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## Optimization of Amine-Based Solid Sorbent Chemistry for Post-Combustion Carbon Capture

*Qianwen Gao, ORISE Postgraduate Fellow, National Energy Technology Laboratory  
626 Cochrans Mill Road, Pittsburgh, Pennsylvania, 15236, United States  
[qianwen.gao@contr.netl.doe.gov](mailto:qianwen.gao@contr.netl.doe.gov), 412-386-6927*

*David C. Miller, U.S. Department of Energy, National Energy Technology Laboratory  
626 Cochrans Mill Road, Pittsburgh, Pennsylvania, 15236, United States  
[david.miller@netl.doe.gov](mailto:david.miller@netl.doe.gov), 412-386-6555*

### Abstract:

Numerous solid sorbent materials have been proposed for application to post-combustion carbon capture. These include both physical sorbents such as zeolites and MOFs as well as chemical sorbents such as amine-impregnated silica. To effectively understand the potential of these materials, they need to be evaluated within the context of a complete process that includes both adsorption and regeneration of the capture material. In addition, that process needs to be synthesized and optimized for the particular material. To help guide the discovery and selection of new materials for carbon capture, this paper describes an approach to not only optimize a carbon capture process, but also to optimize the reactivity parameters for a class of amine-based solid sorbents. A diversity of opinion has been expressed in the literature regarding the desire to have a higher or lower enthalpy of reaction. Our approach enables the enthalpy of reaction for all three reactions associated with amine-based solid sorbents to vary, allowing insight into their interaction and providing guidance for tuning the reactivity of future systems.

CO<sub>2</sub> adsorption on amine-based solid sorbents consists of three reactions [1]: (1) water physisorption, (2) bicarbonate formation, and (3) carbamate formation. The reactions can be expressed as  $K_i = \exp(\Delta S_i/R) \cdot \exp(-\Delta H_i/RT)/P$  and  $k_i = A_i T \exp(-E_i/RT)$ , where  $K$  is the equilibrium constant,  $\Delta S$  is the entropy of reaction,  $\Delta H$  is the enthalpy of reaction,  $R$  is the gas constant,  $T$  is the temperature,  $P$  is the overall pressure,  $k$  is the rate constant,  $A$  is the Arrhenius constant and  $E$  is the activation energy. Preliminary sensitivity analysis indicates that the entropy, enthalpy and Arrhenius constant of the bicarbonate and carbamate reactions ( $\Delta S_2$ ,  $\Delta S_3$ ,  $\Delta H_2$ ,  $\Delta H_3$ ,  $A_2$  and  $A_3$ ) have the largest impact on the overall cost of capture. We utilize a solid sorbent system model developed under the Carbon Capture Simulation Initiative (CCSI) [2] in conjunction with the CCSI-developed Framework for Optimization and Quantification of Uncertainty and Sensitivity (FOQUS) [3] to simultaneously optimize process design variables and reaction parameters to determine how much the cost of electricity (COE) could potentially be reduced by a hypothetical sorbent exhibiting different reactivity. Our results indicate that a reduction of 8 % in COE can be achieved compared with the base case sorbent. The improvement results from increasing the fraction of the overall working capacity resulting from the bicarbonate reaction, which arises from increases in the absolute value of  $\Delta H_2$  and  $A_2$ .

### Introduction

Global awareness of carbon dioxide emissions have been rising due to their impact on global warming. Fossil energy based power plants are the largest source of U.S. CO<sub>2</sub> emissions [4]. Extensive research efforts have been dedicated to developing new technologies that can be applied to existing power plants to capture CO<sub>2</sub>. The use of solid sorbent based technologies is one of several approaches being investigated.

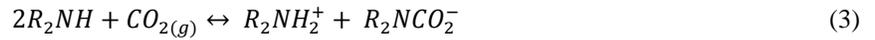
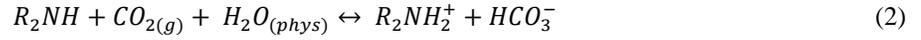
Amines can be immobilized on high surface area solid supports to form a solid sorbent. The U.S. Department of Energy's National Energy Technology Laboratory (NETL) has developed a range of mesoporous sorbent impregnated with polyethyleneimine (PEI) and aminosilanes [5]. The adsorption kinetics of one of these sorbents,

NETL-32D, was studied, and a lumped kinetic model was developed to describe the overall behavior of the sorbent [1].

In this paper, potential modifications of the sorbent chemistry, as represented by the parameters in the lumped parameter kinetic model, are evaluated by simultaneously optimizing the system design and the kinetic model parameters to determine a set of target properties for the sorbent. The cost of electricity (COE) resulting from the power plant with integrated carbon capture system is used as the objective function.

### Sorbent System Modeling

Lee et al. [1] proposed a lumped kinetic model to describe the reactions occurring on amine impregnated porous solid sorbents. This kinetic model assumes three steps involved in the adsorption of CO<sub>2</sub>. Under dry conditions, the amine reacts with carbon dioxide to form carbamate. In the presence of moisture, two other reactions contribute to CO<sub>2</sub> adsorption. Water in the gas phase is physically adsorbed to the sorbent, and adsorbed water can react with amine and CO<sub>2</sub> to form bicarbonate.



The rate constants  $k_i$  and equilibrium constants  $K_i$  in the kinetic model are expressed as follows:

$$K_i = \frac{\exp\left(\frac{\Delta S_i}{R}\right) \exp\left(-\frac{\Delta H_i}{RT}\right)}{P} \quad (4)$$

$$k_i = A_i T \exp\left(-\frac{E_i}{RT}\right) \quad (5)$$

where  $i$  refers to index of the three reactions,  $\Delta S$  is the reaction entropy,  $\Delta H$  is the heat of reaction,  $A$  is the Arrhenius constant,  $E$  is the activation energy,  $P$  is the overall pressure,  $T$  is the temperature.

NETL-32D is a solid sorbent incorporating physically-mixed amines (a branch PEI and N-[3-(trimethoxysilyl)propyl]ethylenediamine) supported on silica gel. The equilibrium and kinetic parameters were determined by fitting experimental data to the proposed model and are shown in Table 1.

Table 1 Kinetic parameters of NETL-32D [1]

Equilibrium parameters				Rate parameters						
$\Delta H_1$	J/mol	-52,100	$\Delta S_1$	J/(mol·K)	-78.5	$A_1$	56,200	$E_1$	J/mol	28,200
$\Delta H_2$	J/mol	-36,300	$\Delta S_2$	J/(mol·K)	-88.1	$A_2$	2.5	$E_2$	J/mol	58,200
$\Delta H_3$	J/mol	-64,700	$\Delta S_3$	J/(mol·K)	-174.6	$A_3$	98.9	$E_3$	J/mol	57,700

The kinetic model is embedded within a model of a Bubbling Fluidized Bed (BFB) reactor [6]. The post-combustion sorbent-based carbon capture system consisting of a 3 bed BFB adsorber, solids heat exchangers and a 2 BFB bed regenerator is shown in Figure 1 and is modeled in Aspen Custom Modeler (ACM) [7]. The BFB's provide favorable mass transfer conditions for solid-gas reactions, and embedded heat exchange tubes provide heating and cooling as required.

The solids heat exchanger model integrates three heat exchangers, two of which are heat integrated and the third uses cooling water. Flue gas containing CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O enters the system at 54 °C. It is first cooled and a portion of the water is knocked out. It then passes through a blower before entering the first bed in the adsorber. After adsorption, the solid sorbent stream is preheated before entering the regeneration unit. The sorbent is regenerated by a temperature swing process with the maximum temperature limited by the sorbent's properties. The majority of the

CO<sub>2</sub> released in the regenerator is compressed and sent for storage, while a small portion is recirculated to maintain fluidization in the regenerator beds. The lean sorbent is cooled and sent back to the adsorber.

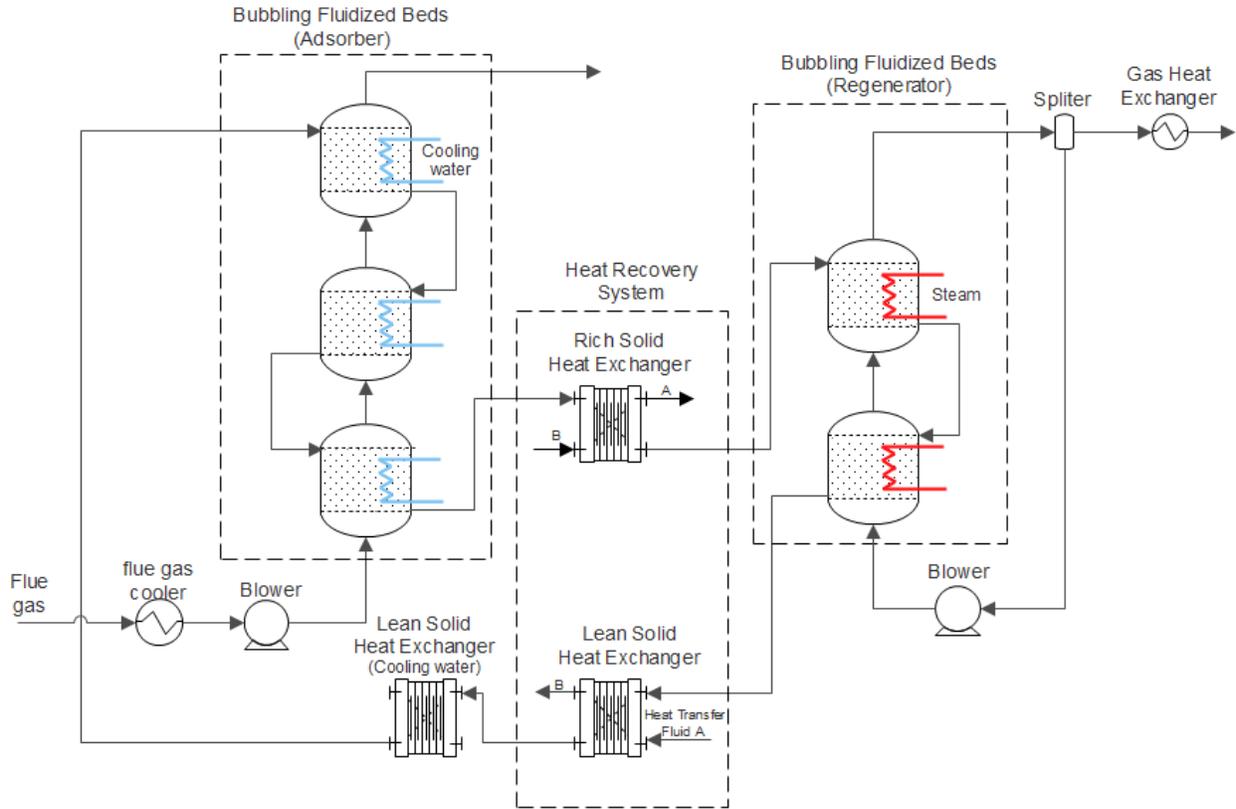


Fig. 1 Solid sorbent-based carbon capture system

Adding carbon capture to a power plant will add to the overall cost of the resulting electricity by both adding capital costs as well as reducing the net power produced from a given boiler and steam cycle. Thus, COE is used to evaluate the performance of the carbon capture system. A base load supercritical pulverized coal power plant is used as the basis for the evaluation [8].

COE is calculated as the ratio of total cost of the power plant to the net power output. The calculation of total costs (TC) is presented in Eq. 6, in which TCC is the total capital costs, OMC is the operating & maintenance costs, CCF is the capital charge factor and CF is the capacity factor. The net power output is calculated in Eq. 7, in which PO is the power output in base power plant without carbon capture while PD is the power demand for sorbent regeneration and other auxiliary equipment in the capture system.

$$TC = TCC \times CCF + OMC \times CF \quad (6)$$

$$NPO = PO - PD \quad (7)$$

Because cost estimation has a large uncertainty, the costs presented in this paper are normalized based on the COE for the base case, NETL-32D sorbent.

### Process Optimization

Multiple nonlinear relationships among the design parameters and sorbent properties affect the COE. Thus, sensitivity analysis on any single parameter is insufficient to obtain a thorough understanding of potential modifications to the sorbent's properties. Instead, a simultaneous optimization approach is applied which enables all

these factors to be considered. The Framework for Optimization Quantification of Uncertainty and Sensitivity (FOQUS) is used to enable large-scale, simulation-based derivative-free optimization of the carbon capture system and sorbent [3].

A rigorous CO<sub>2</sub> capture process model was built in ACM and a spreadsheet for cost calculations is utilized. The CO<sub>2</sub> capture process model and cost analysis are linked to FOQUS for optimization. The optimization problem is formulated as follows.

$$\begin{aligned}
 & \text{Min } f(x) = \text{Cost of Electricity} & (8) \\
 & \text{s. t. } CO_2 \text{ Capture Process model} \\
 & \quad \text{Cost Calculation} \\
 & \quad 0.9 - CO_2 \text{ capture rate} \leq 0 \\
 & \quad x_{min} \leq x \leq x_{max}
 \end{aligned}$$

Decision variables,  $x$ , include design variables including equipment dimensions and operating variables such as temperatures and flowrates with significant impact on the system. These variables are manipulated in FOQUS to minimize the COE. Upper and lower bounds are set for these decision variables, which are based on operating constraints and model limits. An additional constraint requires 90% of CO<sub>2</sub> to be removed from the flue gas.

### Sorbent Optimization

Sorbent properties, which directly affect the kinetics of the adsorption process, play an important role in determining the COE. Rather than evaluating thousands of possible sorbents, this paper identifies the properties, which if they can be obtained will result in a lower COE. Thus, the goal is to provide guidance on ways to improve a sorbent by tailoring its reactivity.

Both carbamate formation and bicarbonate formation contribute to sorbent loading. There are several kinetic and equilibrium parameters of the reactions that affect these loadings: heat of reaction ( $\Delta H$ ), reaction entropy ( $\Delta S$ ), Arrhenius constant ( $A$ ) and activation energy ( $E$ ) of carbamate formation and bicarbonate formation. There are several ways to alter these parameters such as using different types of amines and changing the structure of solid particles. Among these variables, the six listed in Table 2 have the greatest impact on COE and are least constrained physically.

Heats of reaction in bicarbonate and carbamate formation affect reaction equilibrium. They also determine the heat requirements for sorbent regeneration. Density functional theory shows it is possible to tune heats of reaction over a substantial range using substituted amines [9]. Experimental data on various amines also provides a reasonable range for potential reaction enthalpy changes. This lumped parameter model represents both kinetic and mass transfer limitations in terms of the Arrhenius constants. This parameter could be varied significantly by changing the structure of the support. Compared with heats of reaction and Arrhenius constants, reaction entropy and activation energy are more constrained. In this optimization formulation, values of reaction entropy are limited to a small range while the values of activation energy are fixed.

The sorbent optimization problem is formulated similarly to Eq. 8 with the addition of these kinetic parameters as decision variables,  $x$ , to be optimized simultaneously with the design and operating variables.

In the sorbent optimization case, the resulting value of COE is 8 % lower than the base case. The absolute value of  $\Delta H_2$  and  $\Delta H_3$  are higher in the hypothetical sorbent case. The optimized result of  $\Delta H_2$  and  $\Delta H_3$  are values which not only balance the effect of kinetics and energy consumption for sorbent regeneration, but also balance the kinetics of these two reactions. There is a great increase in  $A_2$  of the hypothetical sorbent, which implies  $A_2$  greatly limits the kinetics for the base case sorbent, NETL-32D.

The optimized combination of reaction variables leads to an improvement in sorbent working capacity as compared in Table 3. There is a great increase in the loading resulting from bicarbonate formation while the loading from carbamate is decreased as a result of the competition between these two reactions. The overall loading enhancement results in 31% less sorbent recirculation, which further leads to a reduction of 5% and 11%, respectively, in capital costs and operating costs. The hypothetical sorbent also demonstrates lower regeneration energy.

Table 2 Sorbent property optimization results

	Decision variables	Description	Units	NETL-32D	Hypothetical Sorbent
Reaction Variables	$\Delta H_2$	Heat of reaction in bicarbonate formation	J/mol	-36,300	-46,417
	$\Delta H_3$	Heat of reaction in carbamate formation	J/mol	-64,700	-65,174
	$\Delta S_2$	Reaction entropy in bicarbonate formation	J/mol/K	-88.1	-105
	$\Delta S_3$	Reaction entropy in carbamate formation	J/mol/K	-175	-190
	$A_2$	Arrhenius constant in bicarbonate formation		2.45	100
	$A_3$	Arrhenius constant in carbamate formation		98.9	100
Design & Operating Variables	adsN	Number of parallel adsorption trains		7	6
	rgnN	Number of parallel regeneration trains		5	5
	Ads.Lb	Total adsorber height	m	3.9	4.4
	Rgn.Lb	Total regenerator height	m	7.8	9.3
	adsdt	Adsorber diameter	m	14.4	15
	rgndt	Regenerator diameter	m	9.5	7.4
	F_solids	Total sorbent circulation rate	kg/hr	9,757,580	6,700,610

Table 3 Sorbent property optimization results

System performance	Units	NETL-32D	Hypothetical Sorbent
Bicarbonate delta loading	mol/kg	0.01	0.71
Carbamate delta loading	mol/kg	1.09	0.88
Total delta loading (Sorbent working capacity)	mol/kg	1.10	1.59
Steam usage	kmol/hr	27,790	26,723

## Conclusions

The simulation-based optimization approach helps to identify desirable properties for a hypothetical sorbent. By optimizing the kinetic parameters simultaneously with design and operating variables of the carbon capture system, the COE can potentially be lowered by 8% compared with the reference sorbent. The combination of optimized kinetic parameters balances several factors, resulting in both an overall cost reduction and energy savings. The optimization results indicate that increasing bicarbonate formation is a main factor in lowering the costs. This implies that improving the kinetics of bicarbonate should be investigated further.

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