OCDO--97001487

Project Number: OCRC/93-4.9

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FINAL REPORT

Kinetic Studies of Dry Sorbent for Medium Temperature Applications

This Project was funded in part
by the Ohio Coal Development Office
Department of Development
State of Ohio

Date: July 12, 1996 (Revised)

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DEPARTMENT OF DEVELOPMENT
OHIO COAL DEV OFFICE

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EXECUTIVE SUMMARY

The purpose of this project is to investigate the fundamental nature of sorbent reactivity and reaction kinetics in the medium temperature range from 600°F (315°C) to 1200°F (649°C) 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 focuses on the mechanisms of sorbent-flue gas interaction under economizer and hot baghouse conditions utilizing the experimental setup and the results of the first four years of research.

During the first year study, it was shown 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 well explored in the literature and yet, thought to be one of the important factors that limit the eventual utilization of calcium-based sorbents. During the second year study, it was shown that the majority of gas-solid reactions with small sorbent particles practically reached its final conversions within the first one 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 one second of reaction time, the sulfation reaction of dolomitic hydrate continues beyond one second of reaction time. Based on the preliminary test results, it was shown that the temperature range of 900°F (482°C) to 1000°F (538°C) appeared to be a favorable zone for the injection of dolomitic sorbent while the range of 1000 to 1200°F (538 to 649°C) was favorable for lime

sorbent under the tested flue gas conditions in the duct work. During the fourth year, the interference of carbonation reaction to sulfation reaction was investigated as well as the concentration dependency of the sulfation reaction. The data showed that the carbonation did not interfere the sulfation reaction rate for reactions taking place less than one second, although the long-term sulfation conversion would be lower with carbonation. However, there was significant decrease in carbonation conversion when the sulfation reaction took place simultaneously. During the fifth year, research work has been focused on studying the reaction mechanisms and kinetics of medium temperature sorbent injection FGD process in terms of the n-th order deactivation kinetic model. The first-order deactivation model has been successfully applied for carbonation, sulfation and simultaneous reaction. For carbonation reaction, a constant concentration model is applied. For sulfation reaction, since the concentration of SO_2 changes significantly after reaction, it is considered a variable in the model development. For the simultaneous reaction, based on the observations from experimental data on conversion changes for both carbonation and sulfation reactions, it is concluded that the nascent form of CaCO_3 produced from carbonation reaction can further react with SO_2 to form CaSO_3 . Kinetic studies have shown that the proposed models fit the experimental data well. This model is particularly useful for the dry sorbent reactions, since the apparent rate constants rapidly decrease during the first one second of exposure to various gaseous reactants.

1 INTRODUCTION

1.1 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 one to cut SO_2 emission by 50%. The Phase I took effect in January 1995 and has affected 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, 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[3]. 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.

1.2 Objective

The overall objective of the university program is to enhance the development of dry sorption processes for the economical removal of high levels of SO_2 .

The specific objective of this task is to develop the reaction mechanisms and kinetics of the 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 fifth year, the objective remains to experimentally and theoretically investigate the kinetics by systematically conducting kinetics experiments (contains dehydration, carbonation and sulfation reactions) on the flue gas - calcium based sorbent reactions and analyzing the experimental data which would enable us to develop a realistic model to provide practical guides for dry FGD process development.

The former test results showed that the majority of reactions between the flue gas and the sorbent did not progress rapidly after 500 ms. This year's research has been focused on studying all aspects of the sorbent-flue gas reaction kinetics within the first 100ms in the medium temperature range from 315°C to 593°C.

2 TECHNICAL DISCUSSION

2.1 Literature Review:

Experimental

Over the last two decades, the number of FGD processes has increased. The FGD processes used commercially can be loosely classified into the following categories[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. Among many established technologies, the dry sorbent economizer zone injection FGD process is potentially most economical.

In dry SO_2 removal processes, the sorbent powder reacts with SO_2 to form a dry product which is removed in the particulate collector. As shown in Figure 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 (1100 - 1250°C).
- 2) Economizer injection of calcium hydroxide (450 - 550°C).
- 3) Post furnace injection of calcium hydroxide into combustion products at higher relative humidity (5 - 15°C above adiabatic saturation).
- 4) Post furnace injection of sodium-based sorbent (130 - 180°C).

These four approaches correspond to particular temperature windows that are available for SO_2 removal: furnace injection at temperature around 1100 - 1250°C using a variety of calcium-based sorbent, economizer injection between 450 - 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.

Figure 1. Dry SO₂ Removal Process

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 (982°C) to approximately 1200°F (649°C), but increased with further reduction in injection temperature as shown in Figure 2. Between 800°F (427°C) and 1200°F (649°C), there exists a second sulfation window [8]. And this temperature around 1000°F (538°C) 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.

At these temperatures, SO₂ appears to react very rapidly and directly with calcium hydroxide in either air or nitrogen environment[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 500-600°C/s) through economizers[4].

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

1. The sorbent injection location at 538°C 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.

Figure 2. Utilization of Genstar PHDL over a Wide Range of Injection Temperature, with Coal Firing [8]

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.

Modeling

Modeling 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 very porous particles[11].

Grain model is another old model which concerns gas-solid reaction. According to the theory, a porous particle consists 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] and Simons et al.[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 this 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. Simons et al.[19] developed a kinetic model for sulfation reaction with CaO for a high temperature range (700 - 1,205°C). Based on the pore branching and pore plugging assumptions, their model included a sulfation rate constant which changed linearly with the partial pressure of SO_2 .

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 at high temperature, but to the special case of flue-gas desulfurization in the medium temperature range (450 - 550°C), the development of proper kinetic models is still being studied.

2.2 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 residence 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 Figure 3, consists of a furnace, a preheating and reaction tube, a heat exchanger, a sorbent feeder (Figure 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 [20], indicates that sorbent particles of less than 10µm size will be heated within a few milliseconds after injection into the reactor, providing an 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 and diluted by large amount of nitrogen gas(in a ratio of dilute gas/reactant gas up to 10 based on need) supplied from N₂ cylinder. The particles were collected on a paper filter. The temperature of the exhausted gas through the paper filter was maintained around 45°C and monitored.

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 3a Drop-Tube Reactor System

The sorbent particles are fed into the reactor by a sorbent feeder shown below. 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 and tests indicated a stable flow of the sorbent particles can be obtained

for about 10 μ m size particles.

In order to verify that the sorbents would stop reacting after they were collected in the collection chamber, 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%. Therefore, we could safely assume that there was no further reaction in the collection chamber. However, in order to prevent the product from reacting with air, the collection chamber and the balance were wrapped with glove bags purged with dry N₂.

An elemental analyzer, LECO analyzer, was used to measure the weight percentages of carbon and hydrogen content. A total sulfur analyzer was used to measure the weight percentage of sulfur content. A brief description on these and other analytical equipment used for the experiments is listed in the following subsections.

Figure 3b Schematic Diagram of Sorbent Feeder

2.2.1 Instruments for Product Analysis

Elemental Analyzer (CHNS-932, from LECO Corp.):

The basic principle of the analysis is to first combust the reaction products at high temperature (up to 1000°C) to form CO₂ and H₂O. The CO₂ and H₂O are then swept through the nondestructive infrared absorption detection system where they can be measured in the amount. The weight percentage of C and H can be obtained from mass balance calculations. It should be noted that the “weight percentage” is measured rather than the “mole percentage” due to the fact that only selective components (C, H, N and S) in a sample are measured. This analyzer is not suitable for sulfur in calcium sulfate (CaSO₄).

Total Sulfur Analyzer (LECO-571-500):

By combusting the sample at 1600°C, SO₂ is produced from all forms of sulfur compounds and then introduced to H₂O₂ solution to form H₂SO₄. Then by neutralization of the NaOH solution with known concentration, the sulfur content can be determined.

The weight percentage of S is obtained by mass balance.

BET Surface area Analyzer (Gemini 2360, from Micromeritics):

N₂ adsorption at 77°K at relative pressure (p/p₀) ranging from 0.01 to 0.35 was performed to measure the BET surface areas of the product samples.

Thermogravimetric Analyzer (TGA-951, from Du Pont):

TGA technique is used in this research for some mass balance calculations and the selection of appropriate experimental conditions.

2.3 Experimental Summary and Data Processing

2.3.1 Experimental Summary

The experimental work was performed systematically according to the experimental conditions. At medium temperature range, using Ca(OH)₂ technical powder 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 to consider as many as possible reactions and their interactions which exist in the FGD processes, we need to study these reactions both individually and simultaneously to follow the reaction kinetics.

Since the study is focused on economizer injection of calcium hydrate, where the temperature is about from 600°F to 1200°F, 600°F, 900°F and 1100°F were chosen as reaction temperatures. Also, since the sorbent-flue gas reactions are not sensitive to the residence time after 0.5 second, 50ms, 75ms and 100ms were selected as reaction residence times.

Groups of carbonation, sulfation and simultaneous carbonation/sulfation tests were carried out under controlled reaction conditions to investigate the influences of temperature and residence time in the economizer section. In addition, the concentration of SO_2 was changed from 3000 ppm to 6000 ppm to investigate the effect of SO_2 concentration on sulfation kinetics. For each combination of residence time and temperature, the tests were repeated to ensure the reproducibility of experimental data. The original and product samples were analyzed by LECO elemental analyzer for carbon and hydrogen contents (weight percentage) and the total sulfur analyzer was used to measure the sulfur content (weight percentage). The conversions of the reactions were calculated based on these results as described in the next section. The BET surface areas of the samples were also measured.

2.3.2 Data Processing

After the weight percentages of C, H and S have been measured, the conversion of each reaction can be calculated based on the mole balance. Since all the reactions mentioned above are equal molar reactions, the mole fraction was used to calculate the conversions.

1) Original sample:

Since the original sample consists of only Ca(OH)_2 , CaCO_3 and CaO , the following mass balance equations are used.

$$W_{\text{CaO}} \% = 100 - \frac{H\%}{2M_{W,H}} \times M_{W,\text{Ca(OH)}_2} + \frac{C\%}{M_{W,C}} \times M_{W,\text{CaCO}_3} \quad (2.1)$$

$$M_T = \frac{H\%}{2M_{W,H}} + \frac{C\%}{M_{W,C}} + \frac{W_{\text{CaO}} \%}{M_{W,\text{CaO}}} \quad (2.2)$$

$$F_{\text{Ca(OH)}_2,0} = \frac{H\%}{2M_{W,H}} \cdot \frac{1}{M_T} \quad (2.3)$$

$$F_{\text{CaCO}_3,0} = \frac{C\%}{M_{W,C}} \cdot \frac{1}{M_T} \quad (2.4)$$

where W_{CaO} is the weight percentage of CaO in original sample,

$M_{W,X}$ is the molecular or atomic weight of substance X

M_T is the total moles in the sample, and

$F_{X,0}$ is the initial mole fraction of substance X.

2) Carbonation reaction:

After carbonation reaction, H% and C% of a product sample are analyzed. By using the same method for the original sample, the mole fraction of CaCO_3 , F_{CaCO_3} , can be obtained. The conversion of carbonation reaction, X_{CaCO_3} , can be expressed by the following equation,

$$X_{\text{CaCO}_3} = \frac{F_{\text{CaCO}_3} - F_{\text{CaCO}_3,0}}{F_{\text{Ca(OH)}_2,0}} \quad (2.5)$$

where $F_{\text{CaCO}_3,0}$ and $F_{\text{Ca(OH)}_2,0}$ are the initial mole fractions of CaCO_3 and Ca(OH)_2 , respectively.

3) Sulfation reaction:

After the sulfation reaction, S% of the solid product is measured in addition to H% and C%. The following material balance equations are used for sulfation conversion, X_{CaSO_x} ,

$$W_{CaO}\% = 100 - \frac{H\%}{2M_{W,H}} \times M_{W,Ca(OH)_2} + \frac{C\%}{M_{W,C}} \times M_{W,CaCO_3} + \frac{S\%}{M_{W,S}} \times M_{W,CaSO_3} \quad (2.6)$$

$$M_T = \frac{H\%}{2M_{W,H}} + \frac{C\%}{M_{W,C}} + \frac{S\%}{M_{W,S}} + \frac{W_{CaO}\%}{M_{W,CaO}} \quad (2.7)$$

$$F_{CaSO_3} = \frac{S\%}{M_{W,S}} \cdot \frac{1}{M_T} \quad (2.8)$$

$$X_{CaSO_3} = \frac{F_{CaSO_3}}{F_{Ca(OH)_2,0}} \quad (2.9)$$

4) Simultaneous reaction:

The same calculation method for sulfation and carbonation reaction are used for the simultaneous reaction and the conversions for both carbonation and sulfation are obtained.

2.4 Results and Discussion

2.4.1 Carbonation Reaction

Carbonation reactions were performed in the drop tube reactor to study the effect of CO₂ on the desulfurization process. For these tests, the reactant gas was a mixed gas that contained 14% CO₂ balanced with N₂. The experimental conditions used are listed below:

Inlet to the reaction zone

Temperature: 600°F (315°C), 900°F (482°C), 1100°F (593°C)

Sorbent Feed Rate: 250 mg/min of Ca(OH)₂ powder

Reaction Gas: 14% CO₂ balanced with N₂, flowrates adjusted to maintain the reaction residence times of 50ms, 75ms and 100ms

Reaction zone

Temperature: Isothermal at 600°F (315°C), 900°F (482°C), 1100°F (593°C)

Outlet of the reaction zone

Quenching Gas: pure N₂ (99.99%) up to 20 times of dilution to maintain about

45°C on the collection filter

Run time : 10 minutes (2.5 g of sorbent injection) for each run

The reaction gas was supplied from commercially a premixed gas cylinder at room temperature and quickly heated to the reaction temperature before contacting with sorbent particles by passing through the "preheating" outer shell section of the reactor assembly as shown in Figure 3a on page 10. The reaction temperature was monitored by thermocouples inserted in the reaction tube and controlled by a three-zone heater element. The reaction residence times were maintained by adjusting the total gas flow rate which would match the residence time in the reaction tube at the specified reaction temperature.

From sample analysis (by LECO Elemental Analyzer), the measured weight percentages of carbon and hydrogen are listed in the first part of Table 1. Equations 2.1 - 2.5 were used to calculate the carbonation conversions and tabulated in the second part of Table 1.

The results from the BET surface area measurements for the product samples of the carbonation reaction are listed in Table 2. It is shown that the surface area decreases with increasing temperature, because more intense carbonation reaction takes place in the powder at higher temperature. Figure 4 is the graph of BET surface areas changing with reaction time and temperature.

From comparison of the data for #1 and #2 which were obtained from two separate runs on the same sample, it shows that most of the data are very close to each other, indicating that the data are reliable.

From the results in Table 1, it is shown that for the carbonation reaction, the conversion increases continuously and significantly from 3% to 30% with increasing temperature. However, it seems that the conversion is not sensitive to the residence time at the same temperature. Figure 5 illustrates the change of reaction conversion with reaction temperature and residence time. The increment of the conversion from 482°C to 593°C is larger than that from 315°C to 482°C. This may imply that 900°F (484°C) is a significant temperature to be taken into account. The BET surface areas of the product decrease with reaction temperature, which matches the corresponding trend of the conversion change.

Table 1. Carbonation Reaction of $\text{Ca}(\text{OH})_2$

	Reaction Temp.	Run No.	50 ms	75 ms	100 ms
H wt% *	600 °F (315°C)	#1	2.556	2.459	2.672
		#2	2.567	2.521	2.524
	900 °F (482°C)	#1	2.194	2.097	2.170
		#2	2.23	2.208	2.161
	1100 °F (593°C)	#1	1.743	1.693	1.713
		#2	1.739	1.648	1.645
C wt% *	600 °F (315°C)	#1	1.454	1.408	1.593
		#2	1.495	1.386	2.067
	900 °F (482°C)	#1	2.426	2.666	2.690
		#2	2.401	2.670	2.656
	1100 °F (593°C)	#1	4.617	4.952	5.004
		#2	4.742	5.010	4.944
Conv. %	600 °F (315°C)	#1	3.57	3.25	4.55
		#2	3.86	3.097	7.92
	900 °F (482°C)	#1	10.52	12.28	12.45
		#2	10.33	12.30	12.22
	1100 °F (593°C)	#1	27.35	30.09	30.51
		#2	28.37	30.56	30.02

* LECO analyzer accuracy was at least 0.1%, translating to 4 significant figures.

Table 2. BET Surface Areas of Spent Sorbents from the Carbonation Reaction.

	Reaction Temp.	Run No.	50 ms	75 ms	100 ms
Surface Area* (m ² /g) Original: 10.1(m ² /g)	600°F (315°C)	#1	5.774	6.044	5.880
		#2	5.782	5.953	5.869
	900 °F (482°C)	#1	5.168	3.900	4.056
		#2	4.380	3.815	-----
	1100 °F (593°C)	#1	2.370	2.616	2.303
		#2	2.294	2.281	2.997

* BET equipment accuracy was between 0.1 and 1%, translating to 3 - 4 significant figures. All 4 digits are reported although the last digit may not be reliable.

Figure 4. BET Surface Area Changes with Temperature and Residence Time for Carbonation Reaction

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

2.4.2 Sulfation Reaction

Experiments for sulfation reaction were carried out without the presence of carbon dioxide in order to isolate the sulfation reaction without the interference of carbonation reaction. The experiments were performed under two levels of C_{SO_2} , 3000 ppm and 6000 ppm to investigate the effect of SO_2 in the reactant gas stream.

a) Sulfation Reaction with C_{SO_2} of 3000 ppm

The following experimental conditions were used.

Inlet to the reaction zone

Temperature: 600°F (315°C), 900°F (482°C), 1100°F (593°C)

Sorbent Feed Rate: 250 mg/min of $Ca(OH)_2$ powder

Reaction Gas: 3000ppm SO_2 (or 6000ppm SO_2), 3% O_2 balanced with N_2 , flowrates adjusted to maintain the reaction residence times of 50ms, 75ms and 100ms

Reaction zone: Isothermal at 600°F (315°C), 900°F (482°C), 1100°F (593°C)

Outlet of the reaction zone

Quenching Gas: pure N_2 (99.99%) up to 20 times of dilution to maintain about 45°C on the collection filter

Run time : 10 minutes (2.5 g of sorbent injection) for each run

As the case of carbonation experiments, the reaction gas was supplied from a commercial premixed gas cylinder at room temperature and quickly heated to the reaction temperature before contacting with sorbent particles by passing through the "preheating" outer shell section of the reactor assembly as shown in Figure 3a on page 10. The reaction temperature was monitored by thermocouples inserted in the reaction tube and controlled by a three-zone heater element. The reaction residence times were maintained by adjusting the total gas flow rate which would match the residence time in the reaction tube at the specified reaction temperature.

The collected samples are analyzed for the carbon and hydrogen contents. The sulfur content is measured by the Total Sulfur Analyzer and converted to sulfation conversion according to the equations in Section 2.3. The results are listed in Table 3.

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

temperature from 315°C to 593°C. At lower temperature, the residence time has little effect on the reaction. But at higher temperature (593°C), the conversion increases with increasing temperature (Figure 6). This indicates that both carbonation reaction without SO₂ and sulfation reaction without CO₂ are mostly completed within the first 50ms. The reproducibility of sulfation reaction data is reasonably good, although some results of the two groups are not so close as for the carbonation reaction. This may be due to the experimental errors caused by the Total Sulfur Analyzer or an additional sulfation reaction in the collection chamber, although the

Table 3. Sulfation reaction of Ca(OH)₂ (SO₂ 3000ppm)

	Reaction Temp.	Run No.	50 ms	75 ms	100 ms
S wt%*	600 °F (315°C)	#1	0.784	0.606	0.820
		#2	0.891	0.786	0.871
	900 °F (482°C)	#1	2.871	2.371	2.533
		#2	2.106	2.189	2.216
	1100 °F (593°C)	#1	3.042	2.533	3.659
		#2	2.884	3.059	3.805
Conv. %	600 °F (315°C)	#1	1.989	1.540	2.087
		#2	2.262	1.995	2.216
	900 °F (482°C)	#1	7.571	6.210	6.628
		#2	5.446	5.698	5.749
	1100 °F (593°C)	#1	8.021	6.960	10.09
		#2	7.584	8.552	10.62

* The Sulfur Analyzer accuracy was between 0.1 and 1%, translating to 3 - 4 significant figures. All possible digits are reported although the fourth digit may not be reliable.

Figure 6. Conversion Changes with Temperature and Residence Time
for Sulfation Reaction

the preliminary screening study reasonably excluded any further reaction in the collection chamber. The conversion of the sulfation reaction is lower than the conversion of the carbonation reaction. But when comparing the concentrations of CO_2 and SO_2 , it is seen that SO_2 is more reactive with $\text{Ca}(\text{OH})_2$.

However, the BET surface area measurements of the products (Table 4) 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. This may be due to the fact that the overall conversion of sulfation reaction is much smaller than the conversion of carbonation reaction.

Table 4. BET Surface Areas of Spent Sorbents from the Sulfation Reaction.

	Reaction Temp.		50 ms	75 ms	100 ms
Surface Area (m^2/g) Original: 10 m^2/g	600°F (315°C)	#1	8.168	5.972	8.444
		#2	7.843	9.670	7.378
	900 °F (482°C)	#1	6.015	8.267	8.877
		#2	6.519	6.751	7.175
	1100 °F (593°C)	#1	6.353	6.725	8.386
		#2	5.344	6.227	7.731

b) Sulfation Reaction with C_{SO_2} of 6000 ppm

Sulfation reactions with higher concentration of SO_2 (6000 ppm) were performed in the drop tube reactor to compare with the results obtained from sulfation reactions with lower concentration of SO_2 (3000 ppm). The experimental conditions for this sulfation reaction were the same as those listed in the previous section except that SO_2 concentration was raised to 6000 ppm. The inlet and preheating conditions were also identical to those of experiments with 3000 ppm SO_2 . The results for conversion and BET surface area from sulfation reactions are listed in Table 5 and Table 6, respectively.

When comparing the above results with those obtained for $C_{SO_2}=3000$ ppm, it can be seen that, although the concentration of SO_2 has been doubled from 3000ppm to 6000ppm, the conversion of sulfation has not changed much. Figure 7 shows the comparison of sulfation reaction with $C_{SO_2} = 3000$ ppm and with $C_{SO_2} = 6000$ ppm.

Also, like the sulfation reaction with 3000ppm SO_2 concentration, the BET surface area for sulfation reaction with 6000ppm has no clear relationship either with reaction temperature or with residence time.

Table 5. Sulfation Reaction of $Ca(OH)_2$ (SO_2 6000ppm)

	Reaction Temp.	Run No.	50ms	100ms
S wt%	900°F (482°C)	#1	1.959	2.468
		#2	2.145	3.121
	1100°F (593°C)	#1	2.827	3.604
		#2	2.529	3.415
Conv.	900°F (482°C)	#1	5.153	6.496
		#2	5.634	8.294
	1100°F (593°C)	#1	7.517	9.565
		#2	6.687	9.146

* The Sulfur Analyzer accuracy was between 0.1 and 1%, translating to 3 - 4 significant figures. All possible digits are reported although the fourth digit may not be reliable.

Table 6. BET Surface Areas of Spent Sorbents from Sulfation Reaction (SO_2 6000ppm)

	Reaction Temp.	Run No.	50ms	100ms
BET Surface Area(m ² /g)	900°F (482°C)	#1	7.005	6.254
		#2	6.465	6.693
Original: 10 m ² /g	1100°F (482°C)	#1	7.243	6.443
		#2	7.409	7.287

* BET equipment accuracy was between 0.1 and 1%, translating to 3 - 4 significant figures. All 4 digits are reported although the last digit may not be reliable.

Figure 7. Comparison of Conversions for Sulfation Reaction with $C_{SO_2} = 3000\text{ppm}$ and $C_{SO_2} = 6000\text{ppm}$

2.4.3 Simultaneous Reaction

Simultaneous carbonation and sulfation reactions were also performed in the drop tube reactor. Both CO_2 and SO_2 react with Ca(OH)_2 . And reactant gases with different SO_2 concentrations have been used to explore the concentration effect for simultaneous reaction.

a) Simultaneous reaction with C_{SO_2} of 3000 ppm

The experimental conditions used were as follows.

Inlet to the reaction zone

Temperature: 600°F (315°C), 900°F (482°C), 1100°F (593°C)

Sorbent Feed Rate: 250 mg/min of Ca(OH)_2 powder

Reaction gas: 14% CO_2 , 3000ppm SO_2 , 3% O_2 balanced with N_2 , flowrates adjusted to maintain the reaction residence times of 50ms, 75ms and 100ms

Reaction zone: Isothermal at 600°F (315°C), 900°F (482°C), 1100°F (593°C)

Outlet of the reaction zone

Quenching Gas: pure N_2 (99.99%) up to 20 times of dilution to maintain about 45°C on the collection filter

Run time : 10 minutes (2.5 g of sorbent injection) for each run

The inlet and preheating conditions were kept the same as those of previous single reaction cases. The product samples were also analyzed for the H, C, and S contents by the LECO Elemental Analyzer and by the Total Sulfur Analyzer. The results of the conversions of carbonation and sulfation reactions under different experimental conditions were obtained after the data treatment as described in Section 2.3 and are listed in Table 7.

From the results, it is seen that for the simultaneous carbonation/sulfation reaction, carbon content increases continuously with increasing temperature. The increment of the carbonation conversion from 482°C to 593°C is also higher than the increment from 315°C to 593°C. But with residence time, the conversion of carbonation behaves somewhat differently compared to the carbonation reaction. At temperatures of 315°C and 482°C, the conversion of carbonation almost doesn't change with increasing residence time. But at 593°C, the conversion

Table 7. Simultaneous Carbonation/sulfation Reaction of $\text{Ca}(\text{OH})_2$

	Reaction Temp.	Run No.	50ms	75ms	100ms
H wt%	600°F (482°C)	#1	2.757	2.595	2.782
		#2	2.756	2.578	2.817
	900°F (482°C)	#1	2.293	2.173	2.464
		#2	2.286	2.204	2.420
	1100°F (482°C)	#1	1.604	1.498	1.617
		#2	1.502	1.406	1.403
C wt%	600°F (482°C)	#1	1.379	1.263	1.231
		#2	1.307	1.252	1.190
	900°F (482°C)	#1	2.231	2.113	2.110
		#2	2.230	2.104	2.197
	1100°F (482°C)	#1	4.049	3.684	3.503
		#2	4.583	3.586	3.843
S wt%	600°F (482°C)	#1	1.753	1.197	1.251
		#2	1.503	1.266	1.192
	900°F (482°C)	#1	1.667	2.530	2.363
		#2	2.045	2.684	2.561
	1100°F (482°C)	#1	2.213	2.993	2.900
		#2	1.801	3.356	3.417
Conv. % (Carbon)	600°F (482°C)	#1	3.652	2.754	2.536
		#2	3.105	2.686	2.241
	900°F (482°C)	#1	9.827	9.155	9.094
		#2	9.912	9.124	9.792
	1100°F (482°C)	#1	24.15	21.25	19.99
		#2	28.33	20.35	22.66
Conv. % (Sulfur)	600°F (482°C)	#1	4.539	3.065	3.204
		#2	3.870	3.244	3.047
	900°F (482°C)	#1	4.396	6.744	6.282
		#2	5.425	7.169	6.843
	1100°F (482°C)	#1	6.149	8.256	8.025
		#2	5.036	9.194	9.507

of carbonation is higher at the residence time of 0.05s than at 0.075s and 0.1s (Figure 7). This means that the conversion of carbonation decreases with increasing residence time, contrary to the “carbonation-only” reaction in Section 2.4.1. The conversion of carbonation is lower than that of the individual carbonation reaction without SO_2 at the same reaction conditions since the sulfation reaction competes with the carbonation reaction. Figure 8 shows the conversion of carbonation reaction changes with temperature and residence time in simultaneous sulfation/carbonation reaction.

Both the results of sulfur content and conversion of sulfation show that the trends are somewhat different from those for carbon content and conversion of carbonation. At relatively longer residence times, 0.075s and 0.1s, the sulfur content increases significantly with the increase in temperature. Like sulfation reaction without CO_2 , the change of residence time has some effects on both the sulfur content and conversion. At higher temperature, conversion of sulfation increases with residence time, especially from 0.05s to 0.75s. But this trend is not obvious at the lower temperature condition, as shown in Figure 9. Unlike the sulfur content, the carbon content decreases with residence time increasing from 0.05s to 0.075s at higher temperatures as we mentioned above. It seems that these two different reactions have some effects on each other. 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 $\text{Ca}(\text{OH})_2$. However, at higher temperature, the existence of SO_2 limits the reaction between $\text{Ca}(\text{OH})_2$ and CO_2 at longer residence time. This phenomenon may also indicate that some parts of fresh CaCO_3 react with SO_2 and form CaSO_3 . The high reactivity of SO_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 (593°C), the sum of conversions of both sulfation and carbonation is very close to the conversion of the individual carbonation reaction, which is 30%. This implies that 30% is the maximum conversion under the conditions employed.

The BET surface areas of the products have been measured. The results are listed in Table 8. It is difficult to identify exactly how much of the change in BET surface area is caused by carbonation reaction, and how much is caused by sulfation reaction. As previously mentioned, the BET surface area for carbonation reaction without SO_2 decreased with increasing

temperature, whereas the BET area for sulfation reaction without CO₂ 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 CO₂). It appears that most change in BET surface area for simultaneous carbonation/sulfation is due to the carbonation reaction. Figure 10 shows the BET surface changes with temperature and residence time in simultaneous reaction.

Figure 8. Conversion of Carbonation Changes with Temperature and Residence Time for Simultaneous Reaction

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

Table 8. BET Surface Areas of Spent Sorbents from the Simultaneous Reaction

	Reaction Temp.		50ms	75ms	100ms
Surface Area (m ² /g)	600°F (315°C)	#1	9.037	9.669	9.026
		#2	8.664	10.32	9.549
	900°F (482°C)	#1	5.896	4.953	4.795
		#2	5.432	4.865	8.138
	1100°F (593°C)	#1	6.104	5.162	---
		#2	4.717	4.781	---

b) Simultaneous reaction with C_{SO₂} of 6000ppm

The conditions for the simultaneous carbonation/sulfation (SO₂ 6000ppm) were identical to those in the previous section except for the fact that SO₂ concentration level in the inlet gas is raised to 6000 ppm.

The results of the conversions of carbonation and sulfation reaction with 6000ppm SO₂ under different experimental conditions were obtained after the data treatment according to Section 2.3 and are listed in Table 9. The BET surface areas of carbonation/sulfation reaction with SO₂ concentration of 6000ppm are given in Table 10.

The general tendency of the experimental data obtained from sulfation and simultaneous carbonation/sulfation reactions with SO₂ concentration of 6000ppm is similar to that of sulfation and simultaneous carbonation/sulfation reactions with 3000ppm SO₂. This tendency includes the changes of the conversions as well as the BET surface areas with temperature and residence time. This also shows that the results we obtained are consistent with those of 3000 ppm cases.

However, raising the concentration of SO₂ did not seem to have much effect on the conversion of sulfation in either sulfation or simultaneous carbonation/sulfation reaction(Figure 11). The results obtained here are very close to the data obtained before with lower

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

Table 9. Conversions of Carbonation/Sulfation Reaction (SO₂ 6000ppm)

	Reaction Temp.	Run No.	50ms	100ms
C wt%	900°F (482°C)	#1	1.959	1.872
		#2	1.934	1.887
	1100°F (593°C)	#1	3.943	3.588
		#2	3.246	3.881
S wt%	900°F (482°C)	#1	1.559	2.145
		#2	1.564	2.081
	1100°F (593°C)	#1	2.587	3.375
		#2	1.771	3.511
Conv. % (Carbon)	900°F (482°C)	#1	8.234	7.710
		#2	8.050	7.809
	1100°F (593°C)	#1	24.041	21.115
		#2	18.157	23.278
Conv. % (Sulfur)	900°F (482°C)	#1	4.145	5.744
		#2	4.157	5.569
	1100°F (593°C)	#1	7.302	9.438
		#2	4.870	9.810

concentration of SO₂ (i.e., 3000ppm). This supports the possibility that at some reaction temperature and very short residence time, there exists a maximum conversion of Ca(OH)₂. Like the cases with 3000ppm SO₂, the conversion of carbonation at 6000ppm SO₂ also decreases with residence time at higher temperature. Furthermore, at 482°C and 593°C, the summation of the conversions of carbonation (Figure 12) and sulfation (Figure 10) for the simultaneous carbonation/sulfation reactions under each SO₂ concentration is close to the conversion of carbonation reaction without SO₂ at the corresponding temperature. At 482°C and 593°C, the total conversion of Ca(OH)₂ is about 15% and 30%, respectively. It seems that at some temperature and very short residence time, only a certain part of Ca(OH)₂ can react with reactant gas. It is very possible that there is a coverage of the product on the Ca(OH)₂ surface which hinders the reaction gas to react with Ca(OH)₂ within very short time. To achieve higher

Table 10. BET Surface Areas from Carbonation/Sulfation Reaction
(SO₂ 6000ppm)

	Reaction Temp.	Run Number	50ms	100ms
BET (m ² /g)	900°F (482°C)	#1	5.630	5.193
		#2	5.565	4.956
	1100°F (593°C)	#1	3.459	3.424
		#2	4.416	3.816

conversion, much longer residence time in the order of minutes would be needed.

However, the BET surface area of simultaneous carbonation/sulfation reaction decreases with more reaction taking place (Figure 13). This may be because much more Ca(OH)₂ reacts with CO₂ than with SO₂. From the BET surface area measurements, it is also shown that the BET surface area decreases with conversion only when CO₂ takes part in the reaction. This behavior is also similar to that of reactions in which the concentration of SO₂ was 3000ppm.

Figure 11. Comparison of Conversion for Simultaneous Reaction
with $C_{SO_2} = 3000\text{ppm}$ and $C_{SO_2} = 6000\text{ppm}$

Figure 12. Conversion of Carbonation in Simultaneous Reaction
with $C_{so_2} = 6000\text{ppm}$

Figure 13. BET Surface Area Changes with Temperature and Residence Time in Simultaneous Reaction with $C_{so_2} = 6000\text{ppm}$

3. KINETIC MODELING

Kinetic models of the carbonation, sulfation and simultaneous carbonation/sulfation reactions have been developed. Deactivation models have been used to describe all the above reactions since during these reaction processes, the activity of the solid particle decreases due to the fact that the molar volumes of the products ($36.9\text{cm}^3/\text{mol}$ for CaCO_3 , and $45.8\text{cm}^3/\text{mol}$ for CaSO_3) are larger than the molar volume of Ca(OH)_2 ($23.4\text{cm}^3/\text{mol}$) or CaO ($16.9\text{cm}^3/\text{mol}$), which makes the porosity of particles decreases after reaction. In the medium temperature range, not only Ca(OH)_2 will react with reactant gas, but also the CaO which is produced by dehydration of Ca(OH)_2 will react. In order to know the reactivities of these two materials in their reactions with CO_2 and SO_2 , Ca(OH)_2 and the newly-formed CaO have been subjected to some TGA runs in which they react with CO_2 (or SO_2), respectively.

3.1 Carbonation Reaction

3.1.1 Reactivity of CaO with CO_2

It has been widely believed that, compared to the Ca(OH)_2 carbonation reaction, the rate of reaction of CaO with CO_2 is very small in the medium temperature range [21,22,23]. Consequently, in a medium temperature hydrated sorbent injection process, the carbonation of CaO formed due to the dehydration of Ca(OH)_2 is traditionally ignored.

However, as described in the experimental section, the experience in handling the dehydration product indicates that the newly formed CaO is very active even at room temperature. Since the reactivity of newly formed CaO to CO_2 is important in understanding the whole picture of the carbonation of Ca(OH)_2 , it is necessary to verify experimentally the reactivity of the fresh CaO .

A series of tests were conducted in the Dupont 951 thermogravimetric analyzer. In order to compare the solitary carbonation rate of Ca(OH)_2 with that of CaO , all the tests were conducted at a temperature around 300°C , where the dehydration of Ca(OH)_2 does not take place during the duration of experiment.

To investigate the reactivity of fresh CaO, the Ca(OH)₂ was first dehydrated in N₂ in a TGA. After the dehydration was completed, the newly formed CaO was cooled down to room temperature in pure N₂ in the TGA reaction chamber. Following this, the TGA reactor was set to a temperature of 300°C. After ensuring an isothermal condition in the reaction chamber, the inlet gas to the TGA was switched quickly from pure N₂ to 14% CO₂ gas balanced with N₂. The weight change history of the CaO after the introduction of CO₂ gas was recorded. A similar procedure was also used for Ca(OH)₂, except that the dehydration step was omitted.

The results of these two tests produced carbonation conversions of 5.47% for CaO and 4.85% for Ca(OH)₂ in the first minute. This observation infers that the freshly dehydrated CaO is as reactive as Ca(OH)₂ within the limit of experimental errors.

3.1.2 Model Development

As described in foregoing statements, in the medium temperature range, the Ca(OH)₂ carbonation reaction is accompanied by or involves the simultaneous dehydration of calcium hydroxide.

The CaO product in the reaction above may then react further with CO₂ to form CaCO₃. Due to the molar volume differences among Ca(OH)₂ (23.4 cm³/mol), CaO (16.9 cm³/mol) and CaCO₃ (36.9 cm³/mol), the formation of CaCO₃, whether by carbonation of Ca(OH)₂ or carbonation of CaO, is accompanied by a net decrease in porosity. Although it is possible that the simultaneous dehydration makes calcium hydroxide more porous, subsequent carbonation makes calcium hydroxide much less porous. On a molar basis, the pore volume consumed by the formation of CaCO₃ during the carbonation of CaO is much greater than the pore volume developed by dehydration of Ca(OH)₂. This analysis suggests that owing to a gradual decrease in porosity, considerable diffusion resistances can develop within the calcium hydroxide particle during exposure to CO₂-containing reactant gas. As a result, the activity of calcium hydroxide to CO₂ gas will decrease continuously.

Since this process of deactivation of $\text{Ca}(\text{OH})_2$ is analogous to the catalyst-poisoning process, where the deactivation of catalyst is also caused by deposition and physical blocking of the surface, a general-order catalyst deactivation model, developed originally by Levenspiel [24], is used here to describe the process of gradual reduction in reactivity of $\text{Ca}(\text{OH})_2$ to CO_2 . The most commonly used models, 1st- and the 3rd-order deactivation kinetics, are briefly described based on plausible physical mechanisms, although their application does not necessarily require accurate physical interpretations.

1st-order Deactivation Model

In this model, the reaction is assumed to be proportional to the remaining amount of reactant and is assumed to take place homogeneously throughout the particles (no diffusion resistance) because the particle is porous and the size is very small. The other assumptions are a first order reaction (proportional to the remaining amount), that the particle volume does not change during the reaction, and that the reaction rate of $\text{Ca}(\text{OH})_2$ is equal to that of CaO for each reactant gas (as shown by the TGA results).

Based on the above assumptions, the carbonation reaction rate, $-r_C$ ($\text{mol}/\text{m}^3\cdot\text{s}$), is defined as

$$-r_C = k_C C_{Cg} a_C, \quad (3.2)$$

where k_C is the carbonation reaction rate constant based on the initial volume of $\text{Ca}(\text{OH})_2$ ($1/\text{s}$) and C_{Cg} is the concentration of CO_2 in the bulk gas phase (mol/m^3). The activity of the pellet, a_C , is assumed to follow a linear “poisoning” relation frequently used in the petroleum industry.

$$a_C = \frac{N_{R_0} - k_{dC} N_C}{N_{R_0}}, \quad (3.3)$$

where N_R , N_{R_0} , and k_{dC} are the number of moles of CaCO_3 produced (mol), the original number of

moles of Ca(OH)_2 (mol) and the intrinsic deactivation constant, respectively.

From Equations (3.2) and (3.3) we obtain

$$\frac{dX_c}{dt} = \frac{k_C C_{Cg}}{\rho_R} a_C = K_C C_{Cg} a_C \quad (3.4)$$

and

$$-\frac{da_C}{dt} = \frac{k_{dC} k_C C_{Cg}}{\rho_R} a_C = K_{dC} C_{Cg} a_C, \quad (3.5)$$

where ρ_R is N_{ro}/V_o , the molar density of solid product CaCO_3 (mol/m³); V_o is the original volume of particle, which has been assumed kept constant during the reaction; K_C is k_C/ρ_R (m³/mol·sec); and K_{dC} is $k_{dC} k_C/\rho_R$, the apparent deactivation constant, (m³/mol·sec).

The term “first-order deactivation” comes from the fact that the decreasing rate of activity is linearly related to the activity itself as expressed in Equation (3.5).

3rd-order Deactivation Model

In this model, the reaction is assumed to take place only at the surface of the particles. Since the molar volume of the reaction product is larger than the original material, the volume of the particle increases and the product layer becomes thicker during the reaction. Figure 14 illustrates the microscopic flat geometry where the reactant core shrinks and the product layer grows as reaction proceeds.

Figure 14. Flat geometry of the reactant core and the product layer for the carbonation reaction.

Both reaction and diffusion take place through the product layer. Therefore, the rate equation is expressed in terms of mass transfer first.

$$-r_C = D_{CO_2} A \frac{(C_{Cg} - C_{Cs})}{L - l} \cdot \frac{1}{A L_0}, \quad (3.6)$$

Where A , C_{Cs} , and D_{CO_2} are the total surface area (m^2), the concentration of CO_2 at the reaction surface of the reactant core (mol/m^3) and the diffusivity of CO_2 through the product layer (m^2/sec), respectively.

The rate equation for the reaction is also expressed in terms of the bulk kinetics.

$$-r_C = k_C C_{Cs} \epsilon_C , \quad (3.7)$$

where ϵ_C is the effectiveness factor, defined as

$$\frac{1}{\epsilon_C} = \sqrt{\frac{k_C}{D_C}} L_0 ,$$

and D_C is the diffusivity of CO_2 through the reactant core.

After rearranging Equations (3.6) and (3.7), the reaction rate equation becomes

$$-r_C = \frac{C_{Cg}}{\frac{(L-l)L_0}{D_{\text{CO}_2}} + \frac{1}{\epsilon_C k_C}} = \frac{k_C C_{Cg} \epsilon_C}{\frac{k_C \epsilon_C (L-l)L_0}{D_{\text{CO}_2}} + 1} . \quad (3.8)$$

By defining the pellet activity, a_C , as

$$a_C = \frac{1}{\frac{k_C \epsilon_C L_0 (L-l)}{D_{\text{CO}_2}} + 1} = \frac{1}{C_1 (L-l) + 1} , \quad (3.9)$$

the thickness of the product layer is related to the activity as

$$L-l = \frac{1}{C_1} \left(\frac{1}{a_C} - 1 \right) , \quad (3.10)$$

where the constant C_1 combines all the constants appearing in Equation (3.9).

$$C_1 = \frac{k_C \epsilon_C L_0}{D_{CO_2}} = \frac{\sqrt{k_C D_C}}{D_{CO_2}} .$$

Finally the growth rate of product layer becomes

$$\frac{dN_C}{dt} = \frac{dA(L-l)}{\rho_C dt} = (-r_C) A L_0 = k_{Cg} \epsilon_C C_{Cg} a_C A L_0 , \quad (3.11)$$

where ρ_C is the molar density of $CaCO_3$.

Substituting Equation (3.10) into Equation (3.11) with the assumption $D_C \approx D_{CO_2}$, and performing a series of algebraic manipulations, the following equation of activity is obtained:

$$-\frac{da_C}{dt} = \frac{k_C C_{Cg} \epsilon_C}{\rho_C} a_C^3 \sqrt{\frac{k_C}{D_C}} L_0 = \frac{k_C C_{Cg}}{\rho_C} a_C^3 . \quad (3.12)$$

Similar to the first-order deactivation model, all the above equations can be summarized into two equations for the third-order deactivation case.

$$-r_C = k_C C_{Cg} \epsilon_C a_C = K_C C_{Cg} a_C \quad (3.13)$$

and

$$-\frac{da_C}{dt} = \frac{k_C C_{Cg}}{\rho_C} a_C^3 = K_{dC} C_{Cg} a_C^3 . \quad (3.14)$$

The right-hand side of Equation (3.14) indicates the third-order dependency of the deactivation rate

on the activity.

General d th-order Deactivation Model

The actual geometry may not match the simple flat geometry of the third-order deactivation model. A d th-order deactivation model is proposed to accommodate the non-ideal geometry of the third-order model:

$$-r_C = K_C C_{Cg} a_C \quad (3.15)$$

and

$$-\frac{da_C}{dt} = K_{dC} C_{Cg} a_C^d . \quad (3.16)$$

The order of deactivation, d , generally lies between 1 and 3.

3.1.3 Model Application and Results

For the carbonation reaction experimental runs performed by the authors, the first order deactivation model appears to be the best suited among the three models mentioned above.

After calculating the CO_2 concentrations at the top and the bottom of the reactor, there is very little change in CO_2 concentration during the reaction (from 14% to 13.5%). Therefore, we can assume the CO_2 concentration to be constant in the reactor. The differential equations (Equations 3.4 and 3.5) can be easily solved and manipulated to provide the carbonation conversion as a function of the reaction time.

$$X_C(t) = \frac{K_C}{K_{dC}} (1 - e^{(-K_{dC} C_{Cg} t)}) . \quad (3.17)$$

The conversions for the carbonation reaction have been previously measured at residence times from 0.05 s to 1 s at temperatures from 600 to 1100°F. By using these conversion data and a

statistical method using the least-sum-of-squares-of-error criterion, K_c and K_{dc} values can be obtained for each temperature listed in Table 11. (See Appendix A for computer programming.) Using these calculated parameters, simulated kinetic curves at different temperatures have been obtained. Figure 15 shows the comparison between the simulated curves and the experimental data. It can be seen that for the carbonation reaction, the first order model fits the experimental data reasonably well.

Table 11. Rate constants for carbonation reaction.

Temp.	K_c	K_{dc}
600°F	0.235	1.883
900°F	1.307	8.140
1100°F	6.537	20.556

As shown in Table 11, the reaction rate constant for the carbonation reaction increases with temperature, as does the apparent deactivation rate constant. From Figure 15, we can also see that the carbonation conversion increases quickly and reaches its highest level in a very short time. During this time the activity of the particle decreases significantly due to the pore closure. This prevents the particle from reacting further with the reactant gas.

Figure 16 gives the relationship between reaction rate constant and temperature. A straight line fit is obtained. From the slope and the intercept of the line, the activation energy (E) and the frequency factor (k_0) are calculated. These values for the carbonation reaction are $E = 4.856 \cdot 10^4$ (J/mol) and $K_{c0} = 4317.5$ (sec^{-1}).

Figure 17 shows the relationship between the deactivation constant and temperature. It also follows the Arrhenius law. From the fit, the deactivation energy and the frequency factor are $E_a = 3.573 \cdot 10^4$ (J/mol) and $K_{dc0} = 2710.6$ (sec^{-1}).

Figure 15. Model validation for the carbonation data using the first-order deactivation model. (Solid curves are model-generated results.)

Figure 16. Arrhenius equation fit for K_C . (Slope is the activation energy.)

Figure 17. Arrhenius equation fit for K_{dc} .
(Slope is the activation energy.)

3.1.4 Conclusion on the Carbonation Model

A first-order deactivation model was developed to simulate the carbonation process of Ca(OH)_2 particles. The model was validated for the carbonation test data with different temperatures. The activation energies and frequency factors for both carbonation reaction and the deactivation process were obtained. Using this kinetic data, the conversion predicted by the model is in good agreement with the conversion obtained experimentally.

3.2 Sulfation Reaction

3.2.1 Reactivity of CaO with SO_2

In previous research on the medium temperature injection process conducted by Bortz et al.[21], in order to confirm that Ca(OH)_2 , and not CaO, is the reactant species, Longview hydroxide was dehydrated in a muffle furnace to form between 50 and 60 mole percent CaO with

the remainder being hydroxide. This material was then injected into a reactor at temperatures ranging from 800 to 1200°F, and solid samples were collected. Utilizations were considerably reduced relative to the raw Longview and were independent of temperature. The authors believed that the 10 percent utilization that did occur with the precalcines was probably due to the remaining hydroxide present in the dehydrated Longview and consequently, the reaction between CaO with SO₂ could be ignored relative to the reaction of Ca(OH)₂.

Since then, it has been widely accepted that compared to the direct sulfation reaction of Ca(OH)₂, the reaction rate of CaO with SO₂ is small enough so that the further sulfation reaction of CaO formed by the dehydration of Ca(OH)₂ can be ignored. However, the carbonation test results presented in the previous sections indicate that newly formed CaO is as active as Ca(OH)₂. Since the reaction between CaO with CO₂ is very similar to that with SO₂, it is possible that the reactivity of the newly-formed CaO to SO₂ cannot be ignored either.

To verify this, a series of tests were conducted in the Dupont 951 thermogravimetric analyzer. In order to compare the solitary sulfation rate of Ca(OH)₂ with that of CaO, all the tests were conducted at a temperature around 300°C, which is low enough so that little dehydration of Ca(OH)₂ will take place. The same procedures used in the investigation presented in the previous section were also used to study the reactivities to SO₂. Just as in the case of the carbonation reactions, the experimental sulfation conversions in the initial 1.5 minutes the two cases were very close, 3.17% for CaO and 3.09% for Ca(OH)₂.

Based on the above tests it was concluded that the further sulfation reaction of the newly-formed CaO is as important as that of Ca(OH)₂ in the medium-temperature range. This contradicts previous researchers' observations[21,22] where partially pre-dehydrated hydroxide was used that could have been pre-carbonated before the sorbent was injected into the reactor. Their CaO sorbents were not formed *in situ*, and were thus less active than the newly-formed CaO.

3.2.2 Model Development

Similar to the carbonation reaction, the sulfation reaction includes three different reactions.

and

In the sulfation reaction, the concentration of SO_2 is very low and changes significantly from the top to the bottom of the reactor. Therefore, we can no longer assume a uniform concentration of SO_2 throughout the reactor. C_{SO_2} is therefore considered a variable in the calculation of the kinetic parameters for the sulfation reaction. Thus, the parameter estimation for the sulfation reaction is somewhat more complicated than that for the carbonation reaction.

Similar to the carbonation reaction, the first order deactivation model was found to be most adequate for the sulfation reaction. The rate equations for sulfation and its activity become

$$-r_A = \frac{dX_S}{dt} = K_A C_{Ag} a_A \quad (3.18)$$

and

$$-\frac{da_A}{dt} = K_{dA} C_{Ag} a_A, \quad (3.19)$$

where the parameters have similar meanings as those for the carbonation reaction except that the subscript A indicates the reactant, SO_2 . The concentration of SO_2 in the gas phase is related to SO_2 uptake in the sorbent as shown below.

$$\frac{dC_{Ag}}{dt} = (-r_A)\alpha = K_A C_{Ag} a_A \alpha, \quad (3.20)$$

where α is the volume fraction of sorbent particles in the gas stream. After comparing Equations (3.18) and (3.20), the following linear relationship is obtained between the gas-phase

concentration of SO₂ and the sulfation conversion of sorbent.

$$C_{Ag} = C_{Ag,0} - \alpha X_S, \quad (3.21)$$

where $C_{Ag,0}$ is the initial concentration of SO₂ in the feed stream. By dividing Equation (3.18) by Equation (3.19), and solving the obtained differential equation, we have the relationship between X_S and α_A .

$$\alpha_A = 1 - (K_{dA}/K_A) X_S = 1 - k_{dA} X_S. \quad (3.22)$$

Substituting Equations (3.21) and (3.22) into Equation (3.18), the following differential equation is obtained for sulfation conversion.

$$\frac{dX_S}{dt} = (C_{Ag,0} - \alpha X_S)(K_A - K_{dA} X_S).$$

After solving the above differential equation, the sulfation conversion is obtained as a function of time.

$$X_S = \frac{K_A C_{Ag,0} (1 - e^{(C_{Ag,0} K_{dA} - \alpha K_A)t})}{K_A \alpha - e^{(C_{Ag,0} K_{dA} - \alpha K_A)t} C_{Ag,0} K_{dA}}. \quad (3.23)$$

3.2.3 Model Application and Results

The experimental values of sulfation conversion were used to fit Equation (3.23) and the rate constants were estimated using programs listed in Appendix A.

Table 12 summarizes the rate constants. Figure 18 shows the comparison of the simulated curves with experimental data for the sulfation reaction. For the sulfation reaction, the

first order deactivation model fits the experimental data reasonably well.

Figure 18. Validation of the sulfation model
(Solid curves are the model generated results.)

Table 12. Rate constants for the sulfation reaction

Temperature	K_A	K_{dA}
600°F	20.895	1017.23
900°F	84.095	1301.36
1100°F	124.20	1485.896

Figures 19 and 20 illustrate the reaction rate constant and the deactivation constant with as a function of temperature. We see that both constants follow the Arrhenius law. From the linear

fit, we obtained the following results for sulfation reaction: $K_0 = 6311.3 \text{ (s}^{-1}\text{)}$, $E = 2.776 \times 10^4$ (kJ/kg-mol), $K_{a0} = 3266.13 \text{ (s}^{-1}\text{)}$, and $E_a = 5716.0$ (kJ/kg-mol).

Figure 19. $\ln K_A$ vs $1/T$ plot for determination of the activation energy for the sulfation reaction.

Figure 20. $\ln K_{dA}$ vs $1/T$ plot for determination of the activation energy for the sulfation deactivation.

Comparing this set of results with that of the carbonation reaction, we can see that the frequency factor for the sulfation reaction is higher than that for the carbonation reaction, and the activation energy is lower than that for the carbonation, indicating the particle is more reactive with SO_2 . This has been shown by the reaction results. Although the conversion of the sulfation reaction is lower than that of the carbonation reaction due to the much higher concentration of CO_2 (about 50 times larger than the concentration of SO_2), the reactivity between $\text{Ca}(\text{OH})_2$ and SO_2 is still larger.

When comparing the deactivation of the carbonation and sulfation reactions, it can be seen that the deactivation energy and the corresponding frequency factor for the deactivation of sulfation reaction are smaller and larger, respectively, than those for the deactivation of carbonation reaction. This means that $\text{Ca}(\text{OH})_2$ deactivates more easily by the sulfation reaction than by the carbonation reaction, while it is more reactive with SO_2 than with CO_2 . This finding is consistent with the fact that the molecular weight of the product CaSO_3 is larger than that of CaCO_3 , making it easier for CaSO_3 to block the pores of the $\text{Ca}(\text{OH})_2$ particle.

3.2.4 Conclusion on the Sulfation Model

The sulfation reactions of $\text{Ca}(\text{OH})_2$ is also accompanied by dehydration at medium temperatures. A series of TGA tests are conducted to determine if the fresh dehydration product, CaO , would react with SO_2 . By comparing the reactivities of CaO and $\text{Ca}(\text{OH})_2$ in the TGA, it was found that the newly-formed CaO has an equivalent reactivity to that of $\text{Ca}(\text{OH})_2$. This result differs the conventional assumption widely used in previous research that the further sulfation reaction of CaO is insignificant. The dehydration reaction not only provides more porous sorbent for SO_2 to diffuse through but also produces an equally reactive reactant.

A first-order deactivation model was developed to simulate the sulfation process. The model considers simultaneous dehydration and sulfation as well as gradual sorbent deactivation due to the pore blocking and reaction surface deposition which occurs as the reactions proceed.

3.3 Simultaneous Dehydration, Sulfation and Carbonation Reactions

In a medium-temperature sorbent injection desulfurization process, the Ca(OH)_2 sulfation reaction is accompanied by simultaneous carbonation and dehydration reactions. The dehydration product, CaO , may then react further with CO_2 and SO_2 in the flue gas to form CaCO_3 and CaSO_3 . In addition, the newly formed CaCO_3 is also reacting with SO_2 . As is the case in solitary carbonation or sulfation processes, due to the molar volume difference among Ca(OH)_2 ($23.4 \text{ cm}^3/\text{mol}$), CaO ($16.9 \text{ cm}^3/\text{mol}$), CaCO_3 ($36.9 \text{ cm}^3/\text{mol}$) and CaSO_3 ($45.8 \text{ cm}^3/\text{mol}$), the formation of CaSO_3 as well as CaCO_3 , whether by reaction with Ca(OH)_2 or reaction with CaO , is accompanied by a net decrease in porosity of the reactant particle.

Similar to the case of solitary carbonation or sulfation, this rate of simultaneous sulfation and carbonation is mainly determined by the deactivation rate of Ca(OH)_2 due to the pore-blocking during the above-mentioned reactions. Since this pore-blocking deactivation process is analogous to a catalysts-poisoning process, in which the deactivation of catalysts is also caused by deposition and physical blocking of the reactant surface, the deactivation model derived from the catalyst reaction described in the previous sections is used here to describe the process of gradual reduction in reactivity of Ca(OH)_2 to CO_2 and SO_2 .

The deactivation model developed to describe the simultaneous sulfation and carbonation process is based on following assumptions:

1. The carbonation and sulfation reactions are parallel and do not interfere with each other in terms of the reaction rate per mole of available Ca(OH)_2 . Consequently, the carbonation and sulfation models and their reaction rate constants obtained in the previous two sections can be used here to calculate the carbonation conversion.
2. The carbonation and sulfation reactivity of newly-formed CaO are the same as those of the parent sorbent Ca(OH)_2 .
3. The carbonation reaction first produces nascent CaCO_3 which is unstable and either reacts with SO_2 to produce CaSO_3 or becomes a stable form of CaCO_3 . The nascent CaCO_3 decays to produce a stable form of CaCO_3 according to first-order kinetics.

Figure 21. Overall kinetic scheme for the simultaneous carbonation and sulfation reaction

Figure 21 illustrates the overall kinetic scheme. In the following subsections, each step is described in detail. The reaction between nascent CaCO_3 and SO_2 is described first.

3.3.1 Reaction with nascent CaCO_3

For the rate of reaction between CaCO_3 and SO_2 , $(-r_{AC})$, it is assumed that the newly formed CaCO_3 (nascent CaCO_3) from the carbonation reaction has the highest potential to react with SO_2 at the time of its formation, and that the reaction rate decays with time due to the fact that the nascent CaCO_3 slowly becomes a stable, hardened form of carbonate. So, the fraction of nascent CaCO_3 formed between time t' and $t' + dt'$ is

$$x_C'(t') dt',$$

and is the differential amount of CaCO_3 formed and not the total conversion of CaCO_3 , x_C , which is affected by further reaction with SO_2 .

Assuming a first-order decay during the time 0 to $t-t'$, the rate of reaction with SO_2 decays due to the reduced amount of nascent CaCO_3 available. The rate constant is then

$$k_{\text{CO}_3} e^{-k_{\text{dCO}_3}(t-t')},$$

where k_{CO_3} is the initial rate constant for the CaCO_3 - SO_2 reaction when the CaCO_3 is fresh. The decay rate constant, k_{dCO_3} , is the first-order rate constant for the decay of nascent CaCO_3 to stable CaCO_3 , which reduces the amount of available solid sorbent for the sulfation reaction. The overall reaction rate at time t for the fraction $x_C'(t')$ dt' is

$$k_{\text{CO}_3} e^{-k_{\text{dCO}_3}(t-t')} C_{\text{Ag}}(t) x_C'(t') dt'.$$

The total reaction rate at time t is obtained by integrating the above expression.

$$-r_{\text{AC}} = k_{\text{CO}_3} C_{\text{Ag}}(t) \int_0^t x_C'(t') e^{-k_{\text{dCO}_3}(t-t')} dt' \quad (3.24)$$

Defining the activity of the CaCO_3 - SO_2 reaction as

$$a_{\text{CO}_3} = \int_0^t x_C'(t') e^{-k_{\text{dCO}_3}(t-t')} dt', \quad (3.25)$$

Equation (3.24) can be simplified to the following general rate-deactivation form.

$$-r_{AC} = k_{CO_3} C_{Ag} a_{CO_3} \quad (3.26)$$

Similar to the solitary carbonation or sulfation reactions, the reaction rate of the simultaneous reaction is mainly determined by the deactivation rate of Ca(OH)_2 . The assumptions are similar to those mentioned above for the individual reaction. However, the conversion by carbonation and sulfation are modified by the reaction from CaCO_3 to CaSO_3 . (The amount of carbonate is reduced and the amount of sulfite is increased to the same extent.) Therefore, the reaction rates for the carbonation and sulfation reactions become

$$-r_C = (-r'_C) - (-r_{AC}) = k_C C_{Cg} a_C - k_{CO_3} C_{Ag} a_{CO_3} \quad (3.27)$$

and

$$-r_A = (-r'_A) + (-r_{AC}) = k_A C_{Ag} a_A + k_{CO_3} C_{Ag} a_{CO_3} \quad (3.28)$$

where $-r'_C$ is the rate of reaction between Ca(OH)_2 and CO_2 , $-r'_A$ is the rate of reaction between Ca(OH)_2 and SO_2 , and $-r_{AC}$ is the rate of reaction between CaCO_3 and SO_2 .

The rate constants, k_C and k_A , are the same values as defined for the solitary carbonation and sulfation reactions in Equations (3.4) and (3.5).

3.3.2 Activity

The rate of change in activity can be obtained by differentiating Equation (3.25).

$$\begin{aligned} \frac{da_{CO_3}}{dt} &= \frac{d}{dt} \int_0^t x'_C(t') e^{-k_{dCO_3}(t-t')} dt' \\ &= x'_C - k_{dCO_3} \int_0^t x'_C(t') e^{-k_{dCO_3}(t-t')} dt' \end{aligned}$$

Recognizing that the last integration is the activity itself, the above equation is simplified to the following form:

$$\frac{da_{CO_3}}{dt} = \frac{dx_C}{dt} - k_{dCO_3} a_{CO_3}, \quad (3.29)$$

where k_{dCO_3} is the deactivation constant for $CaCO_3$ - SO_2 reaction.

The activities of the carbonation and sulfation reactions are defined as linear functions of their respective poisoning substances.

$$a_C = \frac{N_0 - k_{dA} n_C - k_{dCaSO_3} n_S}{N_0} = 1 - k_{dA} x_C - k_{dCaSO_3} x_S \quad (3.30)$$

and

$$a_A = \frac{N_0 - k_{dA} n_S - k_{dCaCO_3} n_C}{N_0} = 1 - k_{dA} x_S - k_{dCaCO_3} x_C, \quad (3.31)$$

where n_S and n_C are the numbers of moles of $CaSO_3$ and $CaCO_3$ produced from $Ca(OH)_2$ without considering the amount modified by the nascent $CaCO_3$ reaction, respectively, and x_S and x_C are the corresponding conversions. These expressions are analogous to those of heterogeneous catalysts where the deactivation is caused by poisoning species gradually occupying the available active sites. The deactivation constants, k_{dA} and k_{dC} , are the same values as defined for the solitary sulfation and carbonation reactions listed in Equations (3.22) and (3.3). The two additional constants, k_{dCaCO_3} and k_{dCaSO_3} , define the additional deactivation of the sulfation and carbonation reactions due to the deposition of $CaCO_3$ and $CaSO_3$, respectively. These constants, therefore, may be understood as the "enhancement" constants for the respective deactivations.

In summary, the following equations are obtained for the simultaneous reaction.

$$\frac{dX_C}{dt} = \frac{1}{\rho_R}(-r_C) = K_C C_{Cg} a_C - K_{CO_3} C_{Ag} a_{CO_3}, \quad (3.22)$$

$$\frac{dX_S}{dt} = \frac{1}{\rho_R}(-r) = K_A C_{Ag} a_A + K_{CO_3} C_{Ag} a_{CO_3}, \quad (3.23)$$

$$-\frac{da_C}{dt} = k_{dC} \frac{dx_C}{dt} - k_{dCaSO_3} \frac{dx_S}{dt} = K_{dC} C_{Cg} a_C - K_{dCaSO_3} C_{Ag} a_A, \quad (3.24)$$

$$-\frac{da_A}{dt} = k_{dA} \frac{dx_S}{dt} - k_{dCaCO_3} \frac{dx_C}{dt} = K_{dA} C_{Ag} a_A - K_{dCaCO_3} C_{Cg} a_C, \quad (3.25)$$

and

$$\frac{da_{CO_3}}{dt} = \frac{dx_C}{dt} - k_{dCO_3} a_{CO_3} = K_C C_{Cg} a_C - k_{dCO_3} a_{CO_3}. \quad (3.26)$$

In this model, four additional kinetic constants, k_{CO_3} , k_{dCO_3} , K_{dCaSO_3} and K_{dCaCO_3} are added in addition to the constants already needed for solitary sulfation and carbonation reactions.

3.3.3 Model Application

The above equations describe the overall simultaneous carbonation and sulfation process. By assuming that the carbonation and sulfation reactions are parallel and not interfering with each other in terms of the reaction rate per mole of available Ca(OH)_2 , reaction rate constants and deactivation constants, K_C , K_A , K_{dC} , and K_{dA} , which are obtained from the individual carbonation and sulfation reactions, can be used in the above equations. However, K_{dCaCO_3} , K_{dCaSO_3} , K_{CO_3} and k_{dCO_3} are unknown and need to be determined. A computer program was written to evaluate these parameters. The computer program first solves the differential equations by the fourth-order

Runge-Kutta method, then optimizes the parameters until the error function, Equation (3.37) reaches a minimum value.(See Appendix A for program listing.)

$$F = \sum [X_C(t_i) - X_{Ci}]^2 + \sum [X_S(t_i) - X_{Si}]^2 \quad (3.37)$$

Figures 22 and 23 show the comparison of fitted curves and experimental data for conversions of carbonation and sulfation. It can be seen that the simulation can represent the simultaneous reaction process well.

Figure 22. Model validation for carbonation conversion with the simultaneous reaction.

Figure 23. Model validation for sulfation conversion with the simultaneous reaction.

Figure 24 shows the relationship between the reaction rate constant, K_{CO_3} , and temperature. From this Arrhenius plot, the activation energy and frequency factor for the reaction of $CaCO_3$ with SO_2 to form $CaSO_3$ can be calculated giving $E_{CO_3} = 4511.2 \text{ kJ/kg mol}$ and $K_{CO_3, 0} = 285 \text{ s}^{-1}$.

3.3.4 Conclusion on the Simultaneous Reaction Model

The residence time also plays an important role in the medium temperature sorbent injection process. Unlike the solitary sulfation reaction presented in the previous section, the observed sulfation conversion increases continuously with residence time even though the rate slows down quickly after the short initial period of reaction. The effect of residence time on the carbonation conversion, however, is more complicated. The carbonation reaction is extremely fast at the initial stage and the carbonation conversion reaches its upper limit quickly. After the initial period, the carbonation conversion begins to decrease with residence time. This reduction

Figure 24. $\ln K_{CO_3}$ vs. $1/T$.
(Slope is the activation energy.)

in carbonation conversion is believed to be due to the further reaction of the newly-formed $CaCO_3$ with SO_2 .

It has been believed in previous research that the carbonation of $Ca(OH)_2$ is a competing and undesired reaction which consumes the available $Ca(OH)_2$ needed for the sulfation reaction. This observed further sulfation, however, compensates the negative effect of the competing carbonation reaction and finally increases the ratio of $CaSO_3$ to $CaCO_3$ in the used sorbent. Consequently, it is possible that, by increasing the residence time of sorbent in the ductwork, the sorbent utilization could also be increased.

A mathematical model was developed to simulate the simultaneous sulfation and carbonation process of a calcium hydroxide particle. The model describes the simultaneous sulfation and carbonation of $Ca(OH)_2$ as well as the further sulfation of the newly-formed $CaCO_3$. The first-order deactivation of sorbent is considered by introducing time-dependent deactivation coefficients which are commonly used to describe a catalyst deactivation process in other fields.

Based on the assumption that the intrinsic sulfation and carbonation reactions are parallel and not interfering with each other, the activation energies and frequency factors previously

obtained in solitary reactions for both the carbonation and sulfation reactions were used in this simultaneous sulfation and carbonation model. The model was validated using the sulfation and carbonation conversion data in the temperature of 600 to 1100°F. The activation energy and frequency factor for the deactivation process were obtained. Using these kinetic data, the predicted conversions were found to be in good agreement with the experimentally obtained conversion.

The simulation results show that the carbonation reaction affects the sulfation reaction behavior by means of two important mechanisms. First, it adds additional diffusion resistance for SO₂ gas because of the formation of CaCO₃, consequently accelerating the deactivation of calcium hydroxide sorbent. The second mechanism is the further sulfation of the newly formed CaCO₃, which compensates the negative effect of the competing carbonation reaction.

Modeling Recommendations

Based on the framework of this simultaneous reaction model, modifications may be made to better represent the realistic situation of a calcium hydroxide particle undergoing the simultaneous dehydration, sulfation and carbonation reactions. This includes the introduction of the effect of the initial surface area and the initial pore size distribution into the model. In addition, the sorbent deactivation due to the further sulfation of the newly-formed CaCO₃ may be included, especially for longer residence times when this deactivation may become significant.

In order to supply sufficient data for model modification, further experiments on the effect of sorbent properties, such as initial surface area and initial pore size distribution are recommended.

4. CONCLUSIONS

The drop-tube reactor has been used to develop the kinetics of the reactions between calcium-based sorbent and SO_2 in the flue gas desulfurization system. Medium temperature range has been chosen to represent typical economizer zone temperature range and to achieve higher sorbent utilization. The reactions were conducted at temperatures from 600°F (315°C) to 1100°F (593°C), and at residence times from 0.05s to 0.1s. From the results of the experimental and kinetic studies, the following conclusions can be established:

1. Using calcium-based sorbent, the reduction of SO_2 in flue gas is achieved within 100ms.
2. All reactions are strongly temperature dependent.
 - i. Conversion of carbonation reaction increases with temperature, especially from 900°F (482°C) to 1100°F (593°C).
 - ii. Conversion of sulfation reaction also increases with temperature, although the increment is not as large as for carbonation reaction.
3. The residence time has small effect on all the reactions.
 - i. For carbonation reaction without SO_2 and for sulfation reaction without CO_2 , the conversions of both reactions increase slightly with an increase in residence time after 100ms.
 - ii. For the simultaneous reaction, the trends for carbonation and for sulfation reactions are different:
 - (a) For carbonation reaction, at lower temperature, residence time less than 100ms does not have much effect. However, at higher temperature (593°C), the conversion decreases with increasing residence time beyond 100ms.
 - (b) For sulfation reaction, conversion increases with residence time beyond 100ms.

The existence of CO_2 does not seem to interfere with the sulfation reaction, while the existence of SO_2 interferes with the carbonation reaction.

The reason is that either the nascent CaCO_3 reacts with SO_2 and forms CaSO_3 or CaCO_3 decomposes at higher temperature, and further reacts with SO_2 or (SO_2 and

O₂).

4. Although the conversion of sulfation is less than that of carbonation due to the much higher concentration of CO₂ (C_{CO_2} was about 50 times larger than C_{SO_2}), the Ca(OH)₂ sorbent is more reactive with SO₂ than with CO₂. High reactivity of Ca(OH)₂ to SO₂ is also shown by the activation energy and frequency factor obtained from modeling work.
5. After the concentration of SO₂ was increased from 3000ppm to 6000ppm, the conversion did not increase significantly. This implies that under the present conditions of temperature and residence time, there exists a reaction limitation due to the decrease of activity of the particle during the reactions.
6. Expressions for the general d-th order deactivation model have been proposed after the mechanisms of the reactions have been developed. A 1st-order deactivation model has been tried and seems to well represent the reaction processes of carbonation and sulfation as well as simultaneous reactions.
7. The reaction rate constants of carbonation and sulfation reaction based upon the kinetic models follow the Arrhenius law. The values of reaction rate constants and activation energy are consistent with the experimental observations.
8. For the simultaneous reaction, nascent CaCO₃ appears to be very active to further react with SO₂. Kinetic models based on this observation fit experimental data well for both carbonation and sulfation reactions in simultaneous reaction.
9. The reaction rate constant for the reaction between CaCO₃ and SO₂ also is shown to follow the Arrhenius law.

5 RECOMMENDATIONS

This research work has been focused on studying the effects of reaction temperature and residence time on all the pertinent reactions involved. Only one kind of sorbent has been used in this study. The effects of the particle properties such as initial particle size, surface area and porosity on the reactions have not been explored to the extent that could lead to any conclusion. More work is recommended.

Deactivation models have been developed for carbonation, sulfation and simultaneous reactions. These models have been shown to fit the experimental data well. Although these models have taken into account the factor of particle activity decrease during the reaction, the changes of surface area and porosity of the particles have not been linked to the model. Future work is recommended in order to follow how the activity of the particle is effected due to the changes in pore structure of the particles after reaction.

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NOMENCLATURE

α	=	M_{R0}/F_{gas}
ϵ	=	Effectiveness factor, dimensionless
ρ_C	=	Molar density of CaCO_3 , mol/m ³
ρ_R	=	Molar density of reactant, mol/m ³
A	=	Total surface area, m ²
a	=	Activity, dimensionless
a_{CO_3}	=	Activity of CaCO_3 react with SO_2 in simultaneous reaction, dimensionless
C_{Ag}	=	Concentration of SO_2 in bulk gas phase, mol/m ³
$C_{ag,0}$	=	Initial concentration of SO_2 , mol/m ³
C_{Cg}	=	Concentration of CO_2 in bulk gas phase, mol/m ³
C_{Cs}	=	Concentration of CO_2 at the reaction surface of reactant core, mol/m ³
D_C	=	Diffusivity of CO_2 into the reactant core, m ² /sec
D_{CO_2}	=	Diffusivity of CO_2 through the product layer, m ² /sec
E	=	Activation energy, J/mol
E_d	=	Deactivation energy, J/mol
F_0	=	Initial mole fraction, moles/moles
F_{gas}	=	Gas volume flow rate, m ³ /s
K_0	=	Frequency factor, m ³ /mol sec ⁻¹
K_{d0}	=	Frequency factor for particle deactivation, m ³ /mol sec ⁻¹
K_C	=	k_C/ρ_R , m ³ /(mol·sec)
k	=	Reaction rate constant, based on the initial volume of Ca(OH)_2 (mol/m ³) ⁻¹ /sec
K_{dC}	=	$k_{dC}^*k_C/\rho_R$, apparent deactivation constant, m ³ /(mol·sec)
k_{dC}	=	the intrinsic deactivation constant, dimensionless
L	=	Total thickness of the particle, m, (flat geometry assumed)
l	=	Thickness of the product layer, m

- L_0 = Original length of the particle, m, (flat geometry assumed)
 M_{Ro} = molar flow rate of Ca(OH)_2 particles, mole/sec
 M_T = Total moles, moles
 M_w = Molecular or atomic weight, g/mol
 N_C = Number of moles of CaCO_3 at current time, mol
 N_S = Number of moles of CaSO_3 at current time, mol
 n_C, n_S = Number of moles of CaSO_3 (or CaCO_3) produced from Ca(OH)_2 , mol
 N_{Ro} = Original number of moles of particle, mol
 $-r$ = Rate of reaction between Ca(OH)_2 and SO_2 , mol/(m³ sec)
 $-r_{AC}$ = Rate of reaction between CaCO_3 and SO_2 , mol/(m³ sec)
 $-r'$ = Rate of reaction from Ca(OH)_2 to CaCO_3 (or CaSO_3) in simultaneous reaction, mol/(m³, sec)
 V_0 = Initial volumes of Ca(OH)_2 particles, m³
 W_{CaO} = Weight percentage of CaO in original sample, %
 X = Conversion of CaCO_3 (or CaSO_3) base on the Ca(OH)_2 , dimensionless
 x = Conversion of CaCO_3 (or CaSO_3) produced from Ca(OH)_2 in simultaneous reaction, dimensionless

APPENDIX A. Computer Programs for Kinetic Model Development

1. Carbonation Reaction

Program to optimize the value of K_C , K_{dC} for carbonation reaction

```
#include <conio.h>
#include <math.h>
#include <stdio.h>

#define dim 2
#define point 5
#define INI_F for(i=0;i<=dim+1;i++) { for (j=0;j<=dim;j++) \
                if (i==0 || j==0) f[i][j]=0;}

float xv[3][point]= {{0.03715195, 0.0317398, 0.06230742, 0.1041, 0.1333},
                    {0.1042422, 0.1229242, 0.1234046, 0.148, 0.1769},
                    {0.2786485, 0.3032921, 0.3027159, 0.3385, 0.3043}};

/* xv conversion */
/* l temperature, m residence time */

float Ci[]={2.901016, 2.259334, 1.969743}; /Initial concentration

float H[]={0.05, 0.075, 0.1, 0.5, 1};

int l;

main()
{
float XT(), Func();
void amoeba();
int i, j, T;
float f[dim+2][dim+1], K[dim+1], y[dim+2];
    /* f, matrix, K, vector of  $K_C$ ,  $K_{dC}$ , y, value of error function */
float *p[dim+2];

clrscr();

for (l=0;l<3;l++) {
    if (l==0) T=600;
```

```

else if (l==1) T=900;
else if (l==2) T=1100;
printf("T=%d\n",T);
f[1][1]=xv[l][0]/0.05;
f[1][2]=-log(0.9)/0.05;
INI_F
for (i=2; i <= dim+1; i++) {
    for (j=1; j<=dim; j++) {
        if ((i-j)==1)
            f[i][j]=f[1][j]+0.5;
        else
            f[i][j]=f[1][j];
    }
}
for (i=1; i<=dim+1; i++) {
    for (j=1; j<=dim; j++)
        K[j]=f[i][j];
    y[i]=Func(K);
}
for (i=1; i<=dim+1; i++) {
    p[i]=f[i];
}
amoeba(p, y, dim, 0.001,Func, 0);
for (j=1; j<=dim; j++)
    printf("%f\t%f\t", p[dim+1][j], p[dim+1][j]/Ci[l]);
printf("%f\t", y[dim+1]);
putchar('\n');
}

}

/* Function */
float Func(K)
float *K;
{
    float q;
    int m;
    for (m=0, q=0; m < point; m++) {
        q += pow( (XT(K[1], K[2], m)-xv[l][m]), 2);
    }
    return(q);
}

float XT(K, Ka, m)

```

```

float K, Ka;
int m;
{
    float q;
    q= K / Ka * (1- exp(-Ka * H[m]));
    return(q);
}

```

2. Sulfation reaction

(1) Program to optimize the values of K_A , K_{dA} for sulfation reaction

```

#include <conio.h>
#include <math.h>
#include <stdio.h>

#define dim 2
#define point 3
#define INI_F for(i=0;i<=dim+1;i++) { for (j=0;j<=dim;j++) \
    if (i==0 || j==0) f[i][j]=0;}

float xv[3][3]= {{0.02126, 0.01768, 0.02152}, /* xv: Conversion */
                 {0.06509, 0.05954, 0.0618592},
                 {0.07803, 0.07287639, 0.0875611}};

/* l temperature, m residence time */

float alpha[3][3]= {{0.2912886, 0.3276996, 0.2912886},
                   {0.2330308, 0.273083, 0.2621597},
                   {0.1747731, 0.2184664, 0.2330308}};

float Ci[]={0.06216463, 0.048414308, 0.042208779};

float H[]={0.05, 0.075, 0.1};

int l;

```

```

main()
{
float XT(), Func();
void amoeba();
int i, j, T;
float f[dim+2][dim+1], K[dim+1], y[dim+2];
float *p[dim+2];

clrscr();

for (l=0; l<3; l++) {
    if (l==0) T=600;
    else if (l==1) T=900;
    else if (l==2) T=1100;
    printf("T=%d\n", T);
    f[1][1]=xv[l][0]/(Ci[l]*0.05)*3;
    f[1][2]=-log(0.9)/(Ci[l]*0.05)*30;
    INI_F
    for (i=2; i <= dim+1; i++) {
        for (j=1; j<=dim; j++) {
            if ((i-j)==1)
                f[i][j]=f[1][j]+0.5;
            else
                f[i][j]=f[1][j];
        }
    }
    for (i=1; i<=dim+1; i++) {
        for (j=1; j<=dim; j++)
            K[j]=f[i][j];
        y[i]=Func(K);
    }
    for (i=1; i<=dim+1; i++) {
        p[i]=f[i];
    }
    amoeba(p, y, dim, 0.001, Func, 0);
    for (j=1; j<=dim; j++)
        printf("%f\t", p[dim+1][j]);
    printf("%f\t", y[dim]);
    putchar('\n');
}

/* Function */

```



```

float Func(K)
float *K;
{
    float xs, q;
    int m;
    for (m=0, q=0; m< point; m++) {
        xs=XT(K[1], K[2], m);
        q += pow((xs-xv[l][m]), 2);
    }
    return q;
}

float XT(K, Ka, m)
float K, Ka;
int m;
{
    float q, em;
    em=exp((Ci[l]*Ka-alpha[l][m]*K)*H[m]);
    q=K*Ci[l]*(1.-em)/(K*alpha[l][m]-em*Ci[l]*Ka);
    return(q);
}

```

(2) Program to calculate conversion and SO₂ concentration

```

/* Calculate Conversion and SO2 concentration */

#include <conio.h>
#include <math.h>
#include <stdio.h>

#define P 1.013e+5
#define R 8.314

float xv[3][3]={ {0.02126, 0.01768, 0.02152},    /* xv: Conversion */
                 {0.06509, 0.05954, 0.0618592},
                 {0.07803, 0.07287639, 0.0875611}};

/* i temperature, j residence time */

float alpha[3][3]= {{0.2912886, 0.3276996, 0.2912886},
                   {0.2330308, 0.273083, 0.2621597},

```

```
{0.1747731, 0.2184664, 0.2330308}};
```

```
float Ci[]={0.06216463, 0.048414308, 0.042208779};
```

```
float H[]={0.05, 0.075, 0.1};
```

```
FILE *fs[3], *fc[3];
```

```
int N;
```

```
main()
```

```
{
```

```
float xi;
```

```
void XT();
```

```
int i, j, T;
```

```
float f[3]={20.894707, 84.094910, 124.200729};
```

```
float fa[3]={1017.230225, 1301.364990, 1481.895996};
```

```
float K, Ka;
```

```
clrscr();
```

```
fs[0]=fopen("s0","w");
```

```
fs[1]=fopen("s1","w");
```

```
fs[2]=fopen("s2","w");
```

```
fc[0]=fopen("c0","w");
```

```
fc[1]=fopen("c1","w");
```

```
fc[2]=fopen("c2","w");
```

```
for (i=0;i<3;i++) {
```

```
    if (i==0) T=600;
```

```
    else if (i==1) T=900;
```

```
    else if (i==2) T=1100;
```

```
    fprintf(fs[i], "T=%d\n", T);
```

```
    fprintf(fc[i], "T=%d\n", T);
```

```
    K=f[i];
```

```
    Ka=fa[i];
```

```
    for (j=0; j<3; j++) {
```

```
        XT(K, Ka, i, j, T);
```

```
        Give subroutine temperatre and time */
```

```
    }
```

```

        fclose(fs[i]);
        fclose(fc[i]);
    }
}

void XT(K, Ka, i, j, T)
float K, Ka;
int i, j, T;
{
    float xs, C, em, h, t, tem;
    int d;
    h=H[j]/100;
    for (t=0, d=0; d<=100; d++, t +=h) {
        em=exp((Ci[i]*Ka-alpha[i][j]*K)*t);
        xs=K*Ci[i]*(1.-em)/(K*alpha[i][j]-em*Ci[i]*Ka);
        C=Ci[i]-alpha[i][j]*xs;
        tem=(T-32)/1.8+273.;
        C = C* (R*tem/P)*1e6;
        fprintf(fs[i], "%f\t%f\n", t,xs*100);
        fprintf(fc[i], "%f\t%f\n", t,C);
    }
    puts("\n", fs[i]);
    puts("\n", fc[i]);
}

```

1. Simultaneous Reaction

Program to optimize the value of K_{CaSO_3} , K_{CaCO_3} , K_{CO_3} and k_{dc} for simultaneous reaction

```

/* */

#include <conio.h>
#include <math.h>
#include <stdio.h>

float Ks, Kc, Kas, Kac, Ki, Kai, Kds, Kdc;

float fas[3]={1017.230225, 1301.364990, 1481.895996};
float fac[3]={1.883369, 8.139619, 20.556135};

```

```
float xvs[3][3]= {{0.03205, 0.03155, 0.03126},    /* xv: Conversion */
                  {0.04911, 0.06597, 0.06563},
                  {0.05728, 0.08725, 0.09507}};
```

```
float xvc[3][3]= {{0.03359, 0.0272, 0.02389},
                  {0.098695, 0.091395, 0.09407},
                  {0.26243, 0.20797, 0.21331}};
```

```
/* i temperature, j residence time */
```

```
float alpha[3][3]= {{0.2912886, 0.3276996, 0.2912886},
                    {0.2330308, 0.273083, 0.2621597},
                    {0.1747731, 0.2184664, 0.2330308}};
```

```
float Cis[]={0.06216463, 0.048414308, 0.042208779};
```

```
float Cic[]={2.901016, 2.259334, 1.969743};
```

```
float H[]={0.05, 0.075, 0.1};
```

```
float xis[3], xic[3];
```

```
float err0;
```

```
FILE *mc[3], *ms[3];
```

```
main()
{
void RK4(), RK0;
float DXsDT(), DXcDT(), DAsDT(), DAcDT(), DAiDT();
int OPT();
int i, j, T;
float fi[3], fai[3];
float fs[3]={20.894707, 84.094910, 124.200729};
float fc[3]={0.234620, 1.307473, 6.536572};
float err1, err2;
int l;    /* 1: Kds, 2: Kdc, 3: Ki, 4: Kai */
int flag;
```

```
float s, t;
```

```
clrscr();  
printf("N=?\n");  
scanf("%d", &N);
```

```
ms[0]=fopen("ms0", "w");  
ms[1]=fopen("ms1", "w");  
ms[2]=fopen("ms2", "w");  
mc[0]=fopen("mc0", "w");  
mc[1]=fopen("mc1", "w");  
mc[2]=fopen("mc2", "w");
```

```
for (i=0; i<3; i++) {  
    Kc=fc[i]*Cic[i];  
    fi[i]=(Kc*0.05-xvc[i][0])*2/(0.05*0.05*Kc*Cis[i]);  
}
```

```
for (i=0; i<3; i++) {  
    if (i==0) T=600;  
    else if (i==1) T=900;  
    else if (i==2)  
        T=1100;  
    printf("T=%d\n", T);  
    fprintf(ms[i], "T=%d\n", T);  
    fprintf(mc[i], "T=%d\n", T);  
    Kc=fc[i]*Cic[i];  
    Ks=fs[i];  
    Kas=fas[i];  
    Kac=fac[i]*Cic[i];  
    Ki=fi[i];  
    Kai=0.01;  
    Kds=1;  
    Kdc=10;  
    flag=1;  
    s=0.5;  
    t=0.1;  
    err0=10;  
    while ( flag != 0) {  
        flag=0;  
        flag=flag+OPT(1, Kds, i, s);  
        flag=flag+OPT(2, Kdc, i, s);
```

```

        flag=flag+OPT(3, Ki, i, s);
        flag=flag+OPT(4, Kai, i, s);
    }
    flag=1;
    while ( flag != 0) {
        flag=0;
        flag=flag+OPT(1, Kds, i, t);
        flag=flag+OPT(2, Kdc, i, t);
        flag=flag+OPT(3, Ki, i, t);
        flag=flag+OPT(4, Kai, i, t);
    }
    printf("%f\t%f\t%f\t%f\t%f\t%f\n", Kds, Kdc, Ki, Kai, err0);
    RK(i);
}
}

```

```

int OPT(1, K, i, r)
int l, i;
float K, r;
{
    int q, change;
    int j;
    float K0, err1, err2;
    q=0;
    change=1;
    K0=K;
    K=K*(1+r);
    while ( change == 1) {
        change=0;
        switch (l) {
            case (1): Kds=K;
                break;
            case (2): Kdc=K;
                break;
            case (3): Ki=K;
                break;
            case (4): Kai=K;
                break;
        }
        RK4(i);
        err1=0;
    }
}

```

```

err2=0;
for (j=0; j<3; j++) {
    err1=err1+(xvs[i][j]-xis[j])*(xvs[i][j]-xis[j]);
    err2=err2+(xvc[i][j]-xic[j])*(xvc[i][j]-xic[j]);
}
if ( ((err1+err2) < err0) && fabs(err1+err2-err0) > 1e-6){
    K0=K;
    K=K*(1+r);
    err0=err1+err2;
    change=1;
    q=1;
}
}
change=1;
K=K*(1-r);
while (change ==1) {
    change=0;
    switch (l) {
        case (1): Kds=K;
            break;
        case (2): Kdc=K;
            break;
        case (3): Ki=K;
            break;
        case (4): Kai=K;
            break;
    }
    RK4(i);
    err1=0;
    err2=0;
    for (j=0; j<3; j++) {
        err1=err1+(xvs[i][j]-xis[j])*(xvs[i][j]-xis[j]);
        err2=err2+(xvc[i][j]-xic[j])*(xvc[i][j]-xic[j]);
    }
    if ( ((err1+err2) < err0) && fabs(err1+err2-err0) > 1e-6){
        K0=K;
        K=K*(1-r);
        err0=err1+err2;
        change=1;
        q=1;
    }
}
switch (l) {

```

```

        case (1): Kds=K0;
            break;
        case (2): Kdc=K0;
            break;
        case (3): Ki=K0;
            break;
        case (4): Kai=K0;
            break;
    }
    return(q);
}

/* Runge-Kutta 4 */
void RK4(i)
int i;
{
    float xs, Cs, xc;
    float t, ac, as, ai;
    float h;
    float beta;
    float k11, k21, k31, k41;          /* 1: xs, 2: xc */
    float k12, k22, k32, k42;          /* 3: as, 4: ac, 5: ai */
    float k13, k23, k33, k43;
    float k14, k24, k34, k44;
    float k15, k25, k35, k45;

    int j;

    float d;

    xs=0;   Cs=Cis[i]; xc=0;
    t=0;    as=1;   ac=1;
    ai=0;
    beta=alpha[i][2];
    h=H[2]/100;

    for (d=0; d< 100; d++, t +=h ) {
        k11 = h * DXsDT(xs, as, ai, Cs, beta);
        k12 = h * DXcDT(xs, ac, ai, Cs, beta);
        k13 = h * DAsDT(xs, as, ac, Cs, beta);
        k14 = h * DAcDT(xs, as, ac, Cs, beta);
        k15 = h * DAiDT(xs, ac, ai, Cs, beta);
    }
}

```



```

k21 = h * DXsDT(xs+k11/2., as+k13/2., ai+k15/2., Cs, beta);
k22 = h * DXcDT(xs+k11/2., ac+k14/2., ai+k15/2., Cs, beta);
k23 = h * DAsDT(xs+k11/2., as+k13/2., ac+k14/2., Cs, beta);
k24 = h * DAcDT(xs+k11/2., as+k13/2., ac+k14/2., Cs, beta);
k25 = h * DAiDT(xs+k11/2., ac+k14/2., ai+k15/2., Cs, beta);

k31 = h * DXsDT(xs+k21/2., as+k23/2., ai+k25/2., Cs, beta);
k32 = h * DXcDT(xs+k21/2., ac+k24/2., ai+k25/2., Cs, beta);
k33 = h * DAsDT(xs+k21/2., as+k23/2., ac+k24/2., Cs, beta);
k34 = h * DAcDT(xs+k21/2., as+k23/2., ac+k24/2., Cs, beta);
k35 = h * DAiDT(xs+k21/2., ac+k24/2., ai+k25/2., Cs, beta);

k41 = h * DXsDT(xs+k31, as+k33, ai+k35, Cs, beta);
k42 = h * DXcDT(xs+k31, ac+k34, ai+k35, Cs, beta);
k43 = h * DAsDT(xs+k31, as+k33, ac+k34, Cs, beta);
k44 = h * DAcDT(xs+k31, as+k33, ac+k34, Cs, beta);
k45 = h * DAiDT(xs+k31, ac+k34, ai+k35, Cs, beta);

xs = xs + (k11+k41+2*(k21+k31))/6.0;
xc = xc + (k12+k42+2*(k22+k32))/6.0;
as = as + (k13+k43+2*(k23+k33))/6.0;
ac = ac + (k14+k44+2*(k24+k34))/6.0;
ai = ai + (k15+k45+2*(k25+k35))/6.0;
for (j=0; j<3; j++) {
    if ( fabs(t+h-H[j]) < 1e-4) {
        xis[j]=xs;
        xic[j]=xc;
    }
}
}

void RK(i)
int i;
{
    float xs, Cs, xc;
    float t, ac, as, ai;
    float h;
    float beta;
    float k11, k21, k31, k41;
    float k12, k22, k32, k42;
    float k13, k23, k33, k43;
    /* 1: xs, 2: xc */
    /* 3: as, 4: ac, 5: ai */

```

```
float k14, k24, k34, k44;  
float k15, k25, k35, k45;
```

```
int j;
```

```
int d;
```

```
xs=0;    Cs=Cis[i]; xc=0;  
t=0;    as=1;    ac=1;  
ai=0;  
beta=alpha[i][2];  
h=H[2]/100;
```

```
fprintf(ms[i], "%f\t%f\n", t, xs*100);  
fprintf(mc[i], "%f\t%f\n", t, xc*100);
```

```
for (d=0; d< 100; d++, t +=h) {
```

```
    k11 = h * DXsDT(xs, as, ai, Cs, beta);  
    k12 = h * DXcDT(xs, ac, ai, Cs, beta);  
    k13 = h * DAsDT(xs, as, ac, Cs, beta);  
    k14 = h * DAcDT(xs, as, ac, Cs, beta);  
    k15 = h * DAiDT(xs, ac, ai, Cs, beta);
```

```
    k21 = h * DXsDT(xs+k11/2., as+k13/2., ai+k15/2., Cs, beta);  
    k22 = h * DXcDT(xs+k11/2., ac+k14/2., ai+k15/2., Cs, beta);  
    k23 = h * DAsDT(xs+k11/2., as+k13/2., ac+k14/2., Cs, beta);  
    k24 = h * DAcDT(xs+k11/2., as+k13/2., ac+k14/2., Cs, beta);  
    k25 = h * DAiDT(xs+k11/2., ac+k14/2., ai+k15/2., Cs, beta);
```

```
    k31 = h * DXsDT(xs+k21/2., as+k23/2., ai+k25/2., Cs, beta);  
    k32 = h * DXcDT(xs+k21/2., ac+k24/2., ai+k25/2., Cs, beta);  
    k33 = h * DAsDT(xs+k21/2., as+k23/2., ac+k24/2., Cs, beta);  
    k34 = h * DAcDT(xs+k21/2., as+k23/2., ac+k24/2., Cs, beta);  
    k35 = h * DAiDT(xs+k21/2., ac+k24/2., ai+k25/2., Cs, beta);
```

```
    k41 = h * DXsDT(xs+k31, as+k33, ai+k35, Cs, beta);  
    k42 = h * DXcDT(xs+k31, ac+k34, ai+k35, Cs, beta);  
    k43 = h * DAsDT(xs+k31, as+k33, ac+k34, Cs, beta);  
    k44 = h * DAcDT(xs+k31, as+k33, ac+k34, Cs, beta);  
    k45 = h * DAiDT(xs+k31, ac+k34, ai+k35, Cs, beta);
```

```
xs = xs + (k11+k41+2*(k21+k31))/6.0;  
xc = xc + (k12+k42+2*(k22+k32))/6.0;  
as = as + (k13+k43+2*(k23+k33))/6.0;
```

```

        ac = ac + (k14+k44+2*(k24+k34))/6.0;
        ai = ai + (k15+k45+2*(k25+k35))/6.0;
        fprintf(ms[i], "%ft%f\n", t+h, xs*100);
        fprintf(mc[i], "%ft%f\n", t+h, xc*100);
    }
}

/* Function */
float DXsDT(xs, as, ai, Cs, al)
float xs, as, ai, Cs, al;
{
    float q;
    q=(Cs-al*xs)*(Ks*as+Ki*ai);
    return(q);
}

float DXcDT(xs, ac, ai, Cs, al)
float xs, ac, ai, Cs, al;
{
    float q;
    q=Kc*ac-Ki*(Cs-al*xs)*ai;
    return(q);
}

float DAsDT(xs, as, ac, Cs, al)
float xs, as, ac, Cs, al;
{
    float q;
    q= -Kas*(Cs-al*xs)*as-Kdc*ac;
    return(q);
}

float DAcDT(xs, as, ac, Cs, al)
float xs, as, ac, Cs, al;
{
    float q;
    q=-Kac*ac-Kds*(Cs-al*xs)*as;
    return(q);
}

float DAiDT(xs, ac, ai, Cs, al)
float xs, ac, ai, Cs, al;
{

```

```

float q;
q=Kc*ac-Kai*ai;
return(q);
}

```

3. Sub Routines

1) Downhill simplex method in multidimensions

```

#include <math.h>

#define NMAX 5000
#define ALPHA 1.0
#define BETA 0.5
#define GAMMA 2.0

#define GET_PSUM for (j=1;j<=ndim;j++) { for (i=1,sum=0.0;i<=mpts;i++)\
sum += p[i][j]; psum[j]=sum;}

void amoeba(p,y,ndim,ftol,funk,nfunk)
float **p,y[],ftol,(*funk)();
int ndim,*nfunk;
{
    int i,j,ilo,ihi,inhi,mpts=ndim+1;
    float ytry,ysave,sum,rtol,amotry(),*psum,*vector();
    void nerror(),free_vector();

    psum=vector(1,ndim);
    *nfunk=0;
    GET_PSUM
    for (;;) {
        ilo=1;
        ihi = y[1]>y[2] ? (inhi=2,1) : (inhi=1,2);
        for (i=1;i<=mpts;i++) {
            if (y[i] < y[ilo]) ilo=i;
            if (y[i] > y[ihi]) {
                inhi=ihi;
                ihi=i;
            } else if (y[i] > y[inhi])
                if (i != ihi) inhi=i;
        }
    }
}

```

```

    rtol=2.0*fabs(y[ihi]-y[iilo])/(fabs(y[ihi])+fabs(y[iilo]));
    if (rtol < ftol) break;
    if (*nfunk >= NMAX) nrerror("Too many iterations in AMOEBA");
    ytry=amotry(p,y,psum,ndim,funk,ihi,nfunk,-ALPHA);
    if (ytry <= y[iilo])
        ytry=amotry(p,y,psum,ndim,funk,ihi,nfunk,GAMMA);
    else if (ytry >= y[ihi]) {
        ysave=y[ihi];
        ytry=amotry(p,y,psum,ndim,funk,ihi,nfunk,BETA);
        if (ytry >= ysave) {
            for (i=1;i<=mpts;i++) {
                if (i != iilo) {
                    for (j=1;j<=ndim;j++) {
                        psum[j]=0.5*(p[i][j]+p[iilo][j]);
                        p[i][j]=psum[j];
                    }
                    y[i]=(*funk)(psum);
                }
            }
            *nfunk += ndim;
            GET_PSUM
        }
    }
}
free_vector(psum,1,ndim);
}

```

```

float amotry(p,y,psum,ndim,funk,ihi,nfunk,fac)
float **p,*y,*psum,(*funk)(),fac;
int ndim,ihi,*nfunk;
{
    int j;
    float fac1,fac2,ytry,*ptry,*vector();
    void nrerror(),free_vector();

    ptry=vector(1,ndim);
    fac1=(1.0-fac)/ndim;
    fac2=fac1-fac;
    for (j=1;j<=ndim;j++) ptry[j]=psum[j]*fac1-p[ihi][j]*fac2;
    ytry=(*funk)(ptry);
    ++(*nfunk);
    if (ytry < y[ihi]) {
        y[ihi]=ytry;
    }
}

```

```

        for (j=1;j<=ndim;j++) {
            psum[j] += ptry[j]-p[ihi][j];
            p[ihi][j]=ptry[j];
        }
    }
    free_vector(ptry,1,ndim);
    return ytry;
}

```

```

#undef ALPHA
#undef BETA
#undef GAMMA
#undef NMAX

```

2) Utility Routines

```

#include <alloc.h>
#include <stdio.h>
#include <stdlib.h>

```

```

void free_vector(v, nl, nh)
float *v;
int nl, nh;
{
    free((char*) (v+nl));
}

```

```

#include <stdio.h>

```

```

void nrerror(error_text)
char error_text[];
{
    void exit();

    fprintf(stderr, "Numerical Recipes run-time error...\n");
    fprintf(stderr, "%s\n", error_text);
    fprintf(stderr, "...now exiting to sys...\n");
    exit(1);
}

```

```
#include <alloc.h>
#include <stdio.h>
#include <stdlib.h>

float *vector(nl, nh)
int nl, nh;
{
    float *v;
    v=(float *) malloc((unsigned) (nh-nl+1)*sizeof(float));
    if (!v) perror("allocation failur in vecor()");
    return(v-nl);
}
```