogen (378K) activation of 100 ml/min. In order to investigate the water adsorption, another series experiments has been conducted. The adsorption steps were conducted at 381 and 314K for 9 circles under 1%, 5% and 6% H₂O balanced with nitrogen. For TGA runs containing moisture, the purge gas stream was run through a sparger to achieve the requisite moisture

content. Full details of the sorbent synthesis and experiment procedures are available in ref. [193]. The experiment provided a set of adsorption curves which can be used to compare with the model outputs.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Results from Experiment

Figure 5.1 displays the TGA curves of CO_2 adsorption and desorption under dry conditions when the adsorption temperature changes from high to low in an empty sorbent. The uptake of CO_2 is represented as the weight fraction of CO_2 adsorbed to the overall sorbent weight, labeled in the vertical axis on the left-hand side. The CO_2 adsorption curves under four CO_2 concentrations (4%, 10%, 18.5% and 100%) were colored in blue, red, black and magenta, respectively. The temperature curve is colored as dark green and labeled at the right vertical axis. As shown in the figure, all four curves have the same trend that the adsorption weight fraction increases as the temperature decreases. For each adsorption curve,

Figure 5.1: TGA results under anhydrous conditions.

the CO_2 weight fraction increases when the operating temperature decreases because of the exothermic process, and it reaches a plateau at each temperature step. However, the CO_2 weight fractions increase after a sharp decrease when the temperature is increased to 338K from 322K for desorption. This indicates that the plateau at 322K is not indicative of equilibrium. Instead, it indicates that a kinetic barrier is reached at such low temperature that further adsorption is cut off. This phenomenon is consistent with the experimental results in literature in Chapter 2, suggesting that there is a diffusion limitation for absorbed CO_2 at the gas-amine interface diffusing into the amine bulk. The CO_2 weight fraction is barely increasing at the temperature lower than 330K because of the slow diffusion. Continuing elevating temperature will shift the equilibrium and decrease the weight fraction of CO_2 . In these four curves, higher CO_2 adsorption capacity is observed under higher CO_2 concentration since the CO_2 weight fraction increases as the CO_2 partial pressure increases from 4% to 100%. However, the difference is small and continuous increases to the CO_2 concentration in the flue gas will not effectively improve the adsorption. The maximum weight fraction of CO_2 is around 0.1 under 100% CO_2 concentration.

Figure 5.2 displays the TGA curves of CO_2 uptake under hydrous conditions. The overall adsorption weight fractions are much higher than under anhydrous conditions at the same operating conditions when 9% water moisture is included in the flue gas. Similar to dry cases, the weight fraction increases as the temperature decreases because of the exothermic process. However, the pseudo-equilibrium plateau does not appear anymore. It can be concluded that there is a much smaller kinetic barrier to limit the diffusion of CO_2 in the amine bulk under wet conditions compared to dry conditions. As CO_2 pressure increases, the weight fractions increase at higher temperatures, but slightly decrease at lower temperatures. This is because of the competition for free amine sites at the surface between CO_2 and H_2O . The continuing increase of weight fraction at 314K is because of the precipitation of water at the surface at this low temperature.

Figure 5.2: TGA results under hydrous conditions.

Figure 5.3: TGA results of H₂O adsorption.

The water adsorption and desorption under different water moisture concentrations

is illustrated in Figure 5.3. The weight fractions increase with the increase of the water concentration and decrease with the increase of temperature. Water moisture is adsorbed and desorbed to equilibrium very fast at 314 and 381K. Almost all water is desorbed at 381K. This behavior implies that water can easily bond or break with amine and there is not such an energy barrier for H_2O transport to the bulk like dry CO_2 adsorption.

5.2 Model Simulations

Figure 5.4 shows the simulated TGA traces of CO_2 adsorption under 10%, 50% and 100% CO_2 as temperature changes between 320K and 400K. It can be clearly seen that the

Figure 5.4: Simulated temperature effect on the adsorption capacity.

weight fraction reaches a plateau in the first 5000 seconds and then starts to increase along with the temperature increases. At around 360K, the weight fraction reaches a peak and starts to decrease to the local minimum as the temperature increases to 400K. Decreasing the temperature will increase the weight fraction and it reaches another plateau after 340K. This

behavior confirmed the existence of the energy barrier for CO₂ diffusion at low temperatures. In the model high temperature is required to overcome this barrier in order to have faster diffusion.

For the dry case, the CO₂ capacity first increases and then decreases as the temperature increases. Figure 5.5 indicates the simulated isotherms of CO₂ adsorption under 322K, 338K, 358K, 365K and 381K when CO₂ partial pressure changes from 0 to 1 bar. The CO₂

Figure 5.5: Simulated CO₂ adsorption as a function of CO₂ partial pressure: Dry.

adsorption weight fraction increases fast at first and then reaches equilibrium slowly as the CO₂ concentration increases. The CO₂ capacity first increases to the maximum adsorption capacity at 358K and then decreases as temperature changes from low to high. This is consistent with the simulation results in Figure 5.4 and previous studies. Figure 5.6 shows the change of CO₂ capacity with adsorption time under 10% CO₂ concentration and five different temperatures. The adsorption reaches equilibrium faster under higher temperature and has the maximum capacity at 358K as expected. By contrast, Figure 5.7 shows the simulated isotherms of CO₂ adsorption under 322K, 338K, 358K, 365K and 381K when CO₂

Figure 5.6: Simulated CO₂ adsorption as a function of CO₂ adsorption time.

Figure 5.7: Simulated adsorption as a function of CO₂ partial pressure: Humid.

partial pressure changes from 0 to 1 bar in wet conditions containing 5% water vapor. It has the maximum capacity at 322K and the capacity decreases as the temperature increases. This behavior indicates that it has a lower energy barrier for CO₂ diffusion under wet conditions compared to anhydrous conditions. Moreover, the equilibrium CO₂ adsorption capacity under wet conditions is much larger than under dry conditions at the same temperature.

The simulation results under dry conditions are compared with experimental results as shown in Figure 5.8. It shows the simulation results and experimental data as the CO₂ concentrations increases from 0 to 100% at different temperatures. The experimental data points were drawn from TGA data. Not only does the same adsorption-desorption trend emerge under different CO₂ concentrations, but also the simulated weight fractions are very close to the experimental data. The average deviation at equilibrium stages is about 8% and the maximum deviation is 17.8% at T = 330K and CO₂ = 4%.[187]

Figure 5.8: Dry CO₂ adsorption simulation results and experimental data under different CO₂ concentrations. Figure from ref. [187]

Figure 5.9 showed the simulation results of water adsorption under experimental conditions. Both the adsorption capacity and the adsorption-desorption process of simulation

curves are consistent with experimental curves. The deviation is only 7% under 6% water concentration and it is slightly higher under lower water concentration. This model qualitatively and quantitatively reproduced the TGA curves of the adsorption-desorption process under various temperature and pressure conditions.

Figure 5.9: Simulation results of H_2O adsorption under different partial pressure.

Figure 5.10 shows the comparison of simulation results and experimental data under hydrous conditions. The overall weight fraction increases as the temperature decreases. The adsorbed weight fraction is twice that under dry conditions in the same CO_2 concentration and operating temperature. The overall weight fraction of adsorption consists of hydronium carbamate, ammonium carbamate, and water. As the CO_2 pressure increases, the weight fractions increase at high temperatures but slightly decrease at lower temperatures. This is because of the competition for free amines at the gas-amine interface between water vapor and CO_2 . Under high CO_2 concentration, water vapor has less chance to react with free amines when compared to CO_2 resulting in the lower intermediate concentration. Therefore fewer hydronium carbamates are formed. Under higher CO_2 concentrations, the weight fraction of hydronium carbamates increases at high temperatures and slightly decreasing at

low temperatures compared to low CO_2 concentrations. The maximum deviation is 38.2% at $T = 381\text{K}$ and $\text{CO}_2 = 4\%$ (this is the experimental result with the lowest absolute value of the adsorbed weight fraction), but the correspondence between model and experiment is generally much closer than this. Quantitative agreement at $T = 322\text{ K}$ is particularly good.[187]

Figure 5.10: Humid CO_2 adsorption simulation results and experimental data under different CO_2 concentrations. Figure from ref. [187]

The overall weight fraction under humid conditions can be separated into three parts, the weight fractions of hydronium carbamate, ammonium carbamate and water. The weight fractions of hydronium carbamate and ammonium carbamate are shown in Figure 5.11 and 5.12. It shows that there is more hydronium carbamate formed than ammonium carbamate and adsorbed water is not the main reason for the capacity increase. The weight fractions of ammonium-carbamate increase as the temperature decreases from 381K to 365K. They start to decrease and reach a plateau when the temperature continues to decrease. When the temperature is low, there is not enough energy to overcome the energy barrier of diffusion and the diffusion rate of amine-stabilized zwitterions is small. By contrast, water-

Figure 5.11: Hydronium carbamate fraction.

Figure 5.12: Ammonium carbamate fraction.

stabilized zwitterions have much smaller energy barrier that lower temperature can provide enough energy to overcome it. Low temperature is favorable to equilibrium; as a result,

the concentration of water-stabilized zwitterions is larger than that at high temperature. The ammonium carbamate weight fractions are smaller than these in anhydrous conditions because of the competition from water for amine sites. The hydronium produced with hydronium carbamate is the source of water adsorption. The mole fraction of hydronium is equal to hydronium carbamate. Therefore, the water weight fraction curves are similar to hydronium carbamate.

Both the experimental data and simulation results showed that the energy barrier under dry conditions is much higher than hydrous conditions. It is consistent with the results from quantum chemistry calculation that the formation of ammonium carbamate has a higher activation energy than hydronium carbamate. Using the quantum chemistry calculations as the reference to equilibrium, kinetic and transport parameters in the model, the simulation results of this model successfully replicated the TGA behaviors for the adsorption of H_2O and CO_2 . This similarity between simulation results and experimental data proved that our model is appropriate to simulate the adsorption and desorption of CO_2 and H_2O . The mechanism using amine and water-stabilized zwitterions as diffusive intermediates succeeded in simulating the adsorption-desorption behaviors of SSA sorbents.

5.3 Results from Calibration

This model was calibrated to the TGA data after the model simulations were matched with experimental data. The capability of dynamic discrepancy function and reduced order model were verified in the calibration process. Two criteria have to be met for a successful calibration: coverage of simulations to experimental data and convergence of the posterior distribution to a confined region in the parameter space.

A number of MCMC sampling steps (94000) have been done for obtaining the posterior. Each MCMC step represents an individual realization of the model simulation. The computational speed of MCMC sampling has been improved to about 5000 steps per day from a couple hundred steps per day after employing the reduced-order model. Coverage of

Figure 5.13: Calibration results under dry condtions

the experimental data is shown by reproducing and overlaying a small set of model realizations against the TGA data. Figure 5.13 and 5.14 shows the coverage of calibration results to TGA data under dry and hydrous conditions. The blue curve is the TGA trace and red curves are 100 model realizations drawn from the posterior. TGA data was well covered by calibration results in these seven cases under dry and humid conditions. It is evidence that the calibration achieved the desired result.

Examining the value of likelihood as a function of the number of MCMC steps is a

(a) Water cases 9% H₂O 0% CO₂

(b) Hydrous cases 7.5% CO₂ with 9% H₂O

(c) Hydrous cases 18.5% CO₂ with 9% H₂O

(d) Hydrous cases 91% CO₂ with 9% H₂O

Figure 5.14: Calibration results under humid conditions

common method to analyze the convergence of posteriors. Steady and constant likelihood values indicate that the sampling routine has dropped in a bounded region that produces similar results. Visualizing the values of model parameters is also a method to determine if it is converged. The movement of the MCMC steps can be seen from the movement of these parameters and if the parameters stay in a bounded region for a long time, it can be considered as converged. Bivariate scatter plots were used to discover the relationship between paired model parameters. It is not feasible to do so for β variables because the

number of β parameters is large.

For this calibration results, the likelihood is shown in Figure 5.15. The value of the likelihood remained constant at a high number of MCMC steps after an unsteady “burn in” period.

Figure 5.15: Likelihood.

The values of some model parameters are shown in Figure 5.16. They maintain in a confined region after a period of bouncing around. The posterior distributions of some model parameters are shown via bivariate scatter plots in Figure 5.17. The parameters are more likely to fall into the yellow color region compared to the blue color region. Strong correlation exists between certain pairs of model parameters. The correlations between $\Delta H_{3.1}$ and $\Delta S_{3.1}$, $\Delta H_{3.3}$ and $\Delta S_{3.3}$, and $\Delta H_{3.4}$ and $\Delta S_{3.4}$ were 0.98, 0.91 and 0.79, respectively. There is a very strong relationship between the formation of enthalpy and entropy as expected. The correlations between $\Delta H_{b_1}^\ddagger$ and $\log_{10}(\zeta_{b_1})$, $\Delta H_{b_2}^\ddagger$ and $\log_{10}(\zeta_{b_2})$, and $\Delta H_{b_3}^\ddagger$ and $\log_{10}(\zeta_{b_3})$ were 0.98, 0.99 and 0.5, respectively.

(a) $\Delta H_{3.2}^\ddagger$

(b) $\log_{10}(\gamma_{3.2})$

(c) $\Delta H_{3.5}^\ddagger$

(d) $\log_{10}(\gamma_{3.5})$

(e) $\Delta H_{b_3}^\ddagger$

(f) $\log_{10}(\zeta_3)$

Figure 5.16: Values of model parameters from MCMC sampling

(a) $\Delta H_{3.3}$ and $\Delta S_{3.3}$

(b) $\Delta H_{b_1}^{\dagger}$ and $\log_{10}(\zeta_{b_1})$

(c) $\Delta H_{3.5}$ and $\Delta S_{3.5}$

(d) $\Delta H_{b_2}^{\dagger}$ and $\log_{10}(\zeta_{b_2})$

(e) $\Delta H_{3.2}^{\dagger}$ and $\log_{10}(\gamma_{3.2})$

(f) $\Delta H_{b_3}^{\dagger}$ and $\log_{10}(\zeta_{b_3})$

Figure 5.17: Bivariate scatter plots of model parameters from MCMC sampling

The confirmation of a converged posterior distribution was statistically verified by the use of a batch means test. In the test, the total number of the post burn-in samples in the posterior distribution, N , is divided by a number of bins, a , and each bin has an equal number of data points, $b = N/a$. The mean for each bin was evaluated:

$$\bar{Y}_j := \frac{1}{b} \sum_{l=(j-1)b}^{jb-1} X_i \quad \text{for } j = 1, \dots, a \quad (5.1)$$

The variance of target distribution, σ_t^2 , is estimated using variance of batch means:

$$\hat{\sigma}_{BM}^2 := \frac{b}{a-1} \sum_{j=1}^a (\bar{Y}_j - \bar{X}_N)^2 \quad (5.2)$$

Equation 5.2 is not a consistent estimator of σ_t^2 , but $\sigma_{BM}^2 \rightarrow \sigma_t^2$ with probability 1 as $n \rightarrow \infty$. [201] In this case it is called consistent batch means (CBM) which has been used to estimate the Monte Carlo standard error of $\bar{X}_N$ as $\hat{\sigma}_{BM}/\sqrt{N}$. The half-width confidence interval is given by:

$$t_{a_N-1} \frac{\hat{\sigma}_{BM}}{\sqrt{N}} \quad (5.3)$$

where t_{a_N-1} is an appropriate quantile from Student's t distribution with $a_N - 1$ degrees of freedom. [202]

This batch means test was used in this study to determine if there is a statistically significant difference between the sample distribution and the target distribution. 95% confidence interval ($\alpha = 0.05$) and 24000 MCMC iterations was used in this test. In this case, $a = b = 154$ and $t_{a_N-1}/\sqrt{N} = 1.9755$. The specifications for the batch mean test is summarized in Table 5.1.

Table 5.1: Specifications for Batch Means Test

Parameters	Value	Unit
CI	95%	—
α	0.05	—
a	154	bins
b	154	points
N	24000	samples
t_N/b	1.9755	—

The results of batch means test for posteriors of θ parameters and a small set of β parameters are shown in Table 5.2 and Table 5.3. μ refers to the global mean, and s refers to the confidence interval from batch means test. Most of the model parameters are in the 95% confidence intervals. Compared to the small deviations of model parameters, β values have larger deviations. The means of the model parameters are also close to the values that come from quantum chemistry calculations.

Table 5.2: Results of θ from Batch Means Test

Variables	μ	s
R_3 (nm)	34.9747	0.7813
n_s	20.9284	0.5843
n_v	15.2443	0.4798
$\Delta H_{3.1}$	-38.8827	0.5136
$\Delta S_{3.1}$	-201.8970	3.1892
$\Delta H_{3.2}$	-5.5110	0.3437
$\Delta S_{3.2}$	-201.5774	1.7186
$\Delta H_{3.2}^\dagger$	5.3404	0.3509
$\log_{10}(\gamma_{3.2})$	-117.2998	2.5018
$\Delta H_{3.3}$	-64.6042	0.5029
$\Delta S_{3.3}$	-57.3115	2.2238
$\Delta H_{3.4}$	76.7483	1.1451
$\Delta S_{3.4}$	11.2524	0.0416
$\Delta H_{3.5}$	-63.5174	1.2661
$\Delta S_{3.5}$	-29.9626	2.4568
$\Delta H_{3.5}^\dagger$	106.3624	0.8569
$\log_{10}(\gamma_{3.5})$	14.5809	0.0502
$\Delta H_{b_1}^\dagger$	54.6540	0.9781
$\log_{10}(\zeta_{b_1})$	-7.6671	0.1155
$\Delta H_{b_2}^\dagger$	30.8214	1.6341
$\log_{10}(\zeta_{b_2})$	-1.7636	0.0564
$\Delta H_{b_3}^\dagger$	35.1341	0.6699
$\log_{10}(\zeta_{b_3})$	-6.2119	0.0997

Table 5.3: Results of β from Batch Means Test

Variables	μ	s
β_1	-6.5330	0.9549
β_{17}	0.5802	0.2200
β_{25}	3.0463	0.1746
β_{51}	-1.9066	0.2616
β_{62}	4.5436	0.2255
β_{81}	-15.0337	0.4067
β_{95}	2.2440	0.2564
β_{133}	-160.8613	2.7608
β_{174}	-212.2684	6.9451
β_{186}	-9.2844	0.4515
β_{217}	6.3874	0.2025
β_{255}	2.5539	0.2903

Based on the results of calibration and batch means test, it can be confirmed that the MCMC routine was run sufficiently long enough to achieve a converged posterior distribution for all of the associated parameters. Both the coverage and convergence criteria of calibration have been satisfied.

It can be concluded that the Bayesian calibration with dynamic discrepancy functions in the BSS-ANOVA form succeeded to calibrate the model to TGA data. The MCMC routine has been run for enough steps and a joint sample-based posterior distribution has been obtained to be incorporated in a process model. The uncertainties in both the model parameters and model form discrepancy have been quantified into the posterior distribution during this process. The reduced-order model was able to reduce the computational time.

5.4 Results from Process Model

100 samples from the posterior joint distribution of model parameters and model form discrepancy were drawn and propagated to the BFB CO₂ capture process model and 79 of them converged. Uncertainties from both model parameters and model form discrepancy were propagated to the upscale model. The process model was run under both dry and humid conditions. Dry flue gas contains 10.9% CO₂, balanced with N₂. Humid flue gas contains 10.9% CO₂ and 5.5% H₂O, balanced with N₂. The temperature of the flue gases is 65°C, which is close to the real situation (the temperature of power plant emissions for CO₂ capture after removing SO_x and NO_x). The histogram and kernel smoothing function fit of carbon capture fraction from the process model are shown in Figure 5.18. Figure 5.18(a) shows the carbon capture fraction under dry condition. The mean carbon capture fraction is 0.54 and the 95% credible region for the carbon capture fraction is 0.14 and 0.94. Figure 5.18(b) shows the carbon capture fraction under humid condition. The mean carbon capture fraction is 0.56 and the 95% credible region is between 0.24 and 0.88. It has a higher mean

Figure 5.18: Distributions of carbon capture rate under dry and humid conditions.

carbon capture fraction with a smaller deviation under humid condition compared to dry condition. However, the difference is not significant because water is barely adsorbed when

the temperature is higher than 75°C . Few hydronium carbamate is formed and ammonium carbamates are the main product same as under dry condition. Forty realizations of carbon capture operating temperature and CO_2 partial pressure, and the amount of CO_2 adsorbed are shown in Figure 5.19, 5.20 and 5.21. Time in the x-axis is the time that particle runs through the bed. The temperature increases because of the exothermic reactions.

Figure 5.19: System condition: temperature under dry and humid conditions

Figure 5.20: System condition: CO_2 partial pressure under dry and humid conditions

Figure 5.21: The amount of CO₂ adsorbed

In order to observe larger improvement to carbon capture from water, the operating temperature has to decrease. An external cooling system (20°C water, 209kg/s) was added to the process model to move the released heat out. Figure 5.22(a) and (b) shows that the operating temperature after cooling system is added.

Figure 5.22: System condition: temperature under humid conditions with external cooling

The CO₂ capture fraction is shown in Figure 5.23. Figure 5.23(a) shows the carbon

(a) Carbon capture rate: dry

(b) Carbon capture rate: humid

Figure 5.23: Distribution of carbon capture rate under dry and humid conditions with external cooling.

capture fraction under dry conditions. The mean carbon capture fraction is 0.56 and the 95% credible region for the carbon capture fraction is 0.28 and 0.84. Figure 5.23(b) shows the carbon capture fraction under humid conditions. The mean carbon capture fraction is 0.73 and the 95% credible region is between 0.47 and 0.99. The mean carbon capture

(a) CO₂ partial pressure: dry

(b) CO₂ partial pressure: humid

Figure 5.24: System condition: CO₂ partial pressure under humid conditions with external cooling

fraction under humid condition is significant larger than under dry condition because of the formation of hydronium carbamate. The CO_2 partial pressure and the amount of adsorbed CO_2 in the process model is shown in Figure 5.24 and Figure 5.25.

Figure 5.25: The amount of CO_2 adsorbed with external cooling

The results clearly show that the small-scale model can be used in large-scale process model for carbon capture, and water can increase the carbon capture rate. Low operating temperature is favored for water adsorption and the formation of hydronium carbamate. Decreasing the temperature of the flue gas injected into the process model will further increase the carbon capture rate under humid condition.

This reaction-diffusion model has been implemented in the BFB model for CO_2 capture. The uncertainties from model parameters and model form discrepancy were propagated to a large-scale process model by passing the posteriors from Bayesian calibration of the small-scale model. Predictions of carbon capture fraction and operating conditions can be obtained. Water can improve the CO_2 capture in the process model. The predictions have a higher carbon capture fraction under humid condition compared to dry condition, especially at lower temperature. The process model has a higher carbon capture fraction and smaller deviation when model form discrepancy is included.

CHAPTER 6

CONCLUSIONS

Quantum chemical calculation shows that zwitterions can be stabilized by nearby amine and water molecules. Stabilized zwitterions serve as diffusive intermediates to transport into the PEI bulk and form carbamate. Water-stabilized zwitterions are more numerous and have a lower activation energy compared to amine-stabilized zwitterions. Hydronium carbamates were formed through water-stabilized zwitterions and ammonium carbamates were formed through amine-stabilized zwitterions. The formation of bicarbonate is not favored because of the high energy of formation and activation energy. A new mechanism and chemistry of five chemical reactions in which water plays an important role have been proposed based on these diffusive intermediates.

A reaction-diffusion model based on this new chemistry has been developed and mathematically implemented using a finite volume method. This model is capable of simulating the adsorption of H_2O , and CO_2 , individually or in conjunction in sorbents. The simulation results were compared to the experimental data from TGA. This model reproduced the experimental adsorption behaviors qualitatively and quantitatively under both dry and humid conditions.

This small-scale model has been calibrated to the experimental data through Bayesian calibration using the priors from quantum chemical calculations. Dynamic discrepancy functions were included in the equilibrium constants and diffusion coefficients in the framework of BSS-ANOVA. Using a MCMC routine, uncertainties from both model parameters and model form discrepancy from the adsorption model were quantified in the form of a joint sample-based distribution which is convenient to upscale. The computational speed of MCMC has been improved by the implementation of a reduced-order model. The calibration results

covered the experimental data very well. Posterior samples have been propagated from the joint distribution of model parameters and model form discrepancy to a bubbling fluidized bed adsorber. The profiles of temperature and CO₂ partial pressure in the process model and predictions of carbon capture fraction have been obtained.

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