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KINETIC STUDIES OF DRY SORBENTS FOR MEDIUM TEMPERATURE
APPLICATION

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by

Soon-Jai Khang
T.C. Keener
Zhenwei Wang

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University of Cincinnati, Cincinnati, OH

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Project Manager: Soon-Jai Khang, Professor, Chemical Engineering Department,
University of Cincinnati, Cincinnati, OH 45221
(513) 556-2789

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EXECUTIVE SUMMARY

The purpose of this project is to study the fundamental nature of the sorbent reactivity and reaction kinetics in the medium temperature range from 600° F to 1200° F available in the convective pass of a boiler upstream of the economizer, where dry sorbents are injected to remove SO₂ from the flue gas. Research focus is on the fundamental mechanisms of sorbent-flue gas interaction under economizer and hot baghouse conditions utilizing the experimental setup and the results of the first three years of research.

During the first year study, it was found that a significant portion of unused sorbent was reacted with carbon dioxide in a simulated flue gas (~14%) and produced calcium carbonate. This behavior had not been actively reported in the literature, and thought to be one of the important factors that limit the eventual utilization of calcium based sorbents. During the second year study, it was found that the majority of gas-solid reactions with small sorbent particles are practically reached its final conversions within the first 1 second of reaction time. Furthermore, dolomitic hydrate was found to have better reactivity because its magnesium carbonate has a lower equilibrium temperature than that of pure calcium carbonate, thus increasing the total amount of available lime for better utilization of sorbent material. During the third year study, the experimental techniques were refined to measure the sorbent kinetics within the first 100 milliseconds. Although the sulfation reaction of hydrated lime levels off below 1 second of reaction time, the sulfation reaction of dolomitic hydrate continues beyond 1 second of reaction time. Based on the preliminary test results, it was found that the temperature range of 900° F to 1000° F appeared to be favorable zone for the injection of dolomitic sorbent while the range of 1000 to 1200° F was favorable for lime

sorbent under the tested flue gas conditions in the ductwork. During the fourth year, the interference of carbonation reaction to sulfation reaction was studied as well as the concentration dependency of the sulfation reaction. The data to date showed that the carbonation did not interfere the sulfation reaction rate for reactions taking place less than 1 second. However, there was significant decrease in carbonation conversion when the sulfation reaction took place simultaneously. The levels of SO_2 concentration had negligible effects on reaction rates when the concentration was maintained above 3000ppm. An n-th order deactivation kinetic model was also developed during the fourth year to model the kinetics of various reactions. This model is particularly useful for the dry sorbent reactions, since the apparent rate constants rapidly decrease during the first 1 second of exposure to various gaseous reactants.

I. INTRODUCTION

A. PROBLEM STATEMENT

Sulfur dioxide (SO_2) is emitted from coal fired combustion through oxidation of sulfur contained in the fuel, and causes the problem of acid rain. SO_2 emissions need to be decreased and controlled to meet environmental regulations. The 1990 Clean Air Act Amendment requires to cut SO_2 emission by 50%. The Phase I, takes effective in January 1995, will affect over one hundred existing power plants in the nation and 41 sources in Ohio whose sulfur dioxide emission exceeds the 2.5 lbs sulfur dioxide per million Btu standard.[1,2]. The combined capacity of about 6,000 MW, which is currently on high sulfur Ohio coal, is affected and more than 863,000 tons/year of sulfur dioxide should be reduced in Ohio alone.

Since the New Clean Air Amendment requires a moderate sulfur dioxide emission cut for the existing plants[3], also since the service lives of the impacted existing power plants are generally less than twenty years, the use of the expensive wet scrubber or spray drier(costing over \$ 1,000 per ton of sulfur dioxide removal) is not an economic approach. Additionally, the limited space for the existing power plants makes it difficult to add the space needed for a wet scrubber or spray drier system.

Control technologies such as flue gas desulfurization (FGD) systems reduce SO_2 emission either during or after combustion. In FGD processes, sorbent is usually injected either directly into the boiler/combustor, the flue gas ductwork or into a special reactor vessel. Sorbent injection method is relatively low in capital and operating cost and easy to retrofit to existing plants, especially for applications where options such as coal-switching are not practical.

B. OBJECTIVE

The overall objective of the total program is to improve and develop cost effective retrofit utilizing dry calcium-based FGD process for removing SO_2 from combustion gases.

The specific objective of this work is to obtain the reaction mechanisms and kinetics of medium temperature sorbent injection FGD process: Investigate the influences of injection region temperature, sorbent residence times in both ductwork and baghouse on the SO_2 removal efficiency. For the fourth year, the objective is to experimentally and theoretically study the kinetics by systematically conducting kinetics experiments (contains dehydration, carbonation and sulfation reactions) on the flue gas - calcium based sorbent reactions and analyze the experimental data which would enable us to develop a realistic model to provide practical guides for dry FGD process development.

II. TECHNICAL DISCUSSION

A. LITERATURE REVIEW:

Over the last two decades, the number of FGD processes has increased. The FGD processes used commercially are[4]:

- a) Sorbent injection processes.
- b) Wet scrubbers.
- c) Spray dry scrubbers.
- d) Regenerable processes.
- e) Combined SO_2/NO_x processes.

Sorbent injection processes involve gas/solid reactions. The sorbent is injected into boiler/combustor and/or adjacent ductwork. Calcium compounds are the most common sorbents, and the reactions are affected by temperature and residence time. One of the most economical technologies is the dry sorbents economizer zone injection FGD process.

In dry SO_2 removal processes, the sorbent powder reacts with SO_2 to form a dry product which is removed in the particular collector. As shown in Fig. 1, four general approaches are available or under development for bringing the sorbent into contact with SO_2 : [5]

- 1) Furnace injection of calcium based compound.
- 2) Economizer injection of calcium hydroxide.
- 3) Post furnace injection of calcium hydroxide into combustion products at a higher relative humidity.
- 4) Post furnace injection of sodium based sorbent.

Figure 1. Dry SO₂ Removal Process

These four approaches correspond to the three temperature windows that are available for SO₂ removal: furnace injection at temperature around 1100°C - 1250°C using a variety of calcium-based sorbent, economizer inlet injection between 450°C - 550°C using hydrates, and duct injection either at temperature within 5 - 15°C of adiabatic saturation for hydrates or at 130 - 180°C for sodium sorbents.

Recent work on the hydrate injection process near 537°C for SO₂ control has been focused on the hydrate and injection parameters to maximize SO₂ removal. Researches show that hydroxide can achieve higher SO₂ removal utilization under favorable concentration and, among the calcium-based sorbents, Ca(OH)₂ is superior in performance to both CaCO₃ and CaO [6,7]. Some tests showed that SO₂ capture levels with Genstar pressure hydrated dolomite decreased as the injection temperature was gradually reduced from 1800°F to approximately 1200°F, but increased with further reduction in injection temperature as shown in Fig. 2. Between 800°F and 1200°F, there exists a second sulfation window [8]. And this temperature around 1000°F is a typical temperature in and above economizer section.

Injection at moderate temperatures may not only result in higher sorbent utilizations but also facilitate injection due to the smaller cross-section (denser, higher velocity gas) and ability to insert lances or injection grids. The process, however is effective only with hydrates.

Figure 2. Utilization of Genstar PHDL over a Wide Range of Injection Temperature, with Coal Firing

At these temperatures, SO₂ appears to react very rapidly and directly with calcium hydroxide[9,10]:

The formation of sulfite, however, has to compete with the reaction between the abundant CO₂ and Ca(OH)₂ to form CaCO₃. Below 550°C, both sulfite and carbonate occur, but sulfite formation dominates. Above 550°C, dehydration of the Ca(OH)₂ accelerates, with carbonation and dehydration

occurring at the expense of sulfite formation. Since sulfite formation is very fast (<250 ms) and the window is approximately 100°C wide, the process is compatible with the high quench rates (typically $500\text{--}600^{\circ}\text{C/s}$) through economizers[4].

In term of engineering, there are three advantages of the medium temperature process:

1. The sorbent injection location at 1000°F is typically just above or in the economizer section, eliminating any possible negative impact of sorbent injection on the radiant heat exchanger.
2. The relatively low injection temperature should allow the insertion of simple sorbent injectors into the flow stream and good mixing should be more easily achieved.
3. Because surface area and porosity decay due to thermal sintering can probably be neglected at these low sorbent temperatures, increasing sorbent reactivity through the usage of high reactivity hydroxides looks very promising as demonstrated with the drop-tube reactor at the University of Cincinnati.

Modelling of noncatalytic gas-solid reactions has received considerable interest in recent years mainly because of unsolved problems concerning the removal of sulfur dioxide in the furnace injection process. Many models have been developed to describe the solid conversion versus time relationship during the course of the high temperature reactions.

Shrinking core model is one of the oldest model which assumes that the reaction occurs first at the outer skin of the particle, the zone of reaction then moves into the solid, and may leave behind completely converted material and inert solid. It is the best simple representation for the majority of reacting gas-solid reaction, but there is a limitation with slow reaction of a gas with a very porous particles[11].

Grain model is another old model which concerns gas-solid reaction. According to the theory, a porous particle is comprised of spherical grains of uniform size separated by pores through which the reacting gases diffuse[12].

Some other models have been developed for the fluid-solid reaction. Random pore model allows for arbitrary pore size distributions in the reaction solid. By comparison with the grain model, a relationship is derived between the effective grain shape factor and a pore structure parameter defined[13]. Pore structure variations during gas-solid reactions and the initial pore structure of solid reactant have very important effects on the kinetics of such reactions. Such change would result in variations in point reaction rate constants and effective diffusion coefficients with respect to time and radial position in the porous solid. In the recent works of Ramachandran and Smith [14,15], the effects of porosity changes and sintering on the gas-solid reactions have been analyzed using the single-pore and grain models. At higher temperature, theoretical models which account for pore size, particle structure, pore closure, calcination, sintering, sulfation and heat and mass transfer have been developed[16,17,18]. In these kind of models, pore diffusion, product-layer diffusion and sintering are considered to be the principal processes that govern the rate of SO_2 capture for the hydrate particles.

Homogenous model is the kind of model dealing with very porous material. The gas diffuses rapidly throughout the entire particle. The diffusion resistance can be eliminated and the reaction takes place based on the remaining of the reactant solid.

Although there are some models which can describe the gas-solid reactions, but to the special case of flue-gas desulfurization, the development of proper kinetic models is still being studied.

B. EXPERIMENTAL PROCEDURE

For dry economizer injection process, in the medium temperature range, some preliminary test results show that the sorbent-flue gas reactions are not sensitive to the resident time after 0.5 second. In this study, a fast reaction reactor, drop-tube reactor, has been built and used for the experimental work.

The drop-tube reactor, as shown in Fig. 3, consists of a furnace, a preheating and reaction tube, a heat exchanger, a sorbent feeder (Fig. 4), a quenching system, and a sorbent collection system. The reactor consists of two concentric stainless steel tubes (0.5 inch I.D. and 1.5 inch O.D., respectively) which are housed within a tube furnace. The furnace is 3-foot-long, 3-inch-I.D. Lindberg model 55347-4 with three independently controlled heating zones, capable of maintaining a temperature up to 1200°C. Reactant gas is preheated in the annular volume between the outer and inner reactor tubes. The reactant gas enters the bottom of the reactor and passes upward through the preheating zone to the top of the reactor and then makes a 120° turn to enter the inner tube forming two hot jets. At the top of the reactor, sorbent particles are injected into the reactor just above the incoming hot jets by means of a feed system described below. Thus, the sorbent stream is impacted by the hot reactant gas jets within a very short period of time. The jet impaction creates severe turbulence and in turn causes rapid heating of the sorbents. Heat transfer calculation [19], indicates that sorbent particles of less than 10 μ m size will be heated within a few milliseconds after injection into the reactor, providing a well mixed isothermal mixture of the gas and solid particles. The gas and particles pass downward through the isothermal reactor tube and as soon as the sorbent particles leave the reaction chamber, they are quickly quenched by pure nitrogen. To monitor the temperature profile inside the reactor, five type-K thermocouples are inserted into the reactor chamber through

the stainless steel thermocouple ports. The output signals from the thermocouples are sent to a computer data acquisition system.

Figure 3. Drop-Tube Reactor System

The sorbent particles are fed into the reactor by a sorbent feeder which is shown in Fig. 4. The sorbent particles are blown into the reactor by the carrier gas, which flows over the surface of a sorbent bed and discharged out of a side branch tube. The feeding rate is controlled by changing the carrier gas flow rate. In the reactor, the flow rate of the particles is assumed as same as the flow rate of carrier gas. A test indicated a stable flow of the sorbent particles can be obtained for about 10 μ m size particles.

A group of TGA tests were conducted under the same temperature range as was in the collection chamber, the results showed that for all the possible reactions the weight changes during reaction time of 15 minutes were below 1%. It indicates that we can safely assume there is no further reaction in the collection chamber. However, in order to prevent the product from reacting with air, the collection chamber and the balance used for sample elemental analysis were wrapped with glove bags purged with N₂.

An elemental analyzer, LECO analyzer, has been used to measure the weight percentages of carbon and hydrogen content. A total sulfur analyzer has been used to measure the weight percentage of sulfur content.

Figure 4. Schematic Diagram of the Sorbent Feeder.

C. WORK PERFORMED AND RESULTS

a. Experimental Work

The experimental studies for the carbonation, sulfation and simultaneous carbonation/sulfation reactions of $\text{Ca}(\text{OH})_2$ were conducted in the drop tube reactor. For the sulfation and simultaneous carbonation/sulfation reactions, SO_2 with different concentrations has been used in the reactions to see if the concentration of SO_2 will effect conversion.

At medium temperature range, using $\text{Ca}(\text{OH})_2$ technical powder as sorbent, the possible reactions are:

In order to study the kinetics of all these reactions between the flue gas and the calcium-based sorbent, and consider as many as possible reactions and their intereffects which exist in the FGD processes, we need to study these reactions both individually and simultaneously to know the kinetics.

Groups of carbonation and sulfation and simultaneous tests were carried out at the residence times from 0.05 to 0.1 second and at the temperature from 600°F to 1100°F to investigate the influences of temperature and residence time in ductwork. For each combination of residence time and temperature, the tests were repeated to ensure the reproducibility of data.

The reaction conditions are:

Reaction Temperature: 600°F, 900°F, 1100°F.

Reaction Residence Time: 50ms, 75ms, 100ms.

1) Carbonation reaction:

For the carbonation reaction, the reaction gas is 14% CO₂ balanced with nitrogen, and quenching gas is 99.99% N₂

The results for carbonation reactions of Ca(OH)₂ at different temperatures and residence times are listed in Table I.

Table I. Carbonation Reaction of Ca(OH)₂

	Rxn Temperature	Run Number	50 ms	75 ms	100 ms
H wt%	600 °F	#1	2.556	2.459	2.672
		#2	2.567	2.521	2.524
	900 °F	#1	2.194	2.097	2.170
		#2	2.23	2.208	2.161
	1100 °F	#1	1.743	1.693	1.713
		#2	1.739	1.648	1.645
C wt%	600 °F	#1	1.454	1.408	1.593
		#2	1.495	1.386	2.067
	900 °F	#1	2.426	2.666	2.690
		#2	2.401	2.670	2.656
	1100 °F	#1	4.617	4.952	5.004
		#2	4.742	5.010	4.944
Conv. %	600 °F	#1	3.57	3.25	4.55
		#2	3.86	3.097	7.92
	900 °F	#1	10.52	12.28	12.45
		#2	10.33	12.30	12.22
	1100 °F	#1	27.35	30.09	30.51
		#2	28.37	30.56	30.02

From the above results, it is shown that for the carbonation reaction, the conversion of carbonation increases continuously and significantly from 3% to 30% with increasing temperature. However, it seems that the conversion is not much sensitive to the residence time at the same temperature. Fig. 5 illustrates the change of reaction conversion with reaction temperature and residence time. The increment of conversion from 900°F to 1100°F is larger than that from 600°F to 900°F. This may imply that 900°F is a significant temperature to be taken into account, and it may effect some other reactions in further study.

The results of BET surface area measurements for the samples from carbonation reactions are listed in Table II. It is shown that the surface area decreases with increasing temperature, because more intense carbonation reaction takes place in the powder at higher temperature. Fig. 6 is the graph of BET surface area changing with reaction time and temperature.

Table II. BET Surface Areas from the Carbonation Reaction.

	Rxn Temperature	Run Number	50 ms	75 ms	100 ms
Surface Area (m ² /g) Original: 10.(m ² /g)	600°F	#1	5.774	6.044	5.880
		#2	5.782	5.953	5.869
	900°F	#1	5.168	3.900	4.056
		#2	4.380	3.815	-----
	1100 °F	#1	2.370	2.616	2.303
		#2	2.294	2.281	2.997

* Data for #1 and #2 were obtained from two separate runs which were under the same reaction condition in order to see if the experiments are reproducible. It is shown that most of the data of

group#1 and group#2 are very close to each other.

Figure 5. Conversion Changes with Temperature and Residence Time in Carbonation Reaction

Figure 6. BET Surface Area Changes with Temperature and Residence Time in Carbonation Reaction

2) Sulfation reaction:

The sulfation reactions without carbon dioxide have been completed also. The experimental conditions are:

Reaction Temperature: 600°F, 900°F, 1100°F

Reaction Residence Time: 50ms, 75ms, 100ms

Reaction Gas: 3000ppm SO₂ balanced with N₂

Quenching Gas: pure N₂ (99.99%)

The collected samples are analyzed for carbon and hydrogen contents. The sulfur content is measured by the Total Sulfur Analyzer. The results are listed in Table III.

Table III. Sulfation reaction of Ca(OH)₂

	Rxn Temperature	Run Number	50 ms	75 ms	100 ms
S wt%	600 °F	#1	0.784	0.606	0.8203
		#2	0.891	0.786	0.871
	900 °F	#1	2.871	2.371	2.533
		#2	2.106	2.189	2.216
	1100 °F	#1	3.042	2.533	3.659
		#2	2.884	3.059	3.805
Conv. %	600 °F	#1	1.989	1.540	2.087
		#2	2.262	1.995	2.216
	900 °F	#1	7.571	6.210	6.628
		#2	5.446	5.698	5.749
	1100 °F	#1	8.021	6.960	10.087
		#2	7.584	8.552	10.619

As shown in the above table, the sulfur content and the conversion increase with temperature

from 600°F to 1100°F. At lower temperature, the residence time seems to have no effect on the reaction. But at higher temperature, the conversion increases a little bit with temperature increasing. The reproducibility of sulfation reaction data is also good, although some results of the two groups do not fit so well as for the carbonation reaction. This may be due to the poor accuracy of the total sulfur analyzer. The conversion of the sulfation reaction is lower than the conversion of the carbonation reaction. But comparing the concentration of CO₂ and SO₂, we see that SO₂ is more reactive.

However, the BET surface area measurements of the product showed that there is almost no obvious relationship between the BET surface area and temperature or residence time, though the sulfur content increases continuously with temperature.

Table IV. BET Surface Areas from the Sulfation Reactions.

	Rxn Temperature		50 ms	75 ms	100 ms
Surface Area (m ² /g) Original: 10(m ² /g)	600°F	#1	8.168	5.972	8.444
		#2	7.843	9.670	7.378
	900 °F	#1	6.015	8.267	8.877
		#2	6.519	6.751	7.175
	1100 °F	#1	6.353	6.725	8.386
		#2	5.344	6.227	7.731

The relationship between conversion of sulfation reaction and residence time and temperature is shown in Fig. 7.

Figure 7. Conversion Changes with Temp. and Residence Time in Sulfation Reaction

3) Simultaneous carbonation/sulfation reaction:

Groups of simultaneous carbonation/sulfation reaction tests were also performed at residence times from 0.05 to 0.1 second and at temperatures from 600°F to 1100°F. Both CO_2 and SO_2 react with the $\text{Ca}(\text{OH})_2$. The experimental conditions used are listed below:

Reaction Temperature: 600°F, 900°F, 1100°F

Reaction Residence Time: 50ms, 75ms, 100ms

Reaction Gas: 14% CO_2 , 3000ppm SO_2 , 3% O_2 balanced with N_2

Quenching Gas: Pure Nitrogen

The product samples are analysed for the H, C, and S contents by LECO Elemental Analyzer and by the Total Sulfur Analyzer. The results of the conversion of carbonation and sulfation reaction under different experimental conditions were obtained after the data treatment and are listed in Table V.

Table V. Simultaneous Carbonation/Sulfation of $\text{Ca}(\text{OH})_2$

	Rxn Temperature	Run Number	50ms	75ms	100ms
C wt%	600°F	#1	1.379	1.263	1.231
		#2	1.307	1.252	1.19
	900°F	#1	2.231	2.113	2.11
		#2	2.23	2.104	2.197
	1100°F	#1	4.049	3.684	3.503
		#2	4.583	3.586	3.843
S wt%	600°F	#1	1.753	1.197	1.251
		#2	1.503	1.266	1.192
	900°F	#1	1.667	2.53	2.363
		#2	2.045	2.684	2.561
	1100°F	#1	2.213	2.993	2.9
		#2	1.801	3.356	3.417
Conv. % (Carbon)	600°F	#1	3.652	2.754	2.536
		#2	3.105	2.686	2.241
	900°F	#1	9.827	9.155	9.094
		#2	9.912	9.124	9.792
	1100°F	#1	24.15	21.25	19.99
		#2	28.33	20.35	22.66
Conv. %	600°F	#1	4.539	3.065	3.204
		#2	3.870	3.244	3.047
	900°F	#1	4.396	6.744	6.282
		#2	5.425	7.169	6.843
	1100°F	#1	6.149	8.256	8.025
		#2	5.036	9.194	9.507

From the results, we can see that for the simultaneous carbonation/sulfation reaction, carbon content increases continuously with increasing temperature. But with residence time, trend is somewhat different compared to the carbonation reaction. At temperatures of 600°F and 900°F, the carbon content almost does not change with increasing residence time. But at 1100°F, the carbon content is higher at the residence time of 0.05s than at 0.075s and 0.1s. That means the conversion of carbonation decreases with residence time increase. The carbon content is lower than that of the individual carbonation reaction without SO_2 at the same reaction conditions since the sulfation reaction competes with carbonation reaction. Fig. 8 shows the conversion of carbonation reaction changes with temperature and residence time in sulfation/carbonation reaction.

Like sulfation reaction without CO_2 , the change of residence time has effect on both the sulfur content and conversion of sulfation. At higher temperature, the conversion of sulfation increases with residence time, but this trend is not obvious at the lower temperature condition, as shown on Fig. 9. But compared to the individual sulfation reaction, it does not seem that the existence of CO_2 has limited the reaction between SO_2 and Ca(OH)_2 . However, at higher temperature, the existence of SO_2 limits the reaction between Ca(OH)_2 and CO_2 for longer residence time. The high reactivity of SO_2 with Ca(OH)_2 at high temperature has also been found in the individual sulfation reaction performed previously. From the data, it is shown that at higher temperature, (1100°F), the sum of conversions of both sulfation and carbonation is very close to the conversion of individual carbonation reaction of 30%. This may imply that 30% is the maximum conversion under the condition employed.

The BET surface areas of the products have been measured. The results are listed in Table VI. The instrument did not identify how much of the change in BET surface area is caused by

carbonation, and how much is caused by sulfation reaction. As we previously reported, since the BET surface area for carbonation reaction without SO_2 decreased with increasing temperature, whereas the BET for sulfation reaction without CO_2 did not show any apparent changes. This may be due to the fact that more carbonation reaction takes place in the reactor (the conversion of carbonation is higher than that of sulfation due to the higher concentration of CO_2). It appears that most change in BET surface area for carbonation/sulfation is due to the carbonation reaction. Fig. 10 shows the BET surface changes with temperature and residence time in simultaneous reaction.

Table VI. BET Surface Area from the Sulfation Reaction

	Rxn Temperature		50ms	75ms	100ms
Surface Area (m^2/g)	600° F	#1	9.037	9.669	9.026
		#2	8.664	10.32	9.549
	900° F	#1	5.896	4.953	4.795
		#2	5.432	4.865	8.138
	1100° F	#1	6.104	5.162	
		#2	4.717	4.781

Figure 8. Conversion of Carbonation Changes with Temperature and Residence Time in Simulation Reaction

Figure 9. Conversion of Sulfation Changes with Temperature and Residence Time in Simultaneous Reaction

Figure 10. BET Surface Area Changes with Temperature and Residence Time in Simultaneous Reaction

b. Modelling Work.

For all the possible reactions in the reactor, we have made the following assumptions:

- A) For the dehydration reaction, a homogeneous reaction is assumed
 - a) Uniform reaction (No pore-diffusion-resistance).
 - b) The rates are proportional to the amounts of respective reactants remaining in sorbent particles.
- B) CaO and Ca(OH)₂ have the same reaction rates with CO₂ and SO₂.
- C) For material balance calculation; we assume that Ca(OH)₂ decomposes based on the rate measured for the dehydration only experiments (No SO₂, CO₂ etc., pure N₂ only).

Based on the above assumptions, the modelling work is done for carbonation and sulfation reactions.

1) Carbonation Reaction.

Based upon the assumption B, the CaO and Ca(OH)₂ have the same reaction rates with CO₂ and SO₂, the carbonation reaction rate becomes:

$$-r_{\text{CO}_2} = k_{\text{CO}_2} (1 - x_{\text{Ca(OH)}_2}) C_{\text{CO}_2}^a a_{\text{CO}_2}$$

where a is the activity of the sorbent, and is a function of time, $-\frac{da_{\text{CO}_2}}{dt} = k_{\text{CO}_2} a_{\text{CO}_2}$,

By solving the activity equation, the activity becomes an independently decreasing exponential function: $a = e^{-k_{\text{CO}_2} t}$

The CO₂ concentration we used was 14%, which was kept constant during the reaction. From

the data results, there is no CaO exists in the product, therefore we can substitute the equation of activity into the reaction rate equation and simplify the reaction rate equation. The equation then becomes:

$$-r_{\text{CO}_2} = K_{\text{CO}_2} (1 - x_{\text{CO}_2}) e^{-k_{\text{aCO}_2} t}$$

where $K_{\text{CO}_2} = k_{\text{CO}_2} * C_{\text{CO}_2}^n$

When $t = 0$, the conversion is 0. We assume that when time is very short ($< 50\text{ms}$), the activity is about 1. Under those initial conditions, we can first solve for K_{CO_2} using the initial slope. Then by using methods of regression and trial and error, we can find another coefficients k_{aCO_2} in the above reaction rate equation.

Fig. 11 shows the simulated curves resulted from the reaction rate equation. Experimental data are also shown for comparison.

Figure 11. Comparison Between Simulated Curves and Experimental Data for Carbonation Reaction

From the results of these curve fittings, we can see that the simulated curves can represent the general trends of the reaction, especially for the relatively lower temperature reactions (600°F and 900°F). The curves fit the experimental data well. However, at temperature of 1100°F, there is some discrepancy between the data and the curve, which will be reanalyzed during the 5th year of this project.

2) Sulfation reaction

For the sulfation reaction, and the sulfation reaction in the simultaneous reactions, the assumptions are similar to those for the carbonation. The similar reaction rate equation are derived:

$$-r_{SO_2} = k_{SO_2}(1-x_{Ca(OH)_2})C_{SO_2}^{n'}a_{SO_2} \quad \text{and} \quad -r_{CaSO_3} = -r_{SO_2}$$

Since we raised the concentration of SO_2 to 6000ppm, (see Fig. 12) and yet it did not seem to affect conversion, we can neglect C_{SO_2} , and use the same way as the previous section. Fig 13 and Fig. 14 show the resulting reaction curves and the experimental data for the sulfation reaction and, the sulfation reaction in the simultaneous reactions, respectively.

Figure 12. Sulfation Conversion

Figure 13. Comparison Between Simulated Curves and Experimental Data of Sulfation Reaction

Figure 14. Comparison of Simulated Curves and Experimental Data of Sulfation in Simultaneous Reaction

By comparing the simulated curves and experimental data in the above figures, we see that the curves fit the data quite well and fit the data better for sulfation reaction than for carbonation reaction. So the assumptions we made may be suitable for these reactions, especially for sulfation reaction. However, more detailed kinetic studies are still needed.

3) Simultaneous reactions

For carbonation in simultaneous reaction, since the CaCO_3 may react with SO_2 , the reaction rate equation is more complicated than that of carbonation reaction with SO_2 .

$$-r_{\text{CaCO}_3} = (-r_{\text{CO}_2}) - k_{\text{CaCO}_3} C_{\text{SO}_2} x_{\text{CaCO}_3}^a - k' x_{\text{CaCO}_3}$$

The coefficients in this equation will be analyzed out in the future work.

III. FUTURE WORK

The major work in the final year will be mainly the modelling work.

We have done most of the experiments and recorded most results. From the results, we made assumptions and fitted the curves, even though the detailed reaction mechanisms and kinetics are still unknown. We will continue the modelling of simultaneous carbonation/sulfation reaction during the next year.

The future work to be performed includes:

- 1) Obtaining the reaction mechanism and kinetics of medium temperature sorbent injection injection FGD process in terms of the n-th order deactivation kinetic model: Investigate the influences of injection temperature, residence times in ductwork on the SO_2 removal.
- 2) Investigating interactions between the sulfation and the carbonation reaction: Investigate the influences of CO_2 on the SO_2 removal process and the sorbent utilization.

IV. CONCLUSIONS

- 1) Simultaneousducibility of the experimental data in the drop-tube reactor is good. The data obtained are thus reliable.
- 2) All the reactions are temperature dependent. For the carbonation reaction, residence time has little effect under the conditions studied. The conversion changes significantly when temperature increases from 900EF to 1100EF. For the sulfation reaction, the residence time has more effect on it, especially for sulfation reaction in simultaneous reaction.
- 3) Sulfation reaction and carbonation reaction compete with each other in the reactor, especially at higher temperature. The existence of CO_2 does not seem to interfere the reaction of SO_2 .

very much. However, the existence of SO_2 interferes with the reaction of CO_2 . The conversion of carbonation decreases with residence time increase. It appears that CaCO_3 reacts with SO_2 .

- 4) All the reactions seem to reach its upper limit after 75ms.
- 5) The sum of x_s and x_c is very close to carbonation conversion without SO_2 : About 30%.
- 6) For the modelling work, the simulated curves fit the experimental data well for the sulfation reaction. The assumption in this report we made may be suitable for that type of reaction.
- 7) For carbonation reaction, the reaction rate equation seems to fits the data at 600EF and 900EF well. But for the reaction at 1100EF, there is some discrepancy between the fitted curve and the data. It will be necessary to consider more factors to closely describe this reaction.

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