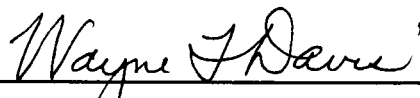


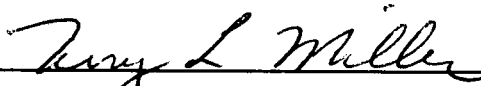
To the Graduate Council:

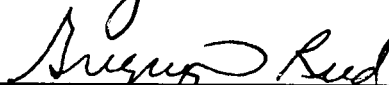
I am submitting herewith a dissertation written by Arijit Pakrasi entitled "Kinetic Studies on the Removal of Hydrogen Chloride from Flue Gas by Hydrated Lime Powders in a Bench Scale Fixed Bed Reactor". I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Ph.D with a major in Civil Engineering.

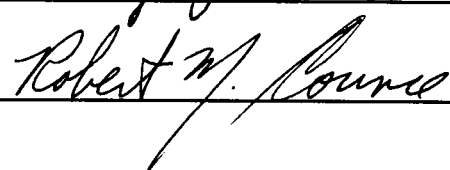


Dr. Wayne T. Davis, Major Professor

We have read this dissertation
and recommend its acceptance:







Accepted for the Council:



Associate Vice Chancellor
and Dean of The Graduate
School

Kinetic Studies on the Removal of Hydrogen Chloride
from Flue Gas by Hydrated Lime Powders in a
Bench Scale Fixed Bed Reactor

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Arijit Pakrasi

August 1992

DEDICATION

This dissertation is dedicated to my loving wife Sarmistha
and my dear son Riddhi
who shared with me the pains and pleasures of my graduate
study and made numerous sacrifices to make this happen

ACKNOWLEDGEMENTS

I would like to express my deep gratitude to my major professor, Dr. Wayne T. Davis, who inspired me throughout my graduate study. His guidance, patience and support helped me immensely in my research. I also thank other committee members Dr. Terry Miller, Dr. Pete Counce and Dr Greg Reed for their valuable comments and support.

I thank Parham Cain, my colleague in graduate school, for her invaluable help in my testing and analysis. My thanks to Rebecca Pullen, fellow graduate student, for helping me whenever I needed. Also I thank Sharon Hale for all her help during the experiments, and Sherman and Clarence at the Berry Hall for building the experimental setup.

I would like to thank Dr. Mohammed Amin, Dr. David Joy and Dr. Spruiell for their help with analysis. Thanks to Ann Lacava at the graduate school for her patient editing. Finally, I thank all persons in the Air Quality Services Division (Knoxville) of International Technology Corporation, specially Tony Babb and Nick Chadda, for their help and support in the past one year in completing my research.

ABSTRACT

The kinetics of the removal of hydrogen chloride gas by hydrated lime powders was determined in a fixed bed bench scale reactor at conditions representative of low temperature dry sorbent injection process.

The kinetic tests showed that relative humidity of the gas was the most important parameter in determining both the rate and extent of conversion. Other operating parameters such as temperature, gas concentration, surface area of the hydrated lime also affected the conversion at different degrees depending on the relative humidity of the test condition. Hygroscopic property of the reaction product i.e. calcium chloride, significantly affected the conversion at relative humidities of 25% and higher. Diffusional resistance in the solid product layer, was determined to be the primary reason for incomplete conversion of the hydrated lime in test conditions <25% relative humidity.

The shrinking unreacted core model based on diffusion of hydrogen chloride through the product layer as the limiting mechanism, was found to be unsuitable for the tests exhibiting incomplete conversion. An empirical model, developed based on empirical correlations from the experimental data of this study, was found to predict reasonably well the reported conversions in other studies.

TABLE OF CONTENTS

CHAPTER	Page
1. INTRODUCTION	1
1.1. Incineration of Municipal Solid Waste ...	1
1.2. Uncontrolled Air Emissions from MSW Incinerators	2
1.3. Current Regulations and Future Trends ...	4
1.4. Overview of the DSI Process	6
1.5. Potential Impact of $\text{HCl}/\text{Ca}(\text{OH})_2$ Reaction in a DSI Process	11
1.6. Kinetic Data on Hydrogen Chloride Removal by Dry Sorbents	13
1.7. Objectives of this Study	13
2. LITERATURE SURVEY	16
2.1. Hydrogen Chloride Removal in Full Scale DSI Systems	16
2.2. Hydrogen Chloride Removal at the Pilot Plant Scale	19
2.3. Hydrogen Chloride Removal in Lab/Bench Scale Reactors	23
2.4. The Reaction of Hydrogen Chloride with Hydrated Lime	30
2.5. Noncatalytic Gas-solid Reactions	34
3. EXPERIMENTAL METHODS	43
3.1. General Approach	43

3.2. Fixed Bed Reactor Tests	43
3.3. Characterization of Sorbent and Reaction Products	59
4. RESULTS AND DISCUSSION	62
4.1. Preliminary Tests on the Fixed Bed Reactor	62
4.2. Characterization of Hydrated Lime Sorbent	65
4.3. Kinetic Tests in The Fixed Bed Reactor .	75
4.4. Analysis of the Reaction Products	105
4.5. Application of Gas-solid Reaction Models	125
5. DEVELOPMENT OF AN EMPIRICAL MODEL	138
5.1. Conceptual Model	138
5.2. Prediction of Conversion by Empirical Model	155
5.3. Comparison of Model with Reported Experimental Data	164
6. CONCLUSIONS	169
7. RECOMMENDATIONS FOR FURTHER STUDY	174
LIST OF REFERENCES	177
APPENDIXES	183
Appendix 1. Physical Properties of F-75 Sand	184
Appendix 2. Physical Properties of Tenn Luttrel Hydrated Lime	186
Appendix 3. Operating Conditions and Sorbent	

Conversions in Kinetic Tests	198
Appendix 4. Parameters of Best Fit Equation for Kinetic Tests	212
Appendix 5. Operating Conditions and Results in Product Analyses Tests	216
Appendix 6. Predictions of Empirical Model at the Test Conditions of This Study ...	219
VITA	244

LIST OF FIGURES

Figure	Page
1.1 Various Options in the Dry Sorbent Injection (DSI) Process	8
2.1 Effect of Temperature on Hydrogen Chloride Emissions in Full Scale DSI Plants	20
2.2 Results of Karlsson's Experiments on Hydrogen Chloride Removal by Hydrated Lime in Fixed Bed Integral Reactor	24
2.3 Results of Gullet's Experiments on Hydrogen Chloride Removal by Hydrated Lime in Short Term Differential Reactor	27
2.4 Results of Jozewicz's Experiments on Hydrogen Chloride Removal by Hydrated Lime in Fixed Bed Integral Reactor.....	29
3.1 Experimental Setup for the Kinetic Tests of Hydrogen Chloride by Hydrated Lime	44
3.2 A Sectional View of the Evaporator'.....	47
3.3 A Sectional View of the Reactor Assembly	50
4.1 Chloride Uptake by the Sample bed in a Blank Test and a Lime Test at 1000 ppmv HCl	64
4.2 Typical Nitrogen Adsorption/desorption Isotherm of Tenn Luttrell Hydrated Lime	71
4.3 SEM Photograph of the Unreacted Tenn Luttrell Hydrated Lime	74

4.4	Sorbent Conversion for the Three Size Fractions of Hydrated Lime at 1000 ppmv HCl .	76
4.5	Sorbent Conversion at 0% Moisture and 1000 ppmv HCl	82
4.6	Sorbent Conversion at 7% Moisture, 1000 ppmv HCl and at 175 F to 400 F	85
4.7	Sorbent Conversion at 10% Moisture, 1000 ppmv HCl and at 175 F to 400 F	86
4.8	Sorbent Conversion at 20% Moisture, 1000 ppmv HCl and at 175 F to 400 F	87
4.9	Sorbent Conversion at 175 F, 1000 ppmv HCl and 0% to 20% moisture	89
4.10	Sorbent Conversion at 200 F, 1000 ppmv HCl and 0% to 20% moisture	90
4.11	Sorbent Conversion at 225 F, 1000 ppmv HCl and 0% to 30% moisture	91
4.12	Sorbent Conversion at 300 F, 1000 ppmv HCl and 0% to 20% moisture	92
4.13	Sorbent Conversion at 400 F, 1000 ppmv HCl and 0% to 20% moisture	93
4.14	Sorbent Conversion at 1000 ppmv HCl and Relative Humidities of 25% and 15%	95
4.15	Sorbent Conversion at 1000 ppmv HCl and Relative Humidities of 8% and <2.2%	96
4.16	Effect of Gas Concentration on Sorbent Conversion at 175 F and 25% Relative Humidity	98

4.17 Effect of Gas Concentration on Sorbent	
Conversion at 200 F and 15% Relative Humidity	99
4.18 Effect of Gas Concentration on Sorbent	
Conversion at 225 F and 8% Relative Humidity	100
4.19 Effect of Gas Concentration on Sorbent	
Conversion at 300 F and 2.2% Relative Humidity	101
4.20 Effect of Specific Surface Area on Sorbent	
Conversion at 1000 ppmv HCl and 10% Moisture	103
4.21 Conversion of Hydrated Lime in Product	
Analysis Tests	110
4.22 Available Porosity at Maximum Conversion	111
4.23 Effect of Conversion on Pore Size Distribution	
of Hydrated Lime at 1000 ppmv HCl	113
4.24 Effect of Conversion on Available Pore Area .	115
4.25 SEM Photograph of the Reacted Sorbent	117
4.26 Water Content of the Reacted Sorbent at	
Various Test Conditions	121
4.27 Effect of Preconditioning of Hydrated Lime on	
Conversion	124
4.28 Conceptual Model of the Shrinking Unreacted	
Core	127
4.29 F(X) versus Time Plot at Relative Humidity of	
25% and 175 F	130
4.30 Shrinking Core Model Predicted Conversions and	
Experimental Conversions at 25% Relative	
Humidity and 175 F	132

4.31 F(X) versus Time Plot at 0.6% Relative Humidity and 400 F	134
4.32 Shrinking Core Model Predicted Conversions and Experimental Conversions at 0.6% RH and 400 F	136
4.33 Comparison of Experimental Conversion with Conversion Predicted by Shrinking Core Model for Tests at <25% Relative Humidity	137
5.1 Effect of Relative Humidity on Reaction Order	144
5.2 Effect of Relative Humidity on Frequency Factor	147
5.3 Effect of Relative Humidity on Activation Energy in >5% Relative Humidity Tests	148
5.4 Effect of Relative Humidity on Activation Energy in <5% Relative Humidity Tests	150
5.5 Effect of Relative Humidity on Time Constant in <5% Relative Humidity Tests	153
5.6 Effect of Relative Humidity on Time Constant in >5% Relative Humidity Tests	154
5.7 Conversion Predicted by the Empirical Model at 175 F and 25% Relative Humidity	159
5.8 Conversion Predicted by Empirical Model at 200 F and 15% Relative Humidity	160
5.9 Conversion Predicted by the Empirical Model at 225 F and 8% Relative Humidity	161
5.10 Conversion Predicted by the Empirical Model at 400 F and 0.6% Relative Humidity	162

5.11 Conversion Predicted by the Empirical Model for All Tests between 500 ppmv and 5000 ppmv HCl Concentration	163
5.12 Comparison of Predictions of the Empirical Model and the Shrinking Core Model with Reported Experimental Data	167

LIST OF TABLES

Table	Page
1.1 Sources and Typical Emissions of Pollutants from MSW Incineration	3
1.2 Performance Standards and Emission Guidelines for MSW Combustors (CAAA, February 1991)	5
2.1 Water Uptake and Solubility of Calcium Chloride	33
4.1 Composition of Tenn Luttrel Hydrated Lime (Product #1)	67
4.2 Physical Properties of Tenn Luttrel Hydrated Lime	68
4.3 Brief Operating Conditions of the Kinetic Tests	78
4.4 Brief Operating Conditions of the Product Analyses Tests	108
4.5 Moisture Content of Tenn Luttrel Hydrated Lime at Various Equilibration Conditions	120
5.1 Frequency Factor " A_0 " and Activation Energy "E" obtained from the Initial Reaction Rate Constant and Temperature	146
5.2 Initial Reaction Rate " $r_a(0)$ and time Constant " t_c " at Different Test Conditions ..	151

5.3	Summary of Correlations used in the Empirical Model	156
5.4	Summary of Operating Conditions and Results of Selected Pilot Scale and Bench Scale Studies for Comparison with Empirical Model	165

CHAPTER 1

INTRODUCTION

1.1 Incineration of Municipal Solid Waste

Adequate disposal of municipal solid waste remains one of the major issues of concern for many communities in the United States. Approximately 180 million tons of municipal waste was generated in this country in 1988. This figure is expected to increase by at least 10% by the year 2000 (JAWMA, 1991). At present, approximately 73% of the municipal solid waste is landfilled. However, over 50 % of the presently operating 6000 landfills are expected to close within next five years. Few new landfills are planned due to high cost of operation and public resistance in the form of NIMBY (Not In My BackYard). This continuous shrinkage in available and planned landfill capacity has made the MSW disposal a critical issue in the recent years.

Incineration has been proposed and practiced as one of the alternatives to landfill. Currently, there are approximately 100 existing waste-to-energy plants and incinerators burning 14% of the municipal solid waste generated in United States. Seventy more such plants have been proposed to be constructed between 1992 and 1997 (JAWMA, 1991). However, despite some of it's obvious

advantages, such as waste volume reduction of up to 90%, destruction of harmful pathogens, and potential of recovery of energy from the waste, wide application of incineration has been restricted mainly due to public concern over the harmful air emissions from the process. Adequately addressing the control of emissions from incineration is therefore considered to be one of the key issues for its acceptance by the public and in the role it can play in mitigating the MSW disposal problem in the coming years.

1.2 Uncontrolled Air Emissions from MSW Incinerators

Air emissions from the MSW incinerators consist of acid gases such as hydrogen chloride, sulfur dioxide, hydrogen fluoride, particulate including metals such as arsenic, beryllium, cadmium, lead, mercury etc. and the organics, commonly represented by dioxins (PCDD), dibenzofurans (PCDF) and products of incomplete combustion (PICs). Uncontrolled emissions from the facilities show considerable variations depending on the type of the incinerators e.g. mass burned or refuse derived fuel, the waste composition, and the operating conditions. Sources of the emissions and typical ranges of the uncontrolled emissions from MSW incinerators in the United States is shown in Table 1.1 (Donnelly, J.R., 1991).

Table 1.1 : Sources and typical emissions of pollutants
from MSW incineration

Pollutant	Principal source	Uncontrolled emission
Particulate	Ash in waste	0.5-4.0 gr/dscf
Acid gases		
HCl	Chlorinated plastics	400-1000 ppm _{dv}
SO ₂ /SO ₃	Sulfur compounds	150-600 ppm _{dv}
HF	Fluorocarbons	0-10 ppm _{dv}
NO _x	Air & fuel nitrogen	120-300 ppm _{dv}
Heavy metals		
Arsenic	Metal components	<0.01-0.1 mg/nm ³
Cadmium	Metal components	0.01-0.5 mg/nm ³
Lead	Metal components	20-100 mg/nm ³
Mercury	Metal components	<0.1-1 mg/nm ³
Organics		
PCDD/PCDF	Incomplete combustion of organics	20-50 ng/m ³

Source : Donnelly, J.R., "Overview of Air Pollution Controls for Municipal Waste", Proceedings of the Second International Specialty Conference, Tampa, FL, 1991.

1.3 Current Regulations and Future Trends

In response to public concern, USEPA issued two sets of regulations in February 1991 to control emissions from Municipal Solid Waste Combustors (MSWC) as part of the Clean Air Act Amendments of 1990. The first set of regulations apply to the new combustors (New Source Performance Standards) and the second set of regulations apply to the existing combustors (Emission Guidelines). At the present, combustors with >250 tpd capacities are being regulated. Combustors below this capacity will be regulated within two years. The performance standards and the emission guidelines are given in Table 1.2.

The new emission levels specified in the guidelines are based on the premise that the "Best Demonstrated Technology" or "BDT" for reducing emissions differs based on the aggregate size of the facility. The best demonstrated technology is that technology which achieves greatest reduction in emissions, considering costs. Good combustion practice is considered BDT in all sizes for control of organics. However, for control of acid gases and metals, the BDT is based on the aggregate size of the facility as follows (Zmuda and Smith, 1991):

Facilities with aggregate capacity of >1100 tpd :

Spray dryer followed by a particulate control device.

Table 1.2 : Performance Standards and Emission Guidelines
for MSW Combustors (CAAA, February, 1991)

	Performance Standards (New Sources)	Emission Guidelines (Existing Sources)	
Capacity	Unit >250	Unit >250 <=2200	Facility >2200
Particulates (gr/dscf)	0.015	0.030	0.015
Opacity (%)	10	10	10
Organics (PCDD/PCDF) (ng/dscm)			
Mass burn	30	125	60
RDF fired	30	250	60
Acid Gases (%/ppm)			
- HCl	95/25	50/25	90/25
- SO ₂	80/30	50/30	70/30
- NOx	180	None	None
CO (ppm)	50-150*	50-250*	50-250*

Note : All emissions limits are referenced at dry gas conditions at 7% oxygen concentration.

* - Range of values reflect different types of MWCs.

Source : Donnelly, J.R., "Overview of Air Pollution Controls for Municipal Waste", 1991 MSW conference, Tampa, FL.

Facilities with aggregate capacity of <1100 tpd :

Dry sorbent injection (DSI) followed by a particulate control device.

As per a recent report on the status of MSW combustors in the USA published by Waste Age magazine (Zmuda and Smith, 1991), out of the existing 148 operational waste incinerator installations, approximately 100 units will be regulated by the new Clean Air Act Amendments and will require emission controls. Out of these, the BDT for at least 30 of the plants will be Dry Sorbent Injection (DSI) based on their aggregate capacity. As more waste incinerators are put on stream or planned to solve the solid waste problems in communities across the nation, more DSI plants are expected to be operational.

1.4 Overview of the DSI Process

Dry Sorbent Injection, or DSI is a process for acid gas control in which dry, pulverized alkaline sorbent (most commonly hydrated lime) is injected into the flue gas stream containing the acid gases. The acid gases are removed by the sorbent from the flue gas through heterogenous gas-solid reaction. The product of reaction together with the unreacted sorbent are collected in a downstream particulate collector, such as a bag filter or

an electrostatic precipitator, while the cleaned gas is vented to the atmosphere through a stack. Disposal of the collected solids is accomplished in the same manner as existing fly ash disposal methods.

One of the main advantages of the DSI process over conventional wet scrubbers and spray dryers is the complete elimination of liquid handling, including the slaking of lime. In the DSI process, the hydrated lime is injected pneumatically, thus eliminating heavy duty atomizers needed in spray drying. In the absence of any large moving parts, the operation of a DSI system is simple and requires little maintenance. The process also has great potential as a retrofit, if the existing ductwork and baghouse can be used, since then it can be incorporated with minimum layout changes and downtime.

Depending on the location of injection of the sorbent, DSI technology can be divided in two different types. In the first type, the sorbent is injected directly into the high temperature zone of the combustor, sometimes referred to as Furnace Sorbent Injection or FSI. In the second form of DSI the sorbent is injected either in the intermediate temperature zone downstream of the furnace or in the low temperature zone downstream of the economizer. In the latter case, a quench tower is sometimes used to cool and humidify the flue gas. The various options of the dry injection process are schematically shown in Figure 1.1.

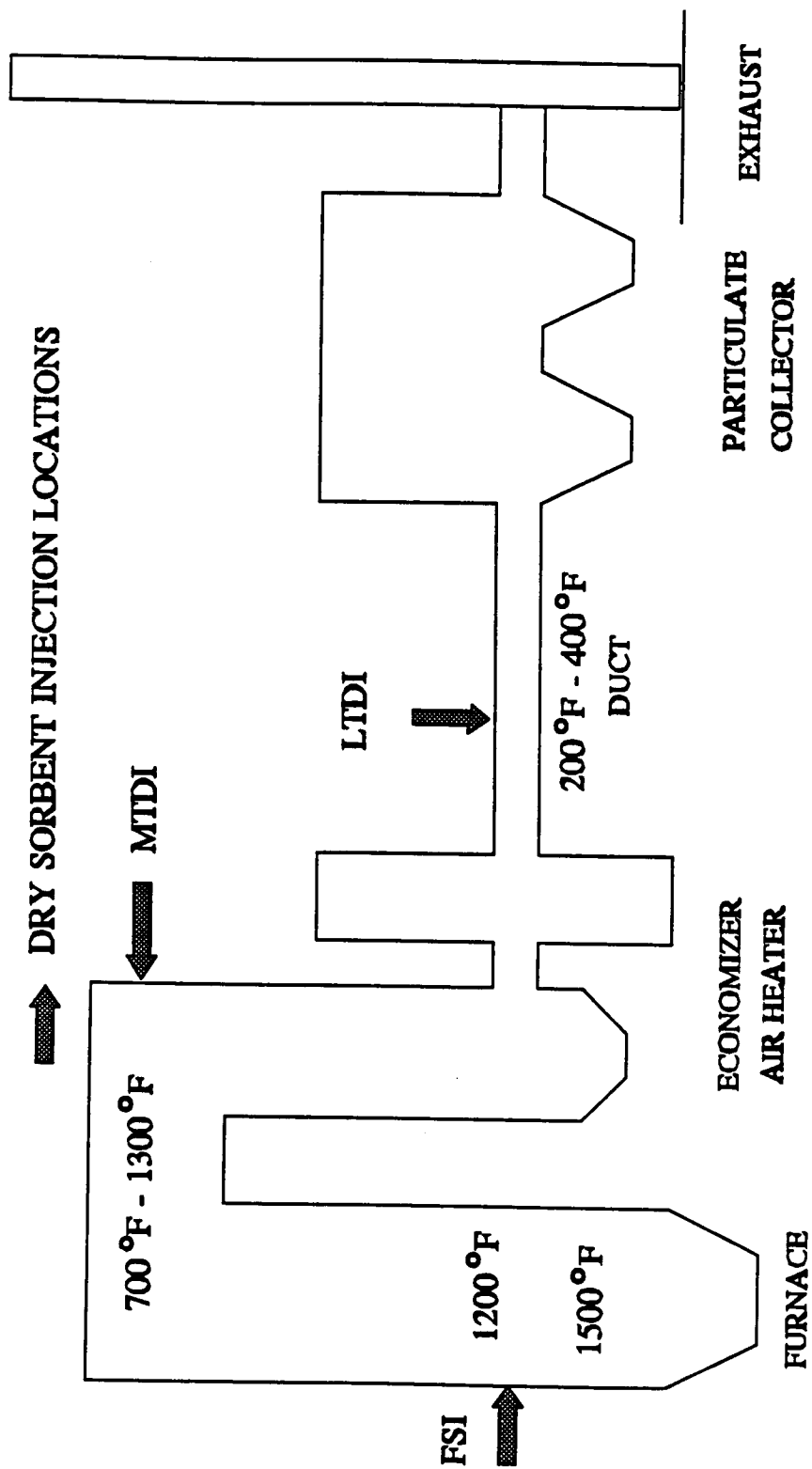


Figure 1.1. Various Options in the Dry Sorbent Injection Process.

In post combustion low temperature DSI processes, the sorbent is injected at various locations in the duct downstream of the economizer, at temperatures ranging from 200 °F to 400 °F. The most common sorbent is hydrated lime although sodium bicarbonate and trona have also been used (White and Vancil, 1989). Calcium based sorbents are preferred because these are available in large quantities in the United States and are much less expensive. Post combustion DSI process has a number of advantages as an acid gas removal technology, such as ease of retrofit, low capital and operating cost, simple design and operation and, higher sorbent utilization compared to FSI. The disadvantages are lower sorbent utilization compared to the spray drying process, limited acid gas removal capability, and significant increase in particulate load.

Though the overall acid removal efficiency and the sorbent utilization is lower in the DSI process compared to the spray drying process, there is one significant advantage in the former process. A large amount of water is injected in the system in the spray drying process in the form of slurry. While this aqueous phase sorbent achieves high acid gas removal efficiency, the water has to be evaporated within the short residence time of the dryer to avoid wet deposits. The reaction between lime and hydrogen chloride produces a hygroscopic calcium chloride salt, which elevates the wet bulb temperature of the slurry

droplets (Klingspor, et. al, 1989). To avoid inadequate drying and wet deposits, the system has to be operated at a higher temperature than if no calcium chloride were present. For example, while the spray dryers in the case of desulfurization of coal fired boiler flue gas usually operate at 140 °F to 150 °F, the operating temperature in a MSWC application is normally maintained at 300 °F or higher. In the DSI process, on the other hand, water and sorbents are separately injected and the primary function of the water is to cool and humidify the gas rather than serve as the medium for transport of the sorbent in a slurry. Subsequent presence of water in the sorbent particle is due to either collision with water droplets or by adsorption of water on the surface of the dry particle. Since this amount of water is usually much smaller and on the surface of the sorbent particle, drying problems are not encountered. Thus, the typical DSI system can be operated at much lower temperatures than a spray dryer. Recent studies in a 50 scfm capacity pilot plant scale showed that the wet deposits were avoided if the DSI system was operated above approach temperatures as low as 40 °F (Jozewicz & Chang, 1989). At approximately 10% moisture content (v/v), this results in an operating temperature of 170 °F, substantially lower than a typical spray dryer operating temperature for MSW applications.

In addition to the lower volume of gas handled, there

is another significant benefit in operating the system at these lower temperatures. The removal of volatile metals such as mercury from the incinerator flue gas is enhanced by condensation of gaseous metals/metal oxides on nuclei present in the flue gas, growth and subsequent removal in particulate devices. The organics are also known to be removed partly by adsorption on the available solid surfaces of the particulate in the flue gas. Both these removal mechanisms are shown to be enhanced at lower temperatures (Gullet, 1989, White and Vancil, 1989, Brna, 1991). Thus, a lower operating temperature in a DSI process is expected to increase the metals and organics removal efficiency substantially, better than currently possible in spray dryers operating at higher temperatures. In view of the current focus on mercury emissions and anticipated regulations for its control from the municipal incinerator flue gases, the lower operating temperature may be a significant advantage of the DSI process.

1.5 Potential Impact of $\text{HCl}/\text{Ca}(\text{OH})_2$ Reaction in a DSI Process

The major constituents of acid gases in the MSW incinerator flue gases are hydrogen chloride and sulfur dioxide. In the DSI process, both these gases are removed

by the sorbent through noncatalytic gas-solid reactions. The overall process is a complex interaction of individual steps involving diffusion of acid gases from bulk gas stream to the surface of the solid sorbent, diffusion of the acid gases through the solid phase of product layer, adsorption and reaction of acid gases on the solid reactant surface. The presence of two acid gases, hydrogen chloride and sulfur dioxide, further complicates the overall process due to competition for available reactant. Additionally, the mechanism and kinetics of hydrogen chloride removal may have significant influence on the removal of sulfur dioxide and thus on the overall removal of the acid gases due to;

a) higher reactivity of hydrogen chloride with lime and b) formation of a higher molar volume solid product (i.e. calcium chloride) which is also hygroscopic. While the hygroscopic nature of the product may promote further removal of the acid gases, the product layer in the sorbent can offer substantial resistance to gas diffusion through the sorbent and even can lead to incomplete conversion due to pore plugging. Thus, understanding the mechanism and kinetics of hydrogen chloride removal by dry hydrated lime is an important step in understanding the overall acid gas removal in DSI process.

1.6 Kinetic Data on Hydrogen Chloride Removal by Dry Sorbents

There is a lack of data on the kinetics of removal of hydrogen chloride gas by dry hydrated lime. The DSI process has been used in full scale applications only in the last five to six years in the United States. The detailed performance data from most of these installations have not been reported. Data reported from the plants are also at differing operating conditions. As it will be discussed in the next chapter, data from the pilot plant tests and lab scale tests are not comprehensive. Most of the lab scale tests focused only on the maximum conversion of a fixed bed of hydrated lime at different operating conditions, and not on the rate of conversion. While data on the maximum conversion is important to compare the potential of hydrated lime with other sorbents, it does not provide insight on the kinetics of the reaction.

1.7 Objectives of this Study

Due to the formation of a solid product layer, the rate of reaction between hydrated lime and hydrogen chloride is expected to be slowed down with progress of the reaction. Since the reaction product i.e. calcium chloride has approximately 52% higher molar volume than the hydrated

lime, there is a possibility of incomplete conversion of the lime due to pore plugging. On the other hand, formation of the hygroscopic calcium chloride may increase the reaction rate under some test conditions. No studies have been reported yet on either the kinetics of this reaction at conditions of low temperature DSI process or on the effect of the properties of the calcium chloride on the kinetics of this reaction.

The objectives of this study are to :

- a) Obtain kinetic data on the removal of hydrogen chloride gas by hydrated lime powders at typical operating conditions of the low temperature DSI process.
- b) Determine the effect of major variables namely, gas temperature, moisture content in the gas, gas phase concentration, and sorbent properties, on the rate of removal of hydrogen chloride.
- c) Determine the effect of higher molar volume of the reaction product i.e. calcium chloride, on the conversion of the hydrated lime sorbent.
- d) Determine the effect of hygroscopicity of the reaction product i.e. calcium chloride, on the conversion of hydrated lime sorbent.
- c) Interpret the results of the kinetic tests in light of appropriate noncatalytic gas-solid

reaction models.

It is expected that the results will be used to examine the efficacy of hydrogen chloride removal by hydrated lime in the DSI process and will form the basis for developing appropriate predictive models for this process.

CHAPTER 2

LITERATURE SURVEY

2.1 Hydrogen Chloride Removal in Full Scale DSI Systems

As mentioned earlier, only a handful of performance data have been reported for the DSI process in full scale MSW incinerators. One of the reasons is the relatively recent application of this process for the MSW incinerators.

A dense phase DSI system was retrofitted on a full scale MWC of >250 tons per day (tpd) capacity by R-C Environmental Services and Technologies (Zmuda and Smith, 1991). The demonstration tests for acid gas control were carried out in August 1990. The uncontrolled emissions of acid gases from the incinerator were 700 ppm_{dv} of hydrogen chloride and 200 ppm_{dv} of sulfur dioxide, corrected to 7% oxygen. Hydrated lime of 95% purity was injected at multiple locations in the MSW combustor. Gas conditions at these locations were not reported. At a stoichiometric ratio of 1.65, reductions of hydrogen chloride and sulfur dioxide were reported to be 53% and 60% respectively. The stoichiometric ratio was defined as the ratio of the actual amount of hydrated lime injected and the theoretical amount needed for complete removal of the acid gases based on

stoichiometry of the reactions. At a different phase of the demonstration program, hydrogen chloride and sulfur dioxide reductions of 75% and 80% were reported at a stoichiometric ratio of 2.1, thus showing the effect of stoichiometric ratio on the removal. No deterioration in the ESP performance was recorded during the demonstration program.

Dry hydrated lime injection system has been installed in each of the three 120 tons per day (tpd) of MSWC at a resource recovery facility in Springfield, MA (McClanahan et. al, 1989). The gas flow from each train was approximately 24,000 acfm at 280 °F. After being evaporatively cooled in a secondary economizer, the flue gas was mixed with finely powdered hydrated lime in a dry absorption reactor. The special internal configuration of this reactor provided optimum mixing of the gas and the reagent and extended the gas-sorbent contact time. This ensured increased chemical reaction and excellent sorbent utilization. Unreacted sorbent collected in the downstream fabric filter was recirculated to maximize sorbent utilization. Operating results showed 94% hydrogen chloride reduction at an inlet concentration of 504 ppmd and 83% sulfur dioxide removal at an inlet concentration of 129 ppmd. The hydrated lime stoichiometric ratio was not mentioned in the report.

A DSI system installed in a 115 tpd incineration plant in St Croix county, Richmond, WI, demonstrated >99% HCl

removal and 78.3% SO₂ removal, at lime recirculation ratio of 2.8 (Darcey et al., 1989). The inlet concentrations of hydrogen chloride and sulfur dioxide were 173-412 ppm and 35-106 ppm, respectively. The flue gas cleaning system in this installation consisted of a heat exchanger, a reaction tower, and a fabric filter with the hydrated lime injection upstream of the heat exchanger. The heat exchanger, which cooled the process gas from 480 °F to 250 °F was considered to be a key component of the DSI system since it provided large reaction surface, long residence time and increased the humidity of the gas. The reaction towers were designed to provide contact of the cooled gases with the sorbent. The system used large recirculation of unreacted sorbent to maximize sorbent utilization.

A MSW incinerator of 200 tpd capacity at Claremont, NH was started up in 1987 with a hydrated lime DSI system and a fabric filter for particulate control (Foster et. al, 1987). The pulverized hydrated lime was injected in a venturi section upstream of the fabric filter. Typical gas conditions during operation were 600 ppmv hydrogen chloride, 180 ppmv sulfur dioxide and a temperature of 400 °F to 525 °F. The DSI system operated at 90% to 95.2% hydrogen chloride removal efficiency at lime stoichiometric ratios of 3.2 to 4.2. The time between consecutive pulsing of the bags was 3 to 5 hours.

Frame (1988) reported the performance of some of the

DSI systems installed by Flakt Inc, in Europe. All these installations were equipped with specially designed reactors, which provided longer residence times and thorough gas solid mixing. The hydrogen chloride and sulfur dioxide removals ranged between 85%-99% and between 38%-97%, respectively. The inlet gas concentrations were 720-1520 mg/nm³ (450-930 ppmv) and 164-387 mg/nm³ (60-135 ppmv) respectively. Detail operating conditions have not been reported for these plants.

In view of the differing operating conditions at the DSI systems installed to date, direct comparison of performance of hydrogen chloride removal can not be made. However, certain similarities are worth noting. In all these installations, high degree of gas solid mixing, large recirculation of solids, long solids residence time, and lower temperature have been used to improve the removal efficiency and sorbent utilization. A general idea of the effect of one of the important variable namely gas temperature is shown in Figure 2.1, based on data collected on some of the plants in USA (White and Vancil, 1989). This figure shows that higher temperature increased the emission of the hydrogen chloride.

2.2 Hydrogen Chloride Removal at the Pilot Plant Scale

Environment Canada, through a joint program with Flakt

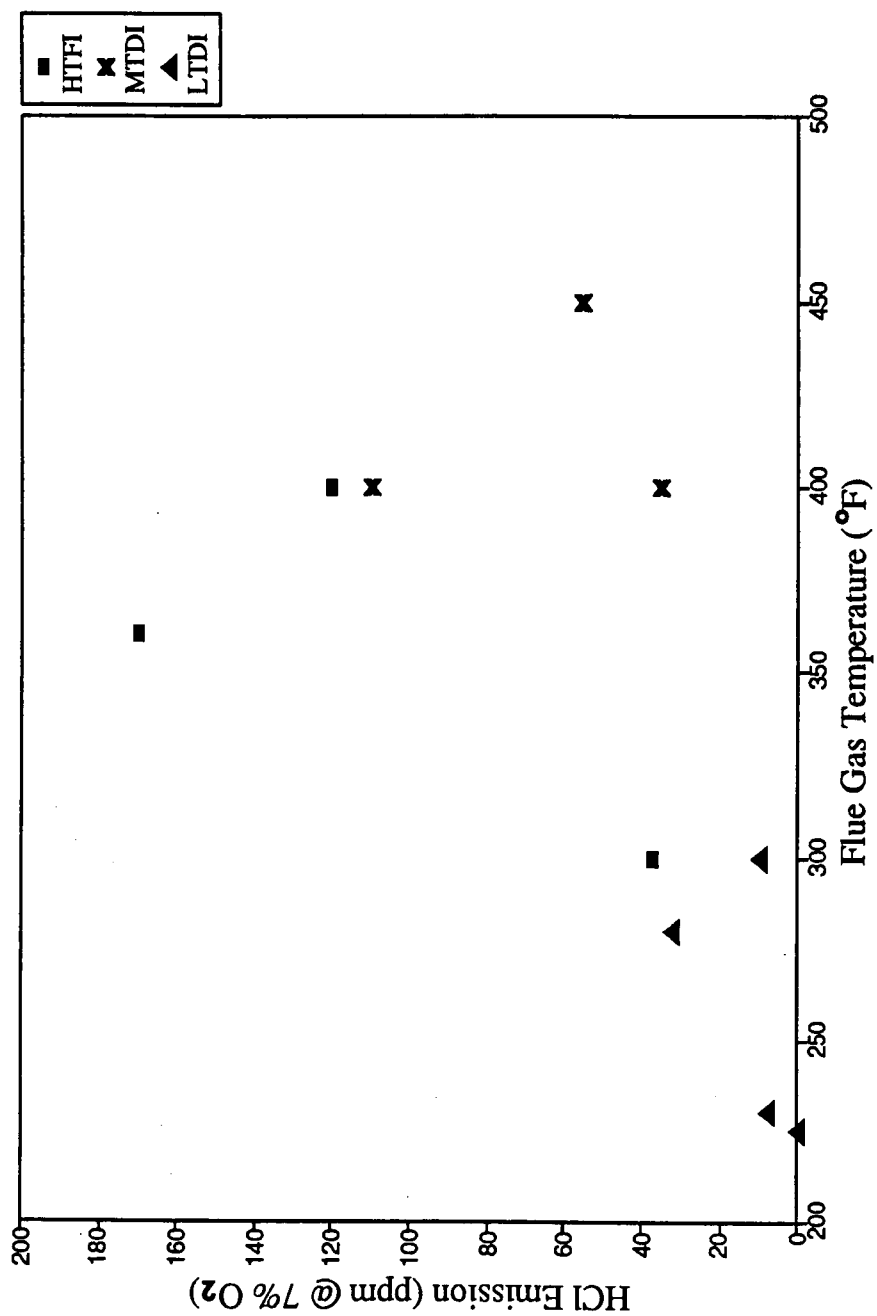


Figure 2.1. Effect of Temperature on Hydrogen Chloride Emissions in Full Scale DSI Plants.

Canada Ltd., conducted a series of tests on a pilot scale DSI system erected as a slipstream on a mass burn incinerator in Quebec City, Canada (Environment Canada, 1986). The pilot installation consisted of a quench tower to cool and humidify the incinerator flue gas, a specially designed dry reactor for acid gas removal and a pulse jet type fabric filter for particulate control. Characterization tests were made at four levels of temperatures at the inlet of the dry scrubber, namely 110 °C, 125°C, 140 °C, and 200 °C. The spent sorbent was not recirculated during these tests. At inlet concentrations of 400 to 450 ppm of hydrogen chloride and 100 to 120 ppm sulfur dioxide, the overall removal efficiencies were >94% and 58-96% respectively. The reported results indicated that the highest efficiencies were achieved at high gas humidities (approximately 20%), with outlet emissions increasing with lower humidity and higher gas temperature.

A pilot scale DSI system of 2000 acfm capacity supplied by ETS Inc. was installed at a MSW incinerator at El Dorado, AR in 1984 (ETS, 1987). The DSI system had two major components, a patented dry reactor and a fabric filter. The specially designed dry reactor ensured intimate gas solid contact and increased contact time. Hydrated lime powders were used in these tests as the sorbent. Removal efficiency of hydrogen chloride ranged between 95% to 99% in nine separate tests at lime stoichiometric ratio ranging

between 2 to 9. At least a 3:1 stoichiometric ratio was considered necessary for a removal efficiency of 99%. Gas conditions, including inlet hydrogen chloride concentrations were not furnished in this report.

Chang et al, (1989) reported the results of HCl removal in a pilot scale DSI system of 50 scfm capacity. The DSI system consisted of a humidifier, a sorbent injection unit at 2 meters from the humidifier exit, and a fabric filter operating at a velocity of 0.01 m/sec (0.4 fps). The gas residence time in the duct between the humidifier and fabric filter was approximately 2 seconds. Over 99% hydrogen chloride removal was reported at stoichiometric ratios of 1 to 3 and approaches to saturation of 28 °C to 44 °C. In other words, the hydrogen chloride was completely removed at these operating conditions. One key finding of this study was that the system could be operated at approach temperatures down to 40 °F without any wet deposits or operational problems in the fabric filter. From limited test results, it also appeared that the removal of sulfur dioxide was influenced by the initial hydrogen chloride concentration in the flue gas.

Itaya et. al (1989) reported the results of a pilot plant DSI system in which the hydrated lime powder was injected upstream of a pulse jet fabric filter operating at filtration velocity of 0.013 to 0.02 m/sec. Gas

temperatures were maintained at various levels of 170 °C, 200 °C, and 230 °C. Inlet hydrogen chloride concentration was maintained at two levels of 300-500 ppm and 800-900 ppm. Wet gas flow varied between 120 to 180 Nm³/hr (72-108 scfm). Under these operating conditions, 60% to 95% hydrogen chloride removal was obtained at stoichiometric ratios of 2 to 4. The stoichiometric ratio and the inlet hydrogen chloride concentration were found to be the only important variables affecting the removal efficiency, in order of importance. Other variables such as operating temperature and filtration velocity did not seem to affect the removal of hydrogen chloride to any significant extent. It was concluded that under these operating conditions, gas diffusion within the particles rather than the intrinsic reaction rate, was the rate determining step. The study also showed that a fabric filter could be used successfully as the reactor for acid gas removal at these test conditions.

2.3 Hydrogen Chloride Removal in Lab/Bench Scale Reactors

Karlsson et. al. (1981) investigated the adsorption-reaction between dry hydrogen chloride gas and solid slaked lime in a fixed bed integral reactor at temperatures between 423-673 °K (302-752 °F). The results of these tests are shown in Figure 2.2. The reactor bed was made up of

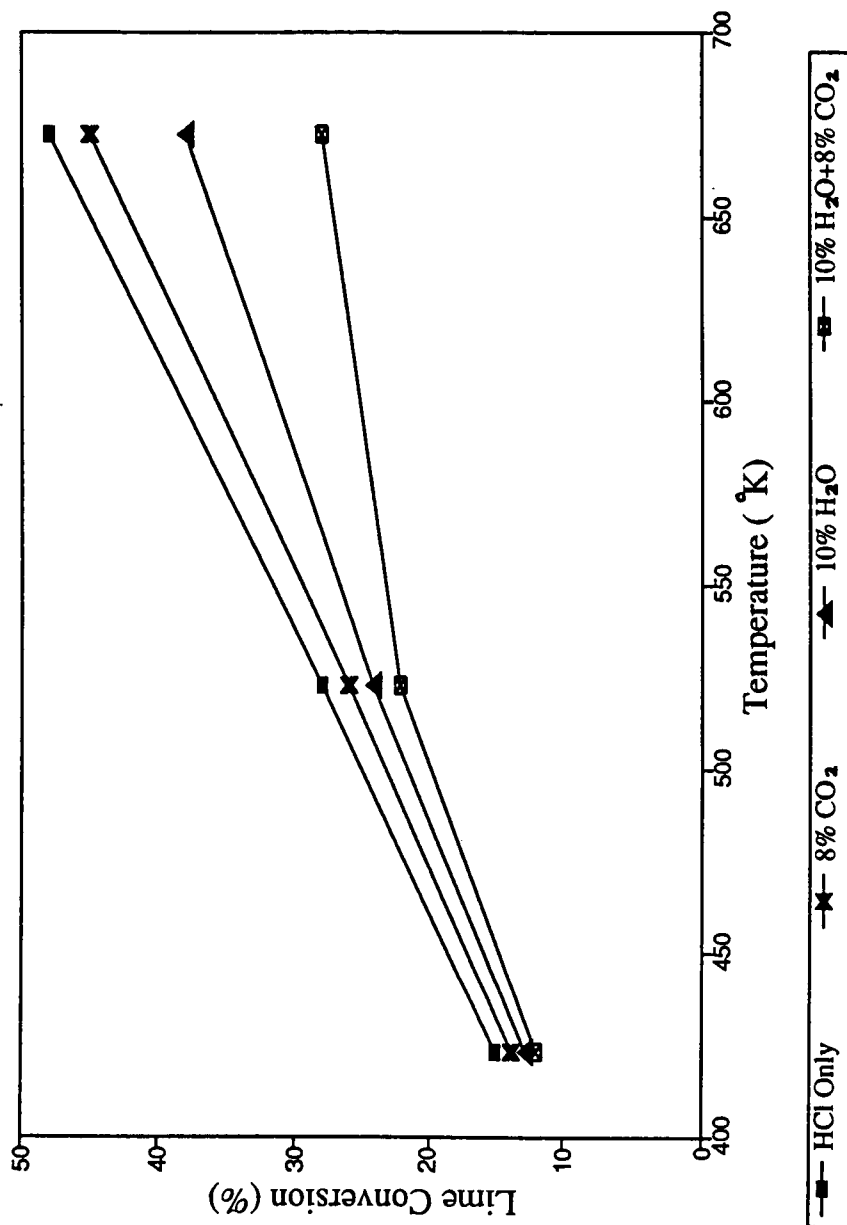


Figure 2.2. Results of Karlssons's Experiments on Hydrogen Chloride Removal by Hydrated Lime in Fixed Bed Integral Reactor.

commercial grade lime (99.5% < 200 micron) mixed with sand in the ratio of 1:20 to maintain a proper gas flow pattern in the bed. A total of 20 experiments were conducted with 1.56 g of lime and 630 ppm of hydrogen chloride at a superficial bed velocity of 6.4 cm/s(12.7 fpm). The hydrogen chloride breakthrough from the bed was determined by the change in conductivity of a deionized water solution downstream of the reactor, in which the gas was absorbed. Each test lasted 10-20 hours depending on the reaction temperature and the amount of information needed from the tests. Lime conversion was measured at the end of these tests at 1% breakthrough of hydrogen chloride. Addition of either water or carbon dioxide to the reacting gas stream decreased the conversion only at higher temperatures. The final conversion of lime at the end of the tests was lower by 1% to 4% at temperatures between 300 °F and 400 °F, but was lower by 20% at 750 °F, due to the combined effect of the addition of 8% CO₂ and 10% H₂O in the dry gas. No reason was offered for this decrease in the reaction rate due to presence of water. This finding was contrary to other performance test data reported in the literature, which showed an enhancement in acid gas removal rate with higher moisture content. Sorbent reactivity tests with calcium hydroxide were carried out in a fixed bed, short time differential reactor (STDR) by Gullet et.al (1989) at 400 °C and 800 °C, to simulate high temperature removal of

hydrogen chloride in FSI. Approximately 4 mg of the sorbent was exposed to a gas stream containing 1000 ppmv hydrogen chloride. The results of these tests are shown in Figure 2.3. Within the range of experimental errors, the results showed no difference in the removal rate between these two temperatures. The data suggested that between these temperatures, the hydrogen chloride removal was not limited by reaction kinetics but by some other mechanism. The results also showed a decrease in rate of conversion with time and a final conversion of less than 50% at both these temperatures. The reaction product from the 800 °C test was analyzed by X-ray diffraction (XRD) and found to be calcium chloride hydroxide ($\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2$), indicating a molar Ca/Cl ratio of 1:1. It was concluded that due to the formation of this intermediate, more than 50% conversion of the calcium hydroxide was not feasible at this temperature. In other words, a 50% conversion calculated based on assuming CaCl_2 as the product of reaction was, in reality 100% conversion based on the actual product of reaction, namely $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2$.

Jozewicz et al. (1990) conducted hydrogen chloride removal studies in a bench scale fixed bed reactor with calcium hydroxide sorbent, as part of a larger study on evaluation of this sorbent for acid emission control. Approximately 1 g of reagent grade $\text{Ca}(\text{OH})_2$ was dispersed in 40 g of sand in a fixed bed reactor and the sorbent was

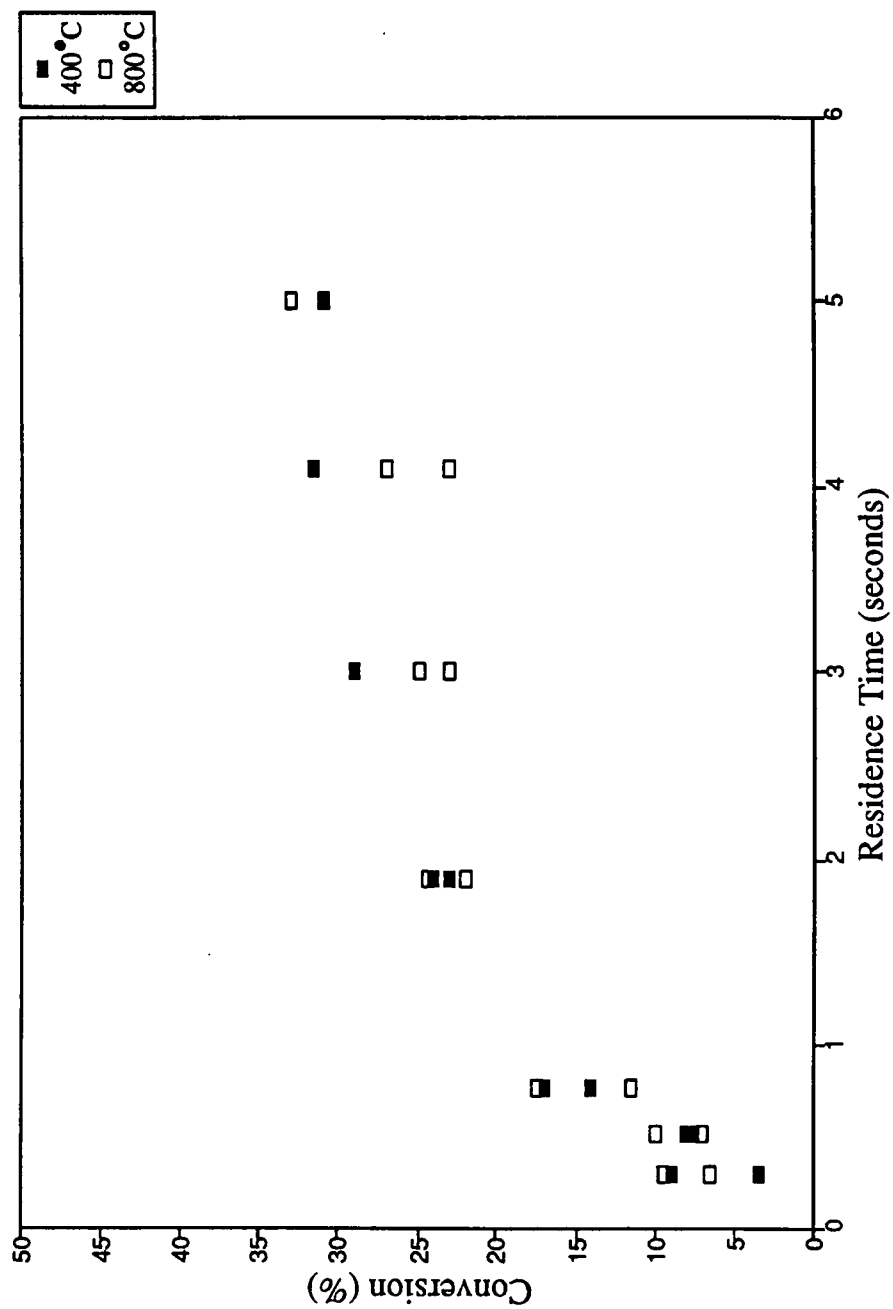


Figure 2.3. Results of Gullet's Experiments on Hydrogen Chloride Removal by Hydrated Lime in Short Term Differential Reactor.

exposed for 1 hour to simulated flue gas containing 1000 ppm of hydrogen chloride and 0.1 g water per g of dry air. The approach to saturation was varied between 10 °C and 110 °C without changing the water content in the flue gas. The relationship between the approach to saturation and hydrogen chloride removal after one hour of reaction (defined as mmoles HCl removed per 100 mmoles of Ca(OH)_2 sorbent) was found to be approximately linear, with the hydrogen chloride removal decreasing with higher approach temperature. Based on these tests, an approach of 54 °F (30 °C) was recommended for at least 80% hydrogen chloride removal from the gas phase. Results of these fixed bed reactor tests are shown in Figure 2.4.

The results from the above mentioned studies have shown the feasibility of achieving hydrogen chloride removal by reaction with hydrated lime powders in DSI systems. The removal efficiency, and the sorbent conversion seem to depend strongly on the operating conditions, especially gas temperature and humidity. The gas phase concentration showed some effect on the removal efficiency over a limited number of pilot plant tests (Itaya, 1989). Sorbent properties such as surface area and porosity were considered to be important in lab/pilot scales (Jozewicz, 1991, Felsvang, 1991), but this is yet to be confirmed in full scale plants.

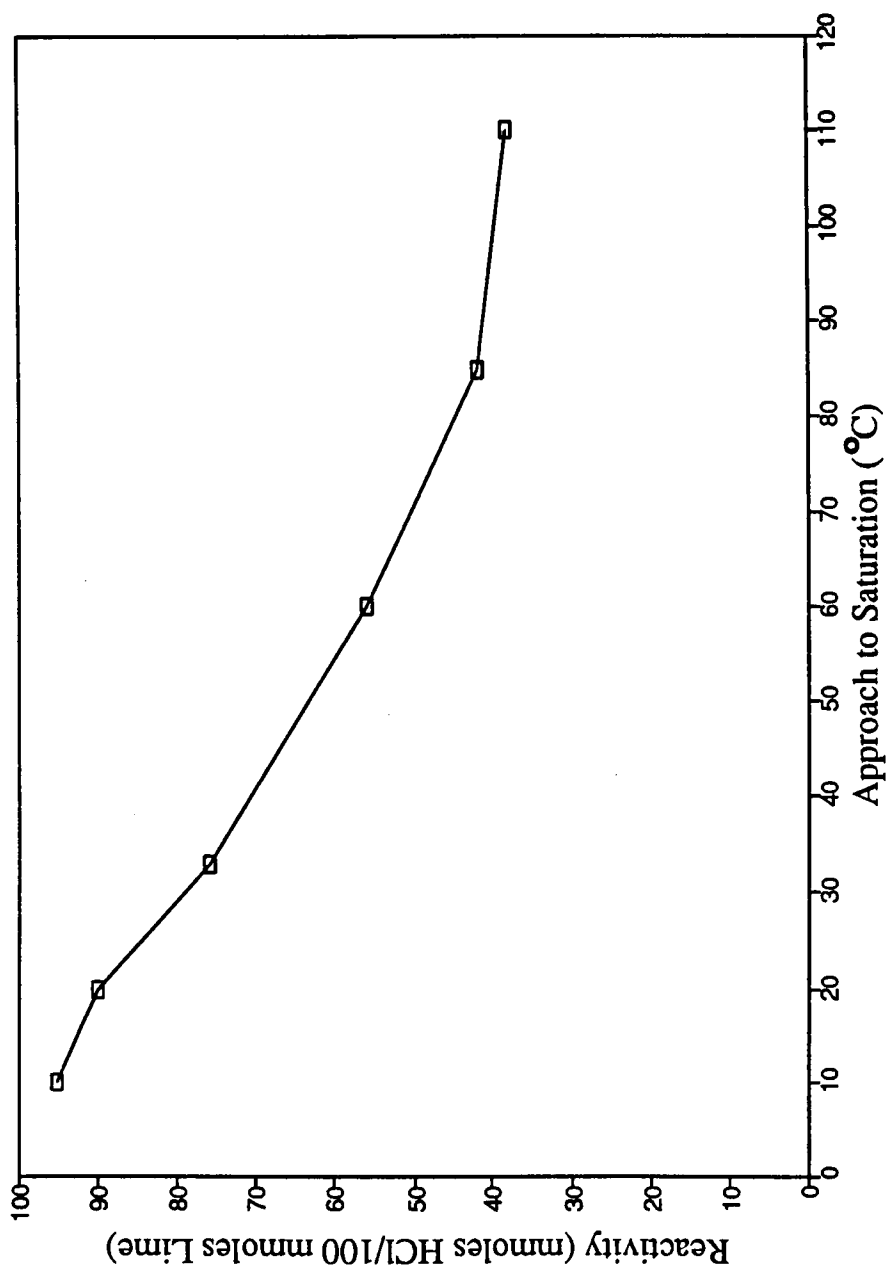
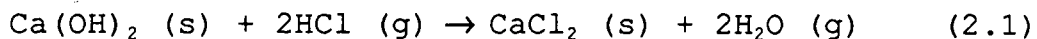


Figure 2.4. Results of Jozewich's Experiments on Hydrogen Chloride Removal by Hydrated Lime in Fixed Bed Integral Reactor.

2.4 The Reaction of Hydrogen Chloride with Hydrated Lime

In the post combustion DSI process, the overall chemical reaction for removal of hydrogen chloride gas by hydrated lime can be expressed as :



Thermodynamic data show that the net change in standard free energy of formation (F_0) for this reaction is approximately -30084 cal/mole. The corresponding value of the equilibrium rate constant (K_{eq}) at 20 °C is 2.76E+22. Since the equilibrium rate constant is the ratio of the rate of forward and reverse reactions at equilibrium, it's high value suggests that the reaction is highly favored in the forward direction at standard temperature. This implies that the conversion of hydrated lime will not be limited at least by the thermodynamics of the reaction. Other mechanisms such as high resistance to mass transport or pore plugging due to higher molar volume of the reaction product, however may be the reason for incomplete conversion of the hydrated lime as reported in the laboratory studies mentioned earlier.

No data have been reported on the kinetics of the reaction between hydrogen chloride and hydrated lime. Such data can be obtained by observing the rate of removal of

hydrogen chloride by hydrated lime, as a function of time at constant operating conditions. No such tests have been reported at conditions simulating the low temperature DSI process. Based on results from an integral fixed bed reactor and a kinetic model of fixed bed adsorption, Karlsson (1981) have reported an expression for the intrinsic rate constant for dry hydrogen chloride removal by a swedish commercial lime in the temperature range of 300 °F to 750 °F. Considering a first order reaction with respect to both the reactants, the intrinsic rate constant was found to be 156 s⁻¹, 246 s⁻¹, and 984 s⁻¹ at 150 °C, 250 °C, and 400 °C respectively. The reaction rate was considered to be increasing too fast with temperature to express the effect in terms of Arrhenius type equation, Instead, a exponential form of equation as shown below was considered to fit the data reasonably well :

$$K_o = 111 * \text{EXP}[(T/554)]^4 \quad (2.2)$$

where,

K_o = Intrinsic rate constant, s⁻¹

T = Reaction temperature , °K

No consideration was made in this analysis for the solid phase diffusion and the decrease in the rate of reaction due to build up of product layer. Such data were not

collected in this study.

The hygroscopic and deliquescent properties of the reaction product namely, calcium chloride, adds further complexity to the rate of removal of hydrogen chloride in case of low temperature DSI process. Hygroscopicity is defined as the lb of water taken up by 1 lb of calcium chloride and depends on the relative humidity of the surrounding air (Kirk and Othmer). Deliquescence is defined as the lowest temperature and relative humidity at which an exposed piece of calcium chloride will take up enough water to dissolve in it (Kirk and Othmer). The hygroscopicity and deliquescence of calcium chloride upto 100 °F is given in Table 2.1. Data at higher temperatures are not available. This table also gives the solubility data of calcium chloride in water. These data shows that at humidities of 20% or higher, calcium chloride may dissolve in the water it absorbs from the humid gas. In such case, no solid product layer will exist on the surface of the reacted particle and absorption of hydrogen chloride may be enhanced by this surface moisture. Since both calcium hydroxide and hydrogen chloride are soluble in water, a wet phase reaction may occur in these conditions. At lower humidities, however, the removal of hydrogen chloride is expected to take place according to the mechanisms of noncatalytic gas solid reactions.

Table 2.1. Water Uptake and Solubility of Calcium Chloride

A. Hygroscopicity ^(1,3)

Relative humidity (%)	36	60	70	80	85	90	95
Water taken up by Calcium Chloride (lb water/lb CaCl ₂)	1.0	1.6	2.0	2.8	3.5	5.0	8.4

B. Deliquescency ^(2,3)

Relative humidity (%)	20	30	40	43
Temperature (°F)	100	74	44	42

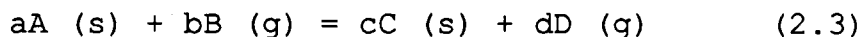
C. Solubility ⁽⁴⁾

Temperature (°F)	140	158	176	194	212
g calcium chloride per 100 g of water	136.8	141.7	147.0	152.7	159

- Notes :
1. Hygroscopicity is defined as the lbs of water taken up by 1 lb of calcium chloride.
 2. Deliquescence is defined as the lowest relative humidity and temperature at which an exposed piece will take up enough water to dissolve.
 3. Source : Kirk and Othmer, "Encyclopedia of Chemical Technology," Vol 4, p12, 1978.
 4. Source : Chemical Engineers' Handbook, Ed. J.H.Perry, p 3-92, 1963.

2.5 Noncatalytic Gas Solid Reactions

A noncatalytic gas solid reaction may be represented by the following scheme :



Where A,B are the reactants, C,D are the products, and a,b,c,d represent the stoichiometry of the reaction.

Gas-solid reactions involve complex interaction of heat and mass transfer through gas and solid phases. The formation of a solid product with structural changes, if any, creates more complexity. Such structural changes occur when the molar volume of the solid product differs significantly from the molar volume of the reacting solid. In these cases, the change in porosity, particle expansion or shrinkage alters the structural property of the solid particle. The molar volume of calcium chloride is approximately 52% higher than calcium hydroxide. Thus, in this reaction, there is a potential for structural changes in the reacting particle of hydrated lime, with the progress of the reaction.

However, treatment of gas/solid reactions are simplified by considering three basic steps in the diffusion-reaction scheme. These are :

1. Mass transfer, either through molecular or turbulent diffusion, of the gaseous reactant from the bulk of the gas stream to the external surface of the solid reacting particle.
2. Gas solid interaction in the solid phase which consists of
 - a) Diffusion of the gaseous reactant to the pores of the solid reactant,
 - b) Adsorption of the gaseous reactant on the solid surface and subsequent reaction,
 - c) Desorption of the gaseous product, if any from the surface of the solid reactant,
 - d) Diffusion of the gaseous product if any, out of the solid phase through the pores of the solid reactant.
3. Mass transfer of gaseous product, if any from the external surface of solid to the bulk gas stream.

As the reaction progresses, if the solid product builds up within the sorbent particles, an additional resistance is provided to the diffusing gases by this product layer. This resistance will change with progress of conversion as thickness of this layer increases and/or structural changes occur within this layer.

The apparent complexity of the system is made amenable to simplified analysis by observing that the rates of all

the above processes are not the same and therefore, one or the other of the processes becomes rate determining. Thus, a simplified expression of the rate determining step could be used to describe the overall process. The three major rate determining steps in the noncatalytic gas solid reactions are as follows :

1. Bulk gas phase mass transfer of the gaseous reactant or the product. The rate of this step is dependent on the dynamics of the flow of the bulk gas around the solid sorbent particles.
2. Solid phase mass transfer of the gaseous reactant or the product gas. This step takes into account both the pore diffusion and product layer diffusion, if any. The rate of this step is strongly dependent on the properties of the sorbent and the product layer.
3. Chemical kinetics of the reaction between the reacting molecules, including the effect of adsorption prior to the reaction. The rate of this step depends on the kinetics and thermodynamics of the adsorption and reaction.

Gas solid reactions are often studied by determining the conversion of the solid sorbent with time under controlled operating conditions. A number of mathematical

and empirical models of gas solid reactions have been proposed in the literature, which describe the conversion-time data as a function of operating conditions and measurable properties of the sorbent. These models are useful in determining the rate controlling step of the reaction and the effect of the operating variables on the sorbent conversion. The conversion of the solid sorbents can be related to removal of the gas phase reactant through stoichiometric relationships of the reactions. Some of the noncatalytic gas solid reaction models are briefly described as follows :

Homogenous Reaction Model

This model applies only in cases where the solid reactant is very porous and thus there is negligible intraparticle diffusional resistance. The concentration of the gaseous reactant is considered to be constant throughout the volume of the solid and the overall rate is controlled by the chemical kinetic step. These models are not applicable for hydrated lime particles which do not have high porosity.

Shrinking Unreacted Core Model

Originally developed by Yagi and Kunii in 1955, this mathematically simple model has been used extensively to describe various fluid-solid reactions. The model considers a spherical reactant particle, in which the reaction front moves radially inward from the external surface to the center of the particle, until complete conversion is achieved. The model can be used where a solid product layer builds up as the reaction progresses. This model is used with great success in cases where the product solid is fairly impervious to the gaseous reactant and also when the reaction rate is much faster than the intraparticle diffusion rate. Though it does not explicitly consider the effect of porosity of the solid reactant, the model has been used successfully for both nonporous and porous solids (Levenspiel, 1976). Recent modifications to this model included incorporation of the effect of structural properties of the solid (Galavas, 1984).

Grain Model

An improvement of the shrinking unreacted core model was first postulated by Szekeley and Evans (1970), by accounting for the sorbent porosity. This model assumed the particle to be made up of large number of small grains of uniform diameter. The gaseous reactant diffuses radially

inward and reacts with these spherical grains which undergo progressive conversion as per shrinking core model. The successive rows of grains undergo various stages of conversion as the reaction front moves inward by interparticle diffusion and eventually complete conversion is achieved. Hartman and Coughlin (1976) modified the original grain model to take into account the increase in pore diffusional resistance due to decrease in porosity of the solid resulting from formation of a larger volume product. In the changing grain size model proposed by Georgakis et. al (1979), a critical initial porosity and a pore plugging time were analytically calculated from the properties of the solid. Batarseh et. al (1989) have extended the scope of this model by incorporating diffusional resistance due to the progressive formation of product layer and applied the model to atmospheric oxidation of FeS_2 rocks. The grain model is more appropriately applied to pellets and solid compacts rather than individual solid particles and thus, may not be appropriate to describe the conversion in DSI systems.

Pore Plugging Models

Contrary to the predictions of the shrinking core and grain model, many gas solid reactions, including the reaction of hydrogen chloride with hydrated lime, show

incomplete conversion of the solid reactant at some operating conditions. A large number of models have been developed to account for this incomplete conversion by considering the physical properties of the solid, namely the porosity and pore size distribution. A single pore model was first postulated by Petersen (1957) to describe the gassification of graphite rods by carbon dioxide. Ramachandran and Smith (1977) modified the model to account for structural changes in porosity due to difference in the molar volume of the product and the reactant solid and applied it to sulfation of calcium oxide. Bhatia and Perlmutter (1981) developed a Random Pore Model (RPM) based on growth and intersection of reaction surfaces in randomly distributed pores within a solid reactant. The model accounted for external gas phase diffusion, intraparticle and product layer diffusion as well as kinetics of reaction. The model was used on experimental data on sulfation of calcium oxide to determine the effective product layer diffusivity.

A semi analytical pore plugging model was proposed by Lee and Georgakis (1981) to describe the sulfation of lime. This model was motivated by the exponential shape of the conversion versus time plots of sulfation. The simplified rate expression allowed to characterize the reaction completely with two kinetic parameters, both of which could be determined from the experimental data of conversion with

time. Thus, this model could be readily applied to experimental data without the need for detailed data on sorbent properties. The model was successfully applied to sulfation of calcium oxide (Lee & Georgakis, 1981) and later on sulfation of sodium carbonate/sodium bicarbonate in a fixed bed differential reactor (Keener, 1982).

Lindner and Simonsson (1981) suggested a semiempirical model taking into account the decreasing gas-solid interfacial area due to growing and overlapping product layers. Similar models accounting for pore closure have been proposed by Christman and Edgar (1983), Dennis and Hayhurst (1986), and Yu and Sotirchos (1987). These models have been used to describe the sulfation of limestone particles.

All these gas solid reaction models had been applied to reacting systems in which hygroscopicity and deliquescence of the product were not encountered. Thus, none of these models account for the effect of the uptake of water by the product and its effect on the transport of the gaseous reactant and product through the product layer. Such condition would be expected for the hydrogen chloride-hydrated lime reaction, specially at high humidities. Even at conditions in which such effects might not be significant, such as low relative humidities and high temperatures, these models could not be applied till date to the hydrogen chloride-hydrated lime reaction due to lack

of kinetic data. The results of this study is expected to fill this gap in kinetic data and allow development of suitable models.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 General Approach

Removal of hydrogen chloride by hydrated lime was studied in a fixed bed reactor. The test conditions were varied to determine the effect of the operating parameters. The important physical properties of the sorbent (i.e. hydrated lime) were determined prior to the kinetic tests. The change in the physical properties of the reacted sorbent were determined in some tests to gain insight to the reaction mechanism.

3.2 Fixed Bed Reactor Tests

The kinetic tests for removal of hydrogen chloride by hydrated lime powders were carried out in a bench scale fixed bed reactor. The schematic of the experimental set up is shown in Figure 3.1. The test gas was a mixture of hydrogen chloride and water vapor at various desired concentrations in an inert carrier gas of nitrogen. In reality, the flue gas from the incinerators will also contain appreciable quantities of carbon dioxide and oxygen. However, Karlsson et al.(1981) have shown that

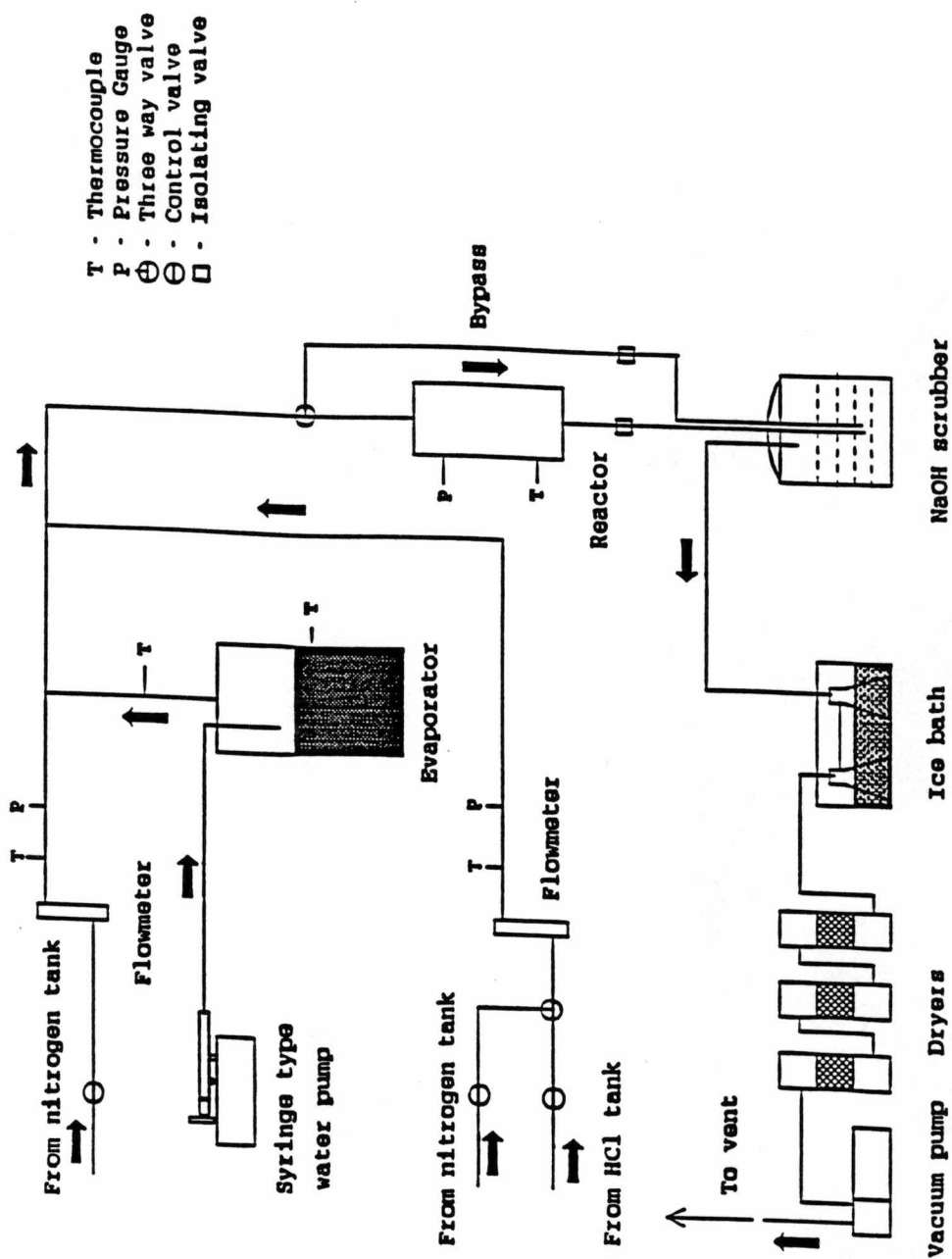


Figure 3.1. Experimental Setup for the Kinetic Tests of Hydrogen Chloride by Hydrated Lime.

10% of carbon dioxide has an insignificant effect on the removal of hydrogen chloride by lime within the temperature range used in this study. Further, Klingspor et al. (1984) have shown that both oxygen and carbon dioxide at concentrations up to 10% had insignificant effect on the reaction rate of sulfur dioxide with dry limestone. Similar conclusions were made in the desulfurization study in bench scale reactors made by Acurex corporation and University of Texas on behalf of Department of Energy (DOE, 1988). Even less effect is expected in the case of hydrogen chloride, which is known to be more reactive than sulfur dioxide. In view of above, all the tests were carried out with hydrogen chloride and nitrogen gas mixture only.

The nitrogen gas from the gas cylinder was first metered through a calibrated rotameter; the gas pressure and the temperature immediately downstream were measured to enable the calculation of the molal flow rate. The gas was then heated to the desired temperature by electric strip heaters wound on the copper tubing through which the gas was passed. The heaters were connected to a variac to allow control of the gas temperature by controlling the heat input rate.

In the next stage, water vapor was added to the hot gas at a controlled rate. A calibrated Harvard syringe pump injected water at predetermined rates to a thermally controlled evaporator, through a 1/8 inch stainless steel

tubing. The evaporator was a 4 inch diameter and 8 inch long steel cylinder, closed at the bottom and with inlet outlet connections at the top. A cross sectional view of the evaporator is shown in Figure 3.2. The evaporator was partially filled up with quartz silica sand and was heated by electric strip heaters wound on the outside surface. The evaporator was heated to 350 °F to 400 °F before the water injection was started. The water dripping on the hot sand bed immediately evaporated. The hot sand bed worked as a heat reservoir and ensured steady evaporation of the injected water. A thermocouple was located 1 cm beneath the surface of the sand at the location where the dripping water contacted the sand surface. Temperatures below 212 °F at this location was considered to indicate water build up in the sand bed. The heat input rate in the evaporator was controlled to maintain the temperature at this point well above 212 °F (usually 450 °F) to ensure complete and steady evaporation of the injected water. A second thermocouple was located at the exit of the evaporator and measured the temperature of the steam generated. By varying the heat input rate, this temperature was maintained at sufficiently high temperatures, usually 450 °F or higher, to avoid condensation of the water vapor upon contacting with the nitrogen gas. Similar designs of the evaporators have been used by other researchers for fixed bed kinetic studies (Jozewicz, 1990, Karlsson, 1981). Calibration tests carried

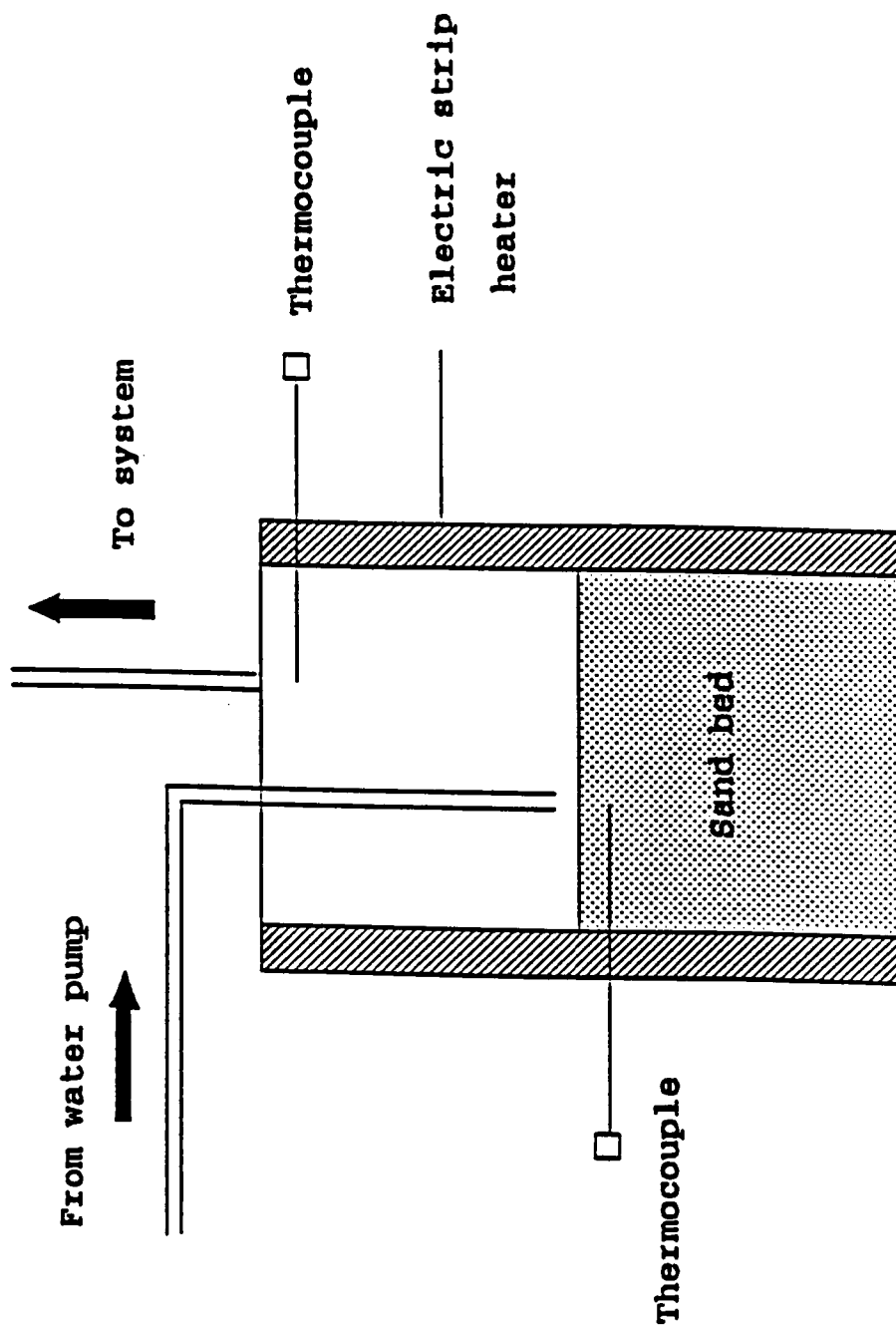


Figure 3.2. A Sectional View of the Evaporator.

out prior to the kinetic tests showed that steady and complete evaporation was being achieved. The evaporated water was directly injected into the hot nitrogen gas stream as shown in Figure 3.1.

Hydrogen chloride gas was then injected into the hot and humid gas stream at the desired concentration. The hydrogen chloride injection after water injection point minimized the possibility of corrosion from condensed water. The hydrogen chloride injection line was connected to the hydrogen chloride cylinder as well as a pure nitrogen gas cylinder by a three way valve as shown in the Figure 3.1. This nitrogen gas was used to purge the injection line to eliminate any residual hydrogen chloride after each test.

In order to avoid handling problems and risks associated with pure hydrogen chloride, a mixture in pure nitrogen was used in these tests. The hydrogen chloride gas mixture was first metered by a calibrated rotameter before being injected in the hot carrier gas stream. The pressure and the temperature of the dry hydrogen chloride gas was measured immediately after the rotameter to enable calculation of the molal flow rates. Unidirectional flow valves were installed both in the hot carrier gas line and the hydrogen chloride gas line prior to the injection point as shown in Figure 3.1. These valves prevented the accidental backflow of hydrogen chloride gas into the

evaporator.

The test gas at the desired temperature and composition then passed through the tubular reactor shell containing the sorbent which was placed on a thin fixed bed of glass filter. A three way valve upstream of the reactor allowed the reactor to be bypassed whenever required, e.g. during withdrawal of the sorbent after reaction. The test gas was heated in the tubes and in the reactor shell by electric strip heaters. The entire system was insulated on the outside to reduce heat loss and for operational safety.

The reactor assembly consisted of a cylindrical reactor shell, a matching flange with a wiremesh support, and a sorbent holder. A sectional view of the assembled reactor is shown in Figure 3.3. The reactor shell was a cylindrical tube made out of 316L SS, and was approximately 20 cm long (8 inches) and 4.75 cm (1.75 inches) inside diameter. The reactor was maintained at the test temperature by electric strip heaters. The heat input rate was controlled by variac, which was operated automatically in an ON/OFF mode by a temperature controller connected to a thermocouple located in the reactor shell at approximately 5 cm (2 inches) above the sorbent bed. A pressure tap in the reactor was connected to a pressure gauge to monitor the gas pressure during testing. The reactor was always maintained under a slight vacuum to prevent any accidental leakage of hydrogen chloride to

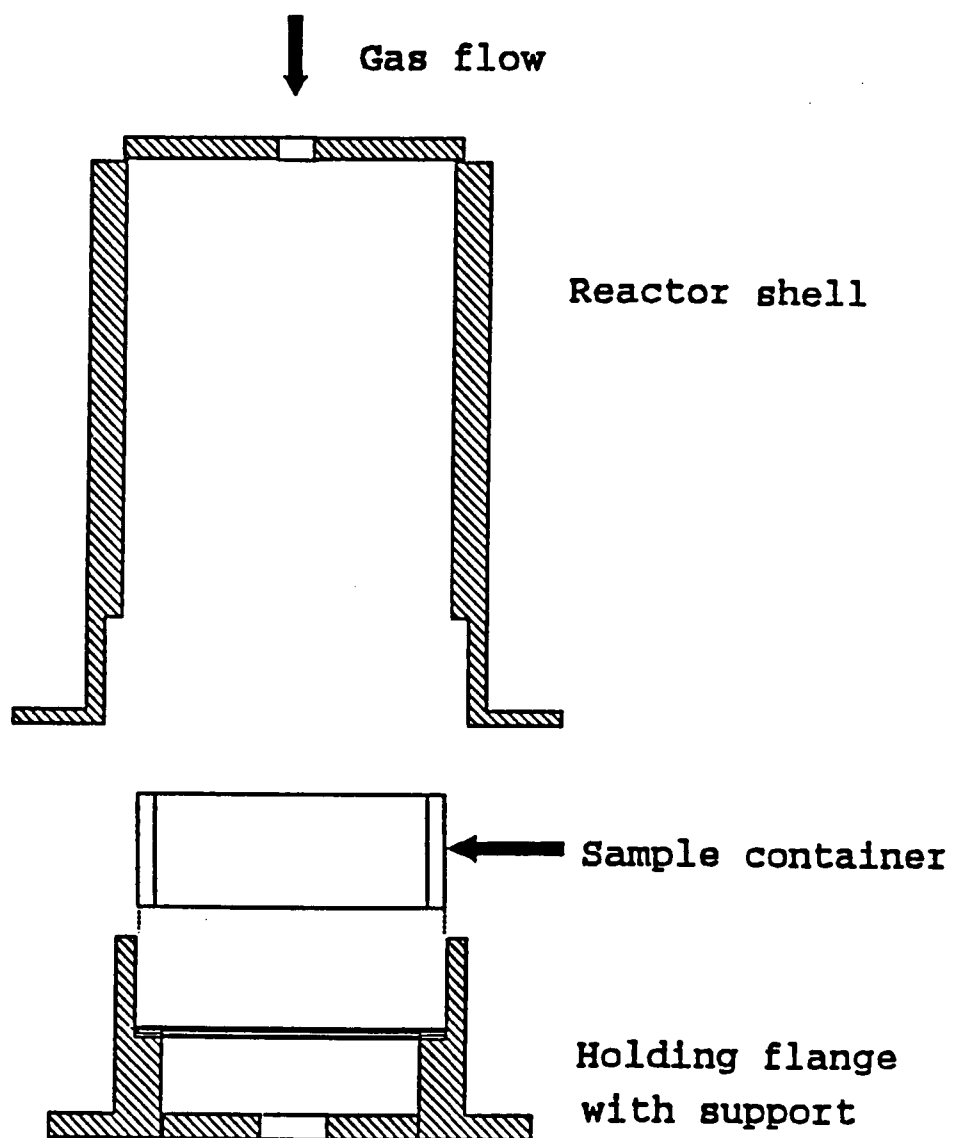


Figure 3.3. A Sectional View of the Reactor Assembly.

the ambient air and also to minimize the corrosion effects of the gas.

The matching flange was also made out of 316L SS and was provided with wiremesh to support the sample holder. A silicone rubber gasket was used between the flanges of the reactor shell and the matching flange to ensure leakfree operation. The outlet from the matching flange was connected to a flexible teflon tubing and then to the gas scrubbing system as shown in Figure 3.1. A gate valve at this point was used to isolate completely the reactor when the reactor was being bypassed e.g. when the sorbent was being placed in or taken out of the reactor.

The sorbent sample was spread over a glass microfiber filter, which was supported on a 316 SS wiremesh in a sample holder. The sample holder was a short cylindrical tube approximately 4 cm in height and 4.75 cm inside diameter as shown in Figure 3.3. During each test, the sorbent was spread on the filter inside the sample holder which was supported on the wiremesh support in the matching flange. After the tests, the matching flange was disconnected from the reactor shell by opening the bolts, and the sample holder was replaced by a sample holder containing new sorbent to be used for the next test. During this time the reactor was bypassed by operating the three way valve and closing the outlet valve on the matching flange. The entire reactor assembly was insulated to

prevent loss of heat and for operator protection.

Both the test gas line from the reactor outlet and the reactor bypass line were connected to the scrubber. The scrubber was a 20 liter glass bottle approximately half filled up with 5N sodium hydroxide solution. The gas was finely dispersed at the bottom of the solution by a fritted glass disperser. The hydrogen chloride from the gas was completely removed in this scrubber. Next the saturated test gas free of hydrogen chloride was passed through two ice-cooled condensers to knock out most of the water, and then through a series of silica gel drying tubes to remove the moisture from the gas. These precautions were taken to prevent the downstream suction pump from being attacked by any hydrogen chloride that may not have been removed in the scrubber for any reason. The 3/4 hp, Gast suction pump provided the suction necessary to create the slight vacuum in the reactor. The outlet of the pump was vented to an exhaust hood.

Several precautions were taken to avoid corrosion from the hydrogen chloride gas within the test stand. The entire hydrogen chloride injection system was made out of teflon tubes and a special teflon flowmeter, nickel cadmium thermocouples and viton or teflon fittings. At all times, even during the shutdown throughout this project, a flow of dry, pure nitrogen was maintained throughout the system to create a positive pressure and avoid infiltration of

ambient moisture. A slight vacuum was always maintained in the reactor during the tests or whenever hydrogen chloride was used. After each test, the hydrogen chloride line was thoroughly flushed with the dry nitrogen. Leak checks on the system were conducted before each day of test to ensure no infiltration of ambient air. Further, hydrogen chloride flow was always initiated only after the system had been at the proper temperature for at least 30 minutes to avoid absorption of the acid gas in any condensed moisture inside the system.

A typical fixed bed reactor test included three steps. These were a) sorbent preparation; b) the kinetic test in the fixed bed reactor, and c) product analyses to determine sorbent conversion.

These steps are now described below.

Sorbent Preparation

Hydrated lime powders have a strong tendency to agglomerate in fixed beds. Large agglomerates are formed which leads to poor flow pattern in fixed beds and nonuniform gas solid contact, both of which are undesirable. The other concern for inadequate gas solid contact was due to the small quantity of the sorbent used in the tests, necessitated by the desire to maintain differential conditions in the reactor with respect to the

gas phase concentration. Following the work of previous researchers (Jozewicz, 1990, Karlsson, 1981), it was decided to mix the hydrated lime powder with quartz silica sand. It was anticipated that the larger volume of the inert sand would help in distributing the small amount of hydrated lime powder uniformly throughout the bed and thus poor gas solid contact would be avoided. The quartz sand selected for this purpose was grade F-75 manufactured by US Silica. Physical and chemical properties of this sand are given in the Appendix 1. It was observed that at least 1 gram of the sand was required to cover the entire bed of the sample holder. Most of the tests were therefore carried out with 1.5 to 2 grams of the sand. The amount of sorbent to be used was determined from trial and error. Optimizing between maintaining differential conditions in the reactor and avoiding analytical limitations, it was determined that 25 milligrams of the sorbent for the low concentration tests (under 5000 ppm HCL) and 50 milligrams of the sorbent for the high gas concentration tests (above 5000 ppm HCL), met the above conditions. Karlsson (1981) have shown that poor channeling in fixed bed with hydrated lime sorbent could be avoided using a sand to hydrated lime mass ratio (D) of $\geq 40:1$. In all the tests in this study, the sand to lime mass ratio was maintained at 40 or higher to ensure adequate gas solid contact. This was further confirmed by the reproducibility of the data during repetition of the tests.

Both the sorbent and sand were weighed in an analytical balance and were mixed in a special nonporous mortar and pestle made out of agate stone. The two solids were mixed thoroughly for approximately 2 to 3 minutes. The mixture was then transferred to the glass microfiber filter placed on the wiremesh support of the sample holder and was evenly distributed over the entire bed. holder. The sample holder was then kept inside a desiccator until it was used in the reactor test. Typically, ten to fifteen such samples were prepared before starting of the tests to ensure an uninterrupted supply of sorbents during the tests.

Fixed Bed Reactor Tests

The system was started by flowing pure nitrogen gas at the desired flow rate for the test and starting the heaters in the system i.e. tube heaters, the reactor heater, and the evaporator heater. The temperature at the various points in the system were conveniently monitored by a network of thermocouples connected to a multichannel digital temperature indicator. The temperatures were controlled by adjusting the heat input rate through individual variacs connected to these heaters. After the temperature in the evaporator sand bed reached approximately 450 °F, water injection was initiated by starting the syringe pump at the desired speed. The reactor

temperature controller was then set to the desired temperature of the test. Steady operating conditions were achieved by running the system in this manner for approximately three hours. Once the steady conditions were ensured, the sorbent sample was inserted in the reactor and allowed to equilibrate with the test gas temperature and humidity. The study by Acurex corporation and University of Texas (DOE, 1988) showed that in a bench scale reactor a mixture of 1 g of hydrated lime and 40 g of sand attained equilibrium with test gas within 2 minutes. However, approximately 15 minutes was allowed for each test in this study.

At the end of this equilibration time, the hydrogen chloride flow was initiated by switching over the three way valve to the hydrogen chloride line, and the gas flow was maintained for the desired reaction time for the test. The hydrogen chloride flow was substituted by nitrogen to stop the reaction after this time. Next, the gas flow was diverted to the bypass line and the reacted sorbent was taken out of the reactor for determination of conversion. A new sample was then inserted in the reactor and the procedure mentioned above was repeated.

Determining Sorbent Conversion

A two step procedure was followed for determining the

conversion of the sorbent. These were i) Preparation of analate; and ii) analysis for chloride and calcium concentrations.

After the test was over, the contents of the sample holder i.e. the mixture of reaction product, the unutilized sorbent, the sand, and the glass microfiber filter bed were placed into a 500 ml glass beaker. Approximately 100 ml of IC eluent solution (made up of a mixture of 0.0045N NaHCO_3 and 0.0056N Na_2CO_3) was poured into this beaker, and four drops of concentrated sulfuric acid were added to dissolve the calcium in solution. The mixture was thoroughly stirred for at least ten minutes and then vacuum filtered. Analates were made by diluting this filtrate with appropriate amount of ultrapure water to reduce the chloride and calcium concentrations within the measurement range of the instruments. This analate was analyzed for calcium and chloride concentration to determine the sorbent conversion.

The concentration of calcium and chloride in the analate was determined by a Perkin Elmer Atomic Absorption Spectrometer (AA) and a Dionex 2000i Ion Chromatograph (IC) respectively. Multilevel calibrations were done with the both the AA and the IC each day prior to the analyses and also at the end of the analyses. Repeat analyses was carried out with the same sample to check the reproducibility of the results.

The conversion of the sorbent was determined from the

ratio of calcium and chloride in the analates. The following equation was used in the sorbent conversion calculation, based on the stoichiometry of the reaction (Equation 2.1),

$$\text{Fractional conversion (X)} = [(\text{moles Cl}/2)/\text{moles Ca}] \quad (3.1)$$

The moles of Ca^{++} and Cl^- were obtained from the AA and IC analyses.

From the time the lime samples were weighed to the time these were placed on the sample holder, operations such as transfer from weighing pan to the mortar, mixing with the sand, and transfer from the mortar to the sample holder bed could have resulted in some loss of lime. The calcium analyses indicated that 8% or less of the theoretical calcium was lost during the transfer and mixing operations. No assumptions were needed to be made for this loss in calculation of conversion, since the same analate was used for both calcium and chloride analyses. The conversion calculations were thus also insensitive to any slight error in dilution volume used during analate preparation.

Care was taken to ensure proper test conditions and reliability of the test data. Certified gases were used with calibrated flowmeters to ensure correct flowrate of gases. The thermocouples were checked periodically to

ensure correct reading of the temperature. The pressure gauges were checked against a water tube manometer to ensure proper pressure readings. The Harvard syringe pump delivering water to the evaporator was calibrated by measuring the water flowrate at specific time intervals in a graduated cylinder. A calibration test of the evaporator was also carried out. Further, leakchecks were performed at the start of each day's tests. The analates were prepared with ultrapure water to eliminate the possibility of chloride contamination. The analates were refrigerated after the tests up to the time these were taken for AA or IC analyses. The glassware was cleaned by deionized (DI) water between consecutive tests to avoid contamination.

3.3 Characterization of Sorbent and Reaction Products

Prior to the kinetic tests on the removal of hydrogen chloride in the fixed bed reactor, relevant physical properties of the hydrated lime i.e particle size distribution, BET surface area, pore size, pore area and pore volume distribution were determined. Also in some later tests, the pore structure and surface area of the reacted sorbent were determined. Particle size analyses was carried out by an automated particle size analyzer, MULTISIZER II, manufactured by Coulter Electronics Inc. A small quantity of the dried sample was dispersed into a

special dispersant supplied by Coulter Electronics. The mixture was well stirred to maintain the particles in suspension. During the analyses, the dispersant containing the sample was drawn through a specially designed orifice in a sample tube, for a predetermined time. As the particles passed through the orifice, the number and size of the particles (i.e. mass mean diameter) were automatically recorded by measuring the change in the conductance between two metal plates on either sides of the orifice. The data on particle size and number were stored in full 256 channels of the analyzer in order to obtain good resolution over the entire size range. A minimum of three samples were analyzed for each of the sorbents used in the reactor tests. At least 100,000 particles were collected during each test before the particle size distribution were determined, to ensure that the results were representative of the original sorbent.

The BET surface area, pore area, and pore volume analyses was conducted using a Micromeritics ASAP 2000 automated surface area and pore size analyzer. A fixed amount of the dry sample (usually 1 g) was first degassed at 350 °C and an absolute pressure of 10-15 mm Hg for approximately 6 to 8 hours. Completion of degassing operation could be checked automatically in the analyzer. After degassing, nitrogen gas at 77 °K was introduced into the sample tube in stages. The amount of the gas adsorbed

by the sample at various partial pressures was automatically recorded by the analyzer. After adsorption phase readings were completed, the desorption readings were obtained by decreasing the partial pressure of nitrogen in the sample tube in small decrements and recording the quantity of nitrogen desorbed. The equilibration time between individual readings was maintained at 5 seconds as per manufacturers suggestions. These adsorption and desorption isotherms provided the necessary information for calculating the surface area, pore size, pore area and pore volume analyses.

The morphology of the lime particles was also determined by Scanning Electron Microscopy. A Cambridge Electronics Scanning Electron Microscope model TII was used to determine the morphology of the lime particles. Magnifications of up to 40K were used to determine the nature of the surface of the particles. In subsequent tests, the reaction products were analyzed by a Hitachi scanning electron microscope. This instruments allowed magnification of upto 250K, which were necessary to identify the small pores in the product. The chemical analyses of the lime were obtained from the manufacturers, however, X-ray diffraction analyses were also conducted to ensure that no foreign material was present in the lime samples in significant quantities.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Preliminary Tests on the Fixed Bed Reactor

Background Levels of Calcium and Chloride

Since a small quantity of hydrated lime (approximately 25 mg) was used in each kinetic test, it was necessary to determine if the results were significantly affected by background levels of calcium and/or chloride in the other materials used in these tests. The ultrapure water, the deionized water and the IC eluent showed practically no calcium and chloride. Analates prepared from the F-75 quartz silica sand and the glass filter also showed very low calcium and chloride levels which were near the lower detection limits of the instruments.

Chloride Uptake of the Sand and Glass Filter in the Reactor

In the kinetic tests, both the sand and the glass filter were exposed to the hydrogen chloride gas along with the hydrated lime. Though both these materials have been found to be inert to acid gases in other studies (Jozewicz

1989, 1990), it was necessary to check whether these affected the chloride uptake of the sample bed significantly. The chloride uptakes of the F-75 sand and glass filter were checked in a kinetic test in the fixed bed reactor. The test condition chosen was 175 °F and 25% relative humidity at 1000 ppmv hydrogen chloride concentration. The test was carried out exactly like an actual kinetic test except that there was no hydrated lime in the sample bed. The results of this test are shown in Figure 4.1, and for comparison this figure also includes the chloride uptake of 25 mg hydrated lime at the same test conditions. The figure clearly shows that the chloride uptakes of the sand and the glass filter are insignificant compared to the hydrated lime. Similar blank tests at other selected test conditions showed the same trend. No corrections were therefore warranted in the conversion calculations of hydrated lime due to the presence of either the sand or the glass filter in the sample bed.

Recovery of Calcium in the Analates

Many transfer and mixing operations were carried out from the time the hydrated lime for a particular kinetic test was weighed in an analytical balance to the time when the calcium was measured in the analate by atomic absorption spectrometry. Since a small quantity of hydrated

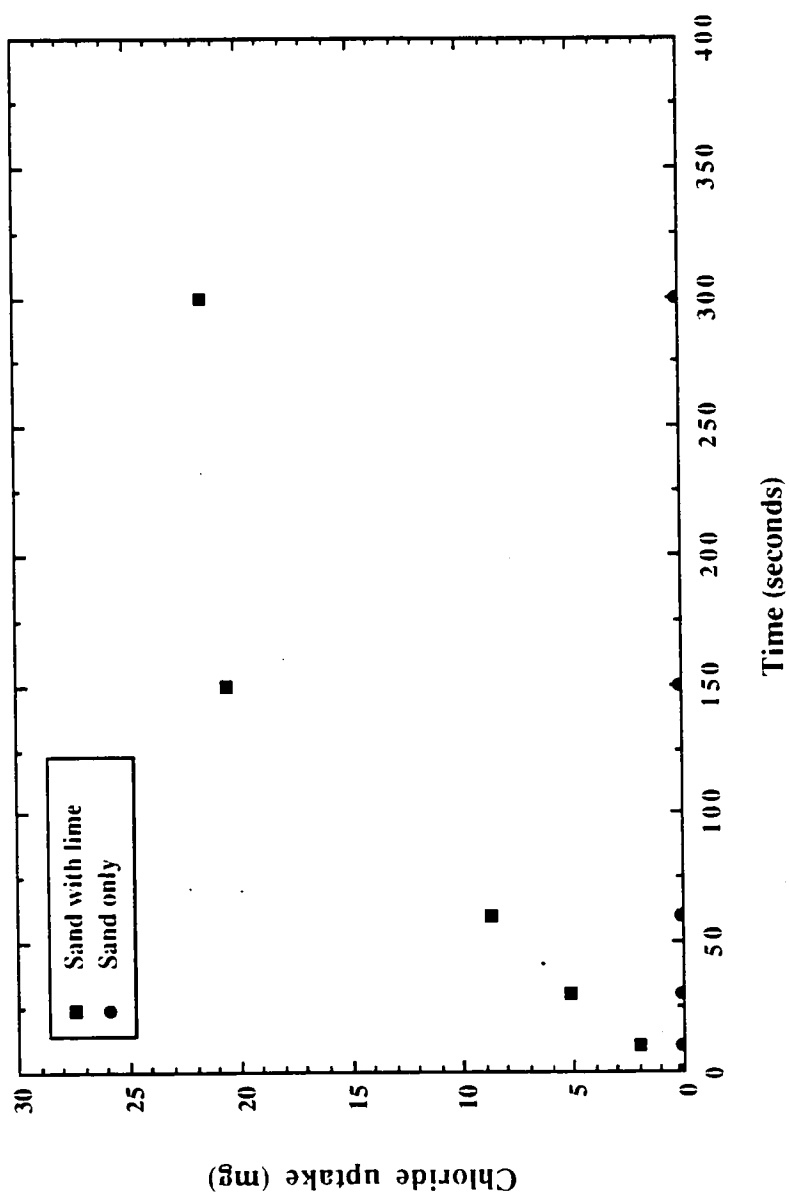


Figure 4.1. Chloride uptake by the sample bed in a blank test and a lime test at 1000 ppmv HCl.

lime was used in the kinetic tests, it was considered necessary to determine the loss of calcium during these operations. To determine this, complete kinetic tests were carried out on preweighed quantities of hydrated lime and sand, except that the test gas contained no hydrogen chloride. Analates were prepared from these samples as described earlier and analyzed for calcium by atomic absorption spectrometry. The results showed that recovery of calcium in the analate was dependent on the amount of sulfuric acid used and that even with an adequate amount of sulfuric acid (approximately 1 ml per 100 ml of analate), 6% to 8% of the calcium theoretically present in 25 mg of calcium hydroxide was still unaccounted for. This unavailable calcium was considered to account for both the less than complete availability of calcium hydroxide in the sorbent (98%) and the overall loss during the tests. It should be noted that the conversion of hydrated lime was calculated from the actual amount of calcium in the analate and not based on the theoretical amount. Thus, the unavailable calcium did not affect the values of the conversion.

4.2 Characterization of Hydrated Lime Sorbent

Commercial grade high calcium hydrated lime (product #1) manufactured by Tenn Luttrell Lime Company, Knoxville,

was selected as the sorbent in this study. Typical chemical composition of this hydrated lime is shown in Table 4.1. The sorbent was initially separated in the following three size ranges by manual sieving with wiremesh sieves :

<u>Size range</u>		<u>ID</u>
0-45 microns	-	TL1
45-53 microns	-	TL2
53-90 microns	-	TL3

The objective was to determine the effect of varying particle size on the conversion in kinetic tests. Important physical properties of these size fractions were next determined.

Particle Size and BET Surface Area

The particle size distribution and surface area of the three size ranges were determined by the methods described earlier in Section 3 (Experimental Methods). Complete analyses of the particle size distribution are given in Appendix 2 and a summary of the results is shown in Table 4.2. The mass mean diameters of the three size ranges were similar and in the range of 6-7.2 microns, which were within the size ranges reported for other commercial hydrated limes i.e. 2-9 microns (Boynton, 1976). The particle sizes were considerably lower than the screens used for the separations. The results indicated that

Table 4.1. Composition of Tenn Luttrell Hydrated Lime
 (Product #1)

Type of Hydration	Atmospheric
Available $\text{Ca}(\text{OH})_2$	98%
% moisture	1%
Particle size (passing 325 mesh)	90%
Loss on Ignition	24%
SiO_2	0.5%
R_2O_3 (metal oxides)	0.7%
MgO	0.6%
Fe	0.25%
Sulfur	0.02%
Phosphorous as P	500 ppm

- Notes :
1. All percentages are by weight.
 2. Ref: Personal communication with Mr. Jim Compton of Tennessee Luttrell Lime Company on 06/06/91.

Table 4.2. Physical Properties of Tenn Luttrell Hydrated Limes

Parameter	TL-1	TL-2	TL-3
Mass mean Dia - Avg. (Range) (microns)	5.96 (4.57-6.68)	7.2 (6.27-8.37)	6.05 (5.57-6.58)
BET surface area (m ² /g)	17.0 ± 0.14	18.7 ± 0.12	18.1 ± 0.14
BJH desorption pore area (m ² /g)	20.2	22.2	21.4
68 Micropore area (m ² /g)	0.669	0.69	0.97
Single point pore volume (cc/g)	0.069	0.071	0.075
Avg. pore diameter (Angstroms)	163.9	152.2	166.56

hydrated lime agglomerated considerably during the manufacturing and/or storage and that manual sieving separated only the different sizes of the agglomerates. The agglomerating property of other types of commercial hydrated limes have been reported in literature (Jozewicz 1990, Chang, 1989). The surface area of the sorbent is an important indicator of reactivity in gas-solid reactions. The surface area of the hydrated lime was measured by the method mentioned in Section 3 (Experimental Methods). A summary of the analyses is given Appendix 2. and the results are reproduced in Table 4.2. The BET surface area of the three size fractions of the hydrated lime were similar and in the range of 17-19 m²/g. The surface area of hydrated lime depends on the conditions of hydration, such as temperature, lime water ratio, and source of quicklime. Reported values of BET surface area of commercial grade atmospherically hydrated limes range from 12-24 m²/g (Boynton, 1976).

Pore Structure

Incomplete conversion of the hydrated lime in reaction with hydrogen chloride have been reported by Karlsson (1981) and Jozewicz (1990), though the causes were not explored in those studies. The product of the reaction between hydrated lime and hydrogen chloride is believed to

be calcium chloride, which has a molar volume approximately 52% higher than the hydrated lime. Therefore, the possibility existed that the reaction in the pores might lead to pore blockage and result in incomplete conversion, if sufficient pore volume was not available. A knowledge of the pore structure of the hydrated lime was necessary to study this aspect of the reaction.

The pore structure of the three size ranges of the hydrated lime used in this study were determined by the nitrogen adsorption/desorption isotherms in a Micromeritics surface area and pore size analyzer. The shapes of these isotherms yield insight into the nature of the pores. The isotherms of the three size ranges of hydrated limes were similar and a typical isotherm is shown in Figure 4.2. The isotherm was classified as a type IV isotherm as per the classification of Brauner et al. This type of isotherm is known to be typical of materials with porosity in the mesopore range (20 to 500 Angstroms), and is accompanied with a hysteresis loop associated with capillary condensation (Gregg and Sing, 1982). Further, the hysteresis loop is of type H3 as per the International Union of Pure and Applied Chemistry (IUPAC) classification (Gregg and Sing, 1982), which suggests that the majority of the pores are parallel plate shaped and slit shaped.

The ideal parallel plate shaped or slit shaped pores exhibit a nearly vertical branch in the desorption isotherm

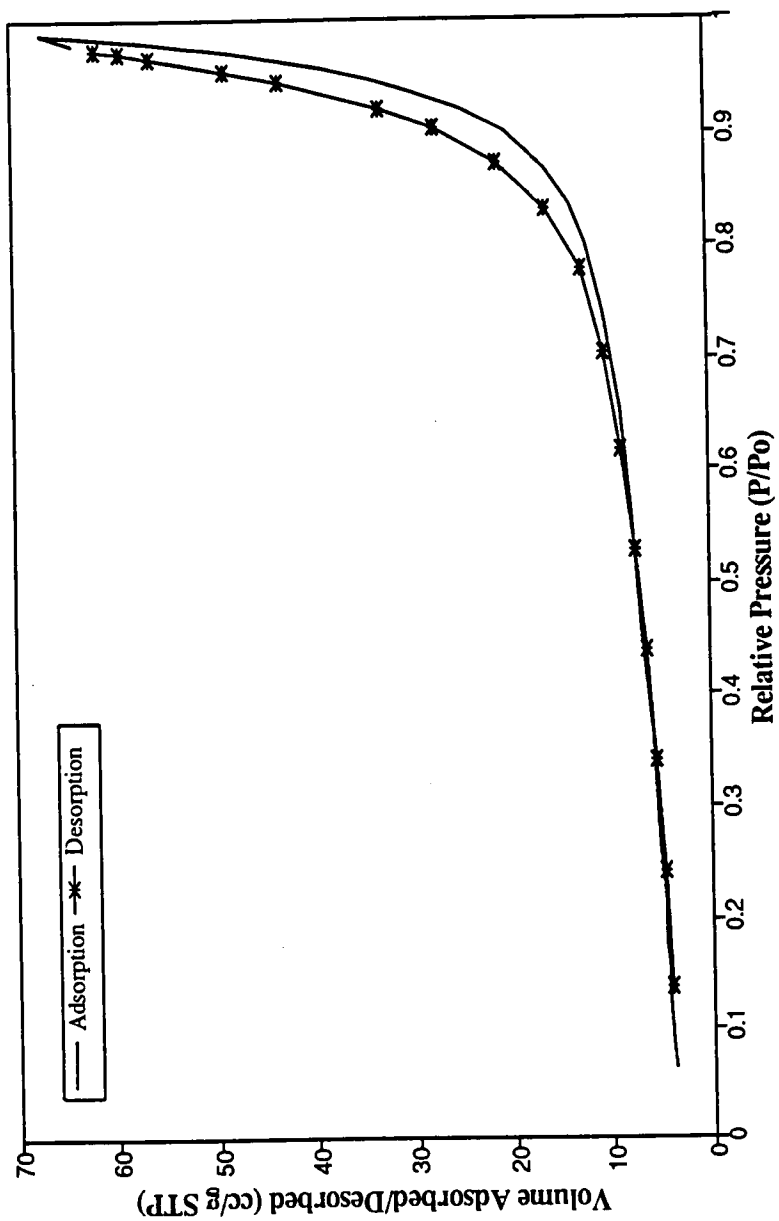


Figure 4.2. Typical Nitrogen Adsorption/Desorption Isotherm of Tenn Luttrell Hydrated Lime.

at the point of loop closure in the mid range of relative pressures (Gullet et al., 1987). Figure 4.2 on the other hand showed a gradual loop closure, which indicated deviation from the ideal parallel plate or slit shaped pores. Gullet observed similar loop closure in calcined hydrated lime and attributed it to the presence of a wide variety of other pore shapes such as wedge shaped, cone shaped pores along with parallel plate and slit shaped pores. Similar conclusions can be drawn for the Tenn Luttrel hydrated lime also. Quick lime, on the other hand, has cylindrical shaped pores as reported by Gullet and Bruce (1987). Other pore structure parameters such as pore area, pore volume and average pore diameter are given in Table 4.2. The table shows that the pore structure of the three size ranges of the hydrated lime are also similar.

Theoretically, the BET surface area is the sum of external and internal surface areas. Assuming the latter to be uniformly distributed, the relationship between the BET surface area and the particle size can be expressed as (Klingspor et al., 1983)

$$S_{\text{BET}} = S_{\text{INP}} + a[3/(R_p \cdot Q_p)] \quad (4.1)$$

Where

$$\begin{aligned} S_{\text{BET}} &= \text{BET surface area (m}^2\text{/g)} \\ S_{\text{INP}} &= \text{Internal pore area (m}^2\text{/g)} \\ a &= \text{Surface roughness correction factor} \end{aligned}$$

(1.0 for smooth sphere)

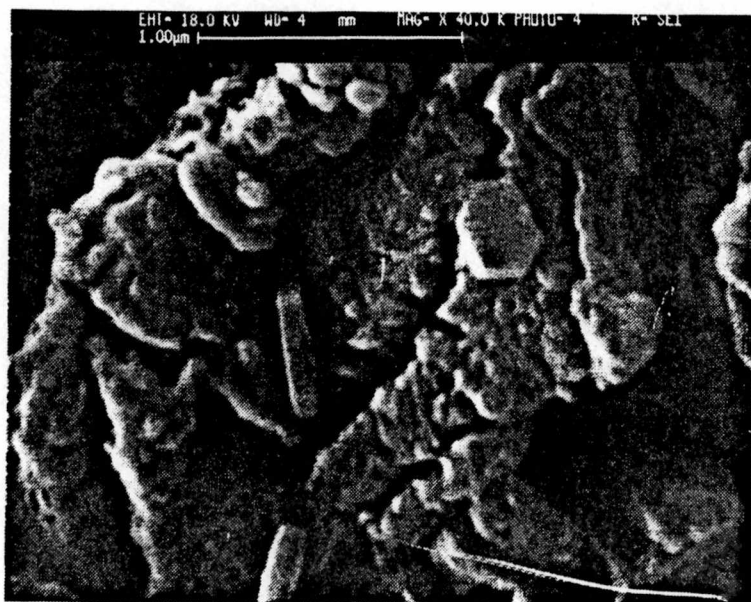
R_p = Particle size (microns)

ρ_p = Particle density (g/cc)

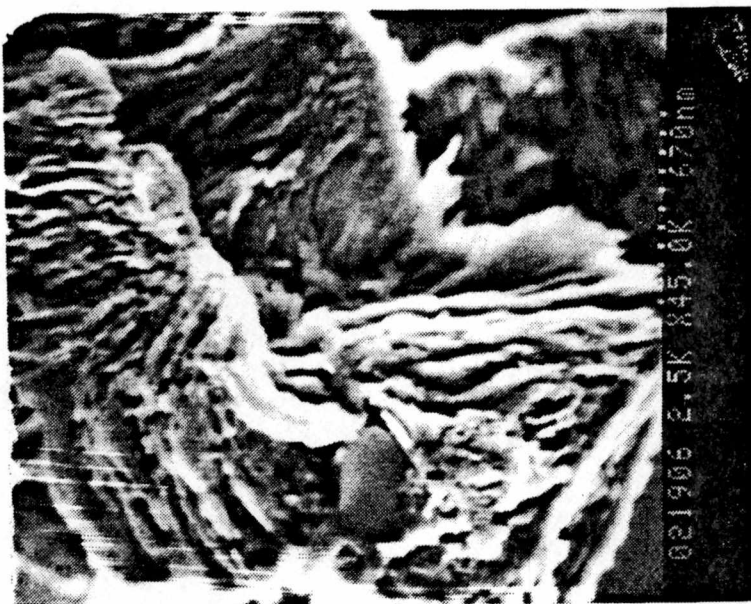
From the particle size, BET surface area, and the pore structure data, the roughness correction factor for the three size ranges of hydrated lime were calculated as 35.94, 47.5, and 37.97, respectively. Such high values of the roughness factor indicated that either the true particle size of the hydrated limes was much smaller from that obtained from the Coulter counter and/or there was considerable surface roughness. Figures 4.3 a,b show the scanning electron microscope (SEM) photographs of the hydrated lime taken at magnifications ranging from 40K to 45K. These figures confirm both the presence of submicron sized particles and considerable surface roughness. Further, the presence of plate, slit shaped pores and to some extent the presence of cylindrical pores are also observed in these figures.

Reactivity with Hydrogen Chloride

All the above tests showed that the physical properties of the three sizes of the hydrated lime were similar. It was expected therefore, that the chemical reactivity of these three size ranges of hydrated lime



(a)



(b)

Figure 4.3. SEM Photograph of the Unreacted Tenn Luttrell Hydrated Lime.

would also be similar. This assumption was checked in a kinetic test at 175 °F, 25% relative humidity, and 1000 ppmv hydrogen chloride concentration. The results are shown in Figure 4.4 and in spite of the scatter in the data, the chemical reactivity of the three sizes can be considered as similar.

Conclusions

Based on the results of all the tests mentioned above, it was concluded that the three size ranges of the hydrated lime were actually the same in terms of physical properties and chemical reactivity with hydrogen chloride. The manual sieving did not result in separation of the hydrated lime into different size distributions. Therefore, all the later kinetic tests were carried out with the unsieved hydrated lime. X-Ray diffraction (XRD) analysis of the hydrated lime showed the presence of only calcium hydroxide.

4.3. Kinetic Tests in the Fixed Bed Reactor

Thirty two kinetic tests were run in this phase to determine the effect of operating parameters such as gas temperature, moisture content in the gas, and the gas concentration on the conversion of hydrated lime. Three tests were run later to determine the effect of surface

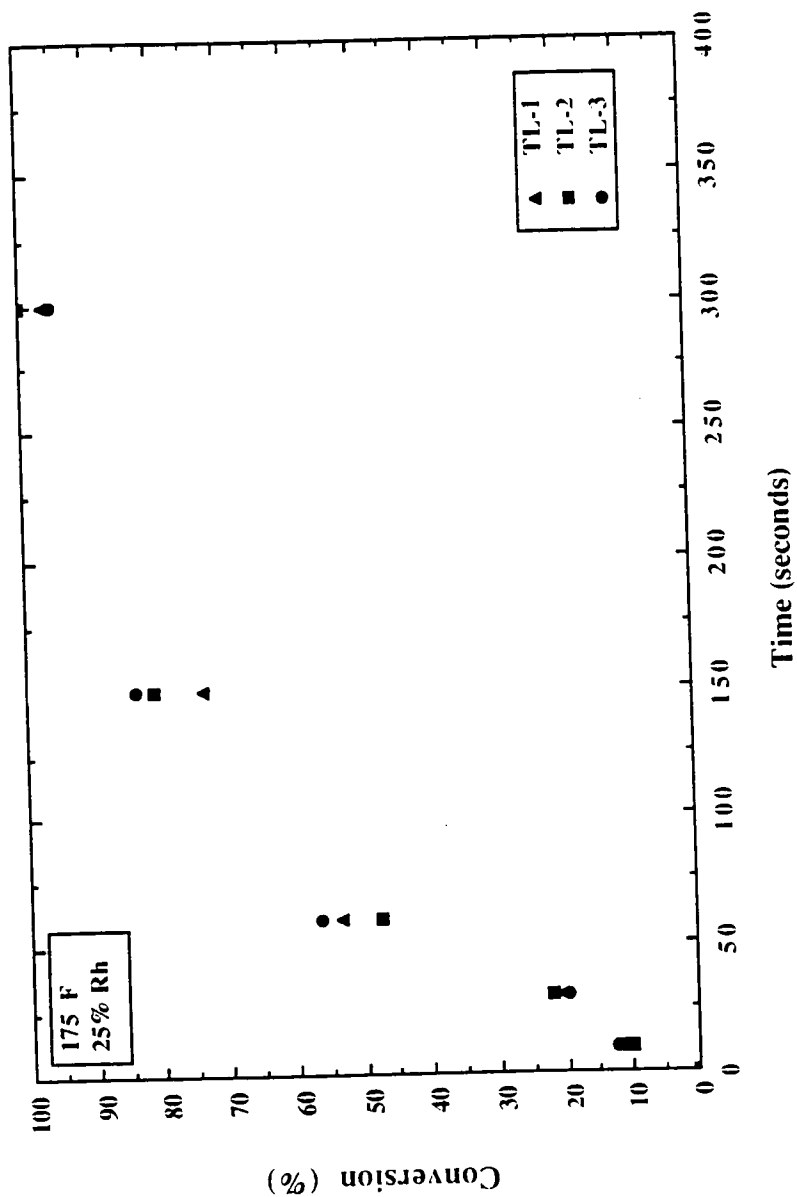


Figure 4.4. Sorbent conversion for the three size fractions of hydrated at 1000 ppmv HCl.

area of hydrated lime on the conversion. Since the manual sieving was not successful in separating the Tenn Luttrel lime in fractions of different surface areas, hydrated lime from another source was used for these surface area tests.

All these tests were run at hydrogen chloride concentration of approximately 1000 ppmv, except the tests in which the effect of gas concentration was determined. These tests were run at gas concentrations of 500 ppmv, 1000 ppmv, 5000 ppmv, and in one condition at 8000 ppmv and 15000 ppmv also. High gas flow and small quantity of hydrated lime sorbent was used in all tests to ensure that the reaction was never limited by the unavailability of hydrogen chloride. Gas temperatures and moisture contents ranged between 175 °F to 400 °F, and 0% to 30% respectively. A brief summary of the operating conditions of these tests are given in Table 4.3. and detailed data are included in Appendix 3. The results of these tests are presented in the following subsection with general discussions of the trends. Quantitative analyses of these trends are presented in the next subsection. In order to calculate the rate of conversion, the experimental conversion data was analyzed statistically to determine the best fit empirical equation for these tests. The empirical equations tested were

1. $\ln(X) = A[\ln(1/t)] + B$

2. $\ln(X) = A[1/t] + B$

Table 4.3. Brief Operating Conditions of the Kinetic Tests

Test ID	Temperature (°F)	Moisture content (% v/v)	Relative humidity (%)	Gas concn. (ppmv)	Reaction Time (seconds)
NM175	175	0	0	1000	30, 60, 150, 300
NM200	200	0	0	1000	30, 60, 150, 300
NM225	225	0	0	1000	30, 60, 150, 300
NM300	300	0	0	1000	30, 60, 150, 300
NM400	400	0	0	1000	30, 60, 150, 300
T15	175	3.2	8	1000	10, 30, 60, 150, 300
T14	175	7	15	1000	10, 30, 60, 150, 300
T18	200	7	8	1000	10, 30, 60, 150, 300
T20	225	7	6	1000	10, 30, 60, 150, 300
T23	300	7	1.5	1000	10, 30, 60, 150, 300
T27	400	7	0.40	1000	10, 30, 60, 150, 300
T13	175	10	25	1000	10, 30, 60, 150, 300
T17	200	10	15	1000	10, 30, 60, 150, 300
T19	225	10	8	1000	10, 30, 60, 150, 300
T22	300	10	2.2	1000	10, 30, 60, 150, 300

Table 4.3. Brief Operating Conditions of the Kinetic Tests (cont.)

Test ID	Temperature (°F)	Moisture content (% v/v)	Relative humidity (%)	Gas concn. (ppmv)	Reaction Time (seconds)
T26	400	10	0.6	1000	10, 30, 60, 150, 300
T12SP	175	20	45	1000	10, 30, 60, 150, 300
T12	200	20	25	1000	10, 30, 60, 150, 300
T16	225	20	15	1000	10, 30, 60, 150, 300
T21	300	20	4.5	1000	10, 30, 60, 150, 300
T24	400	20	1.1	1000	10, 30, 60, 150, 300
T11	225	30	25	1000	10, 30, 60, 150, 300
M13	175	10	25	500	10, 60, 150, 300, 600
M17	200	10	15	500	10, 60, 150, 300, 600
M19	225	10	8	500	10, 60, 150, 300, 600
M22	300	10	2.2	500	10, 60, 150, 300, 600
H13	175	10	25	5000	10, 60, 150, 300
H17	200	10	15	5000	10, 60, 150, 300
H19	225	10	8	5000	10, 60, 150, 300

Table 4.3. Brief Operating Conditions of the Kinetic Tests (cont.)

Test ID	Temperature (°F)	Moisture content (% v/v)	Relative humidity (%)	Gas concn. (ppmv)	Reaction Time (seconds)
H22_1	300	10	2.2	15000	30,100,300,600
H22_2	300	10	2.2	8000	30,100,300,600
H22_2	300	10	2.2	5000	30,100,300,600
S12SP*	175	20	45	1000	10,60,150,300
S19*	225	10	8	1000	10,60,150,300
S26*	400	10	0.6	1000	10,60,150,300

Notes : * - These tests were with Scansorb hydrated lime. All other tests were with Tenn Luttrel hydrated lime.

Detail operating conditions and results are in Appendix 3.

3.
$$X = A[1 - \exp(-t/B)]$$

where "X" was sorbent conversion and "t" was the reaction time. A and B were coefficients of the equation.

The empirical equation 3 yielded the highest average regression coefficient for the tests and was chosen to represent the conversion at any reaction time. The values of the parameters A,B and the regression coefficients are given in Appendix 4.

Tests with Dry Hydrogen Chloride

In the first phase of the kinetic tests, the conversion of the hydrated lime with dry hydrogen chloride was checked at five temperatures of 175 °F, 200 °F, 225 °F, 300 °F, and 400 °F and at four reaction times of 30 seconds, 60 seconds, 150 seconds, and 300 seconds. No moisture was added to the test gas in these tests. The objectives of these tests were to determine the effect of temperature on the reaction and to obtain baseline data for determining the effect of moisture, in later tests.

Figure 4.5 shows the conversion of hydrated lime at the five temperatures mentioned above. The conversion of hydrated lime increased with both temperature and reaction time though the maximum conversion at 400 °F and at 300

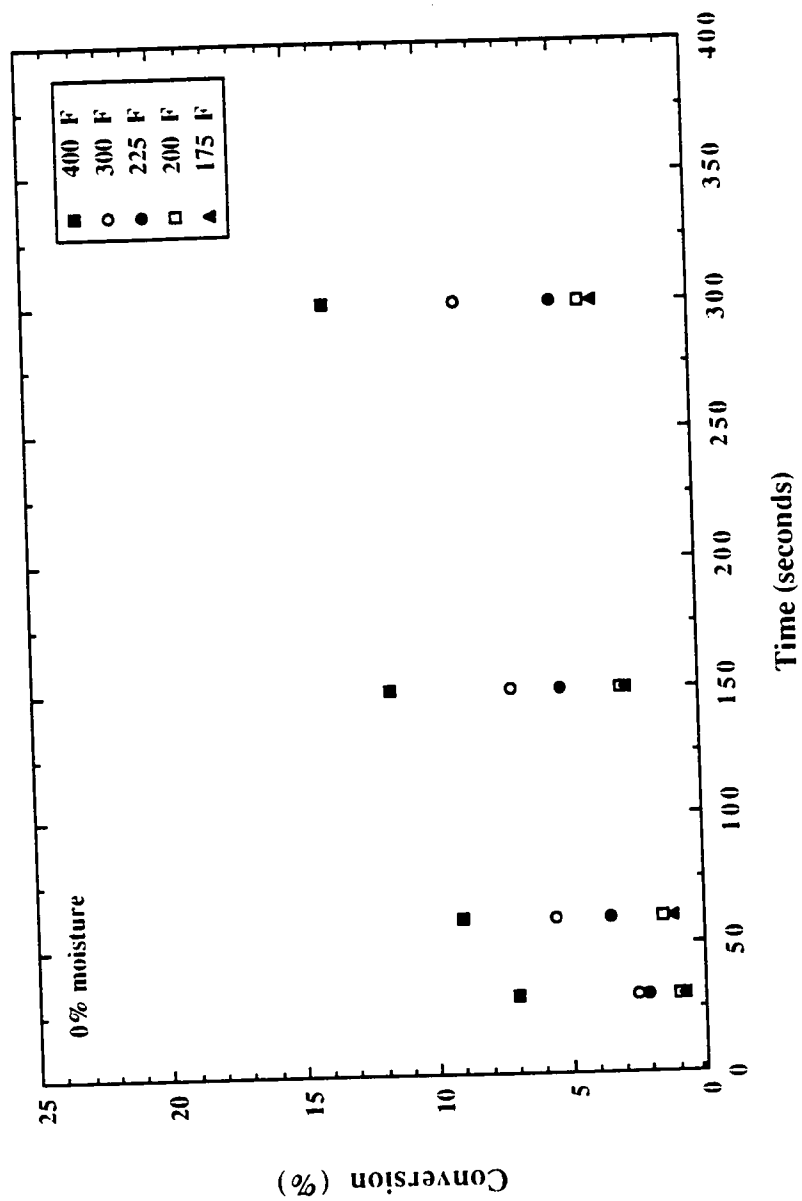


Figure 4.5. Sorbent conversion at 0% moisture and 1000 ppmv HCl.

seconds was only 13.6%, showing poor utilization of the sorbent. There was practically negligible reaction at 175 °F. The rate of conversion decreased to a negligible value within 150 seconds in all tests. These results suggested a high resistance in the product layer to the diffusion of the reacting gas which severely restricted the conversion beyond 300 seconds at all the temperatures. Both the initial rate of conversion and the final conversion increased with temperature, indicating the possibility of a temperature activated reaction mechanism at these test conditions. Karlsson (1981) also found a similar trend between conversion and temperature with dry hydrogen chloride at temperatures between 350 °F and 750 °F as shown in Figure 2.2 for hydrated lime from a different source.

Effect of Moisture on Sorbent Conversion

Moisture in the flue gas is known to enhance the removal of hydrogen chloride by hydrated lime, both in full scale plants (White and Vancil, 1989) and in bench scale fixed bed reactors (Jozewicz, 1990). However, kinetic data on the moisture enhancement of the reaction between hydrogen chloride and hydrated lime have not been reported. The objective of this phase of the testing was to obtain such kinetic data at various levels of moisture and temperatures, representative of the low temperature DSI

process. Seventeen test conditions were selected at different combinations of moisture and temperatures so that the effect of moisture content in the test gas, the temperature of the test gas, and the relative humidity of the test gas, on the sorbent conversion could be determined separately. The tests covered a moisture content range of 5% to 30% (v/v), a temperature range of 175 °F to 400 °F, and a relative humidity range of 0.40% to 45%. All tests were conducted at a hydrogen chloride concentration of 1000 ppmv and the sorbent conversion was obtained at five reaction times of 10, 30, 60, 150, and 300 seconds in each of these tests.

The effects of the moisture on the sorbent conversion are shown in Figures 4.6 to 4.8 at moisture contents of 7% (v/v), 10% (v/v), and 20% (v/v), respectively. There was significant enhancement in the conversion of hydrated lime over the dry hydrogen tests at all moisture contents, and the degree of enhancement increased with increasing moisture. The tests also showed that complete conversion of the hydrated lime was possible at certain moisture contents and temperatures, a fact which had not been shown in earlier studies. However, the reaction products in those tests exhibiting a complete conversion of the hydrated lime were found to be damp and sticky. Thus, complete conversion of the hydrated lime may not be desired in full scale plants to avoid handling problems.

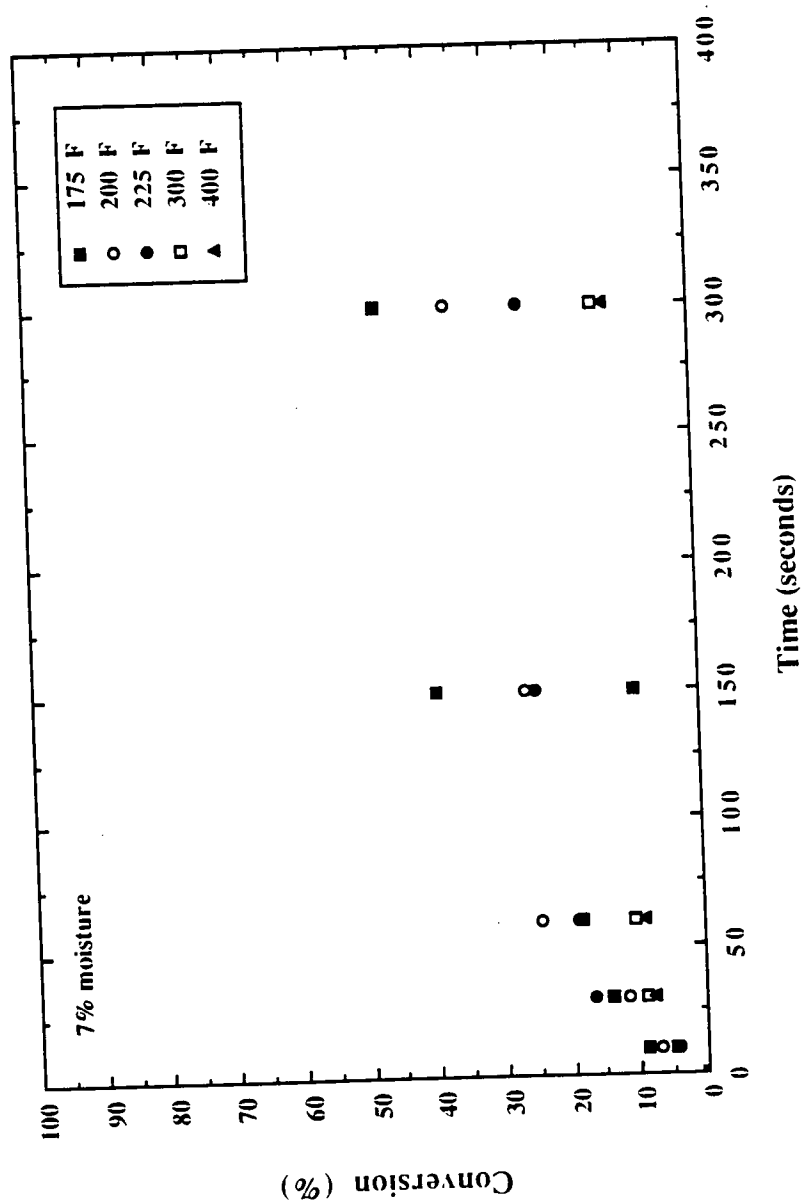


Figure 4.6. Sorbent conversion at 7% moisture, 1000 ppmv HCl and at 175 F to 400 F.

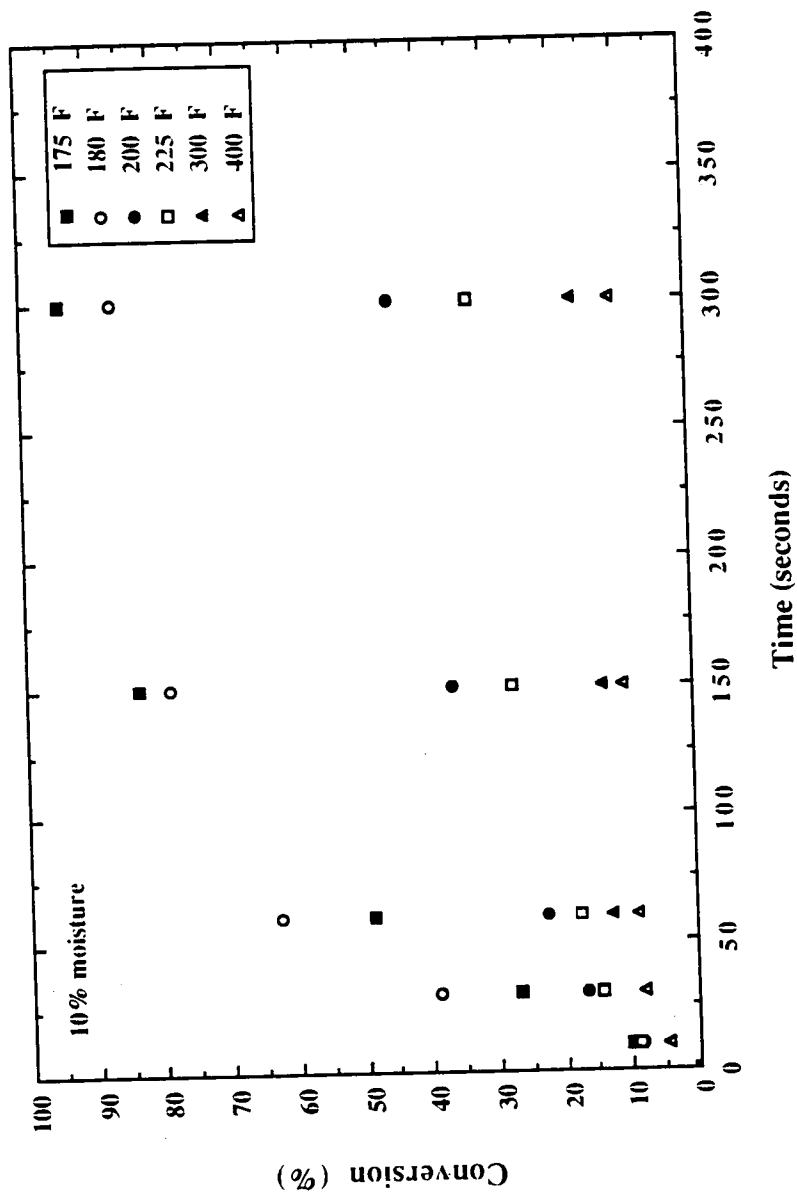


Figure 4.7. Sorbent conversion at 10% moisture, 1000 ppmv HCl and at 175 F to 400 F.

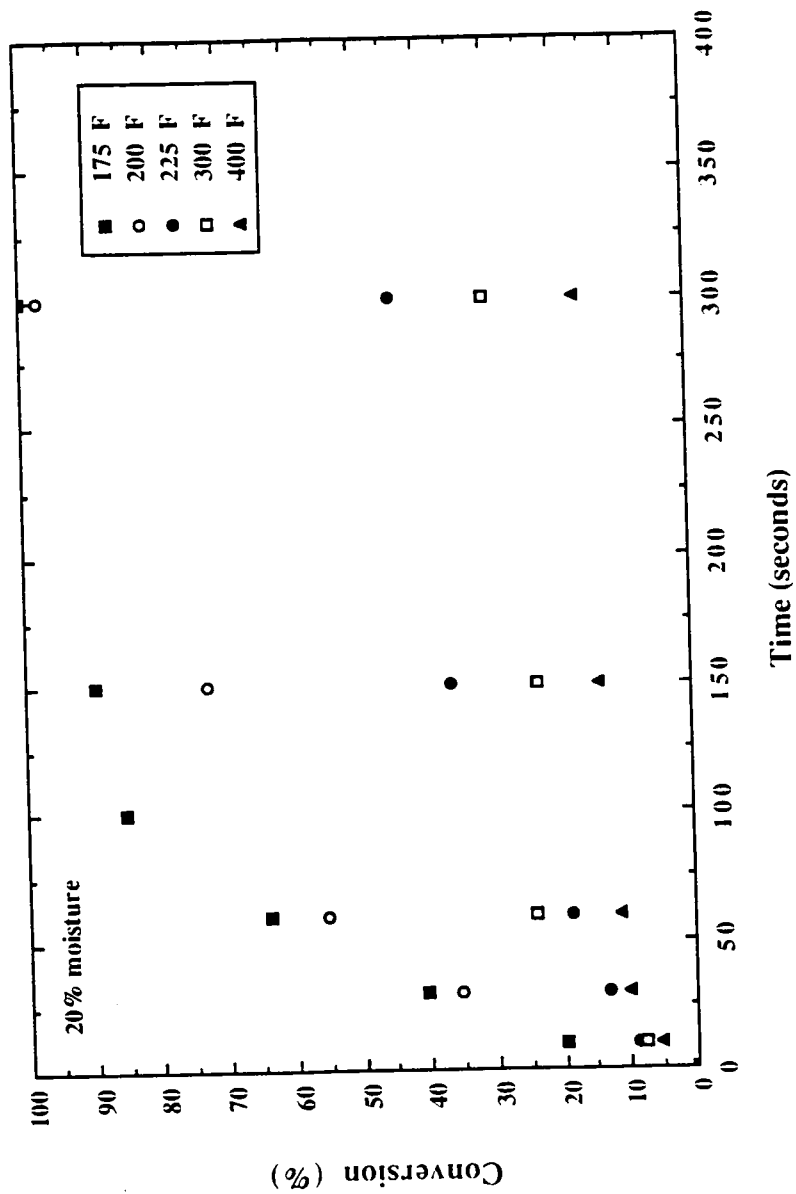


Figure 4.8. Sorbent conversion at 20% moisture, 1000 ppmv HCl and at 175 F to 400 F.

The effect of the formation of reaction product on the rate of reaction is evident at all conditions as noted by the reduction in the conversion rate as the reaction proceeded. The rate of conversion decreased considerably after 300 seconds in the tests which showed incomplete conversion.

To determine the effect of the moisture content at each temperature, the conversion data were plotted with varying moisture contents and at constant test temperatures as shown in Figures 4.9 to 4.13. For comparison, these figures also include the results of dry hydrogen chloride tests at the same temperatures.

The degree of enhancement of the conversion was relatively higher at lower temperatures. For example, while the final conversion at 175 °F changed from 3.6% to 100% between moisture contents of 0% and 20% in the test gas, the change in the final conversion was only from 13.6% to 16.8% for the same moisture contents at 400 °F. Thus, for a fixed moisture content, the conversion decreased with increase in temperature. This trend is completely reverse of the trend in the dry hydrogen tests shown in Figure 4.5, in which the conversions increased at higher temperatures. These results suggested that the mechanism of reaction of hydrated lime with dry and moist hydrogen chloride were different. The effects of the temperature and moisture content seemed to be interrelated, thus neither of these

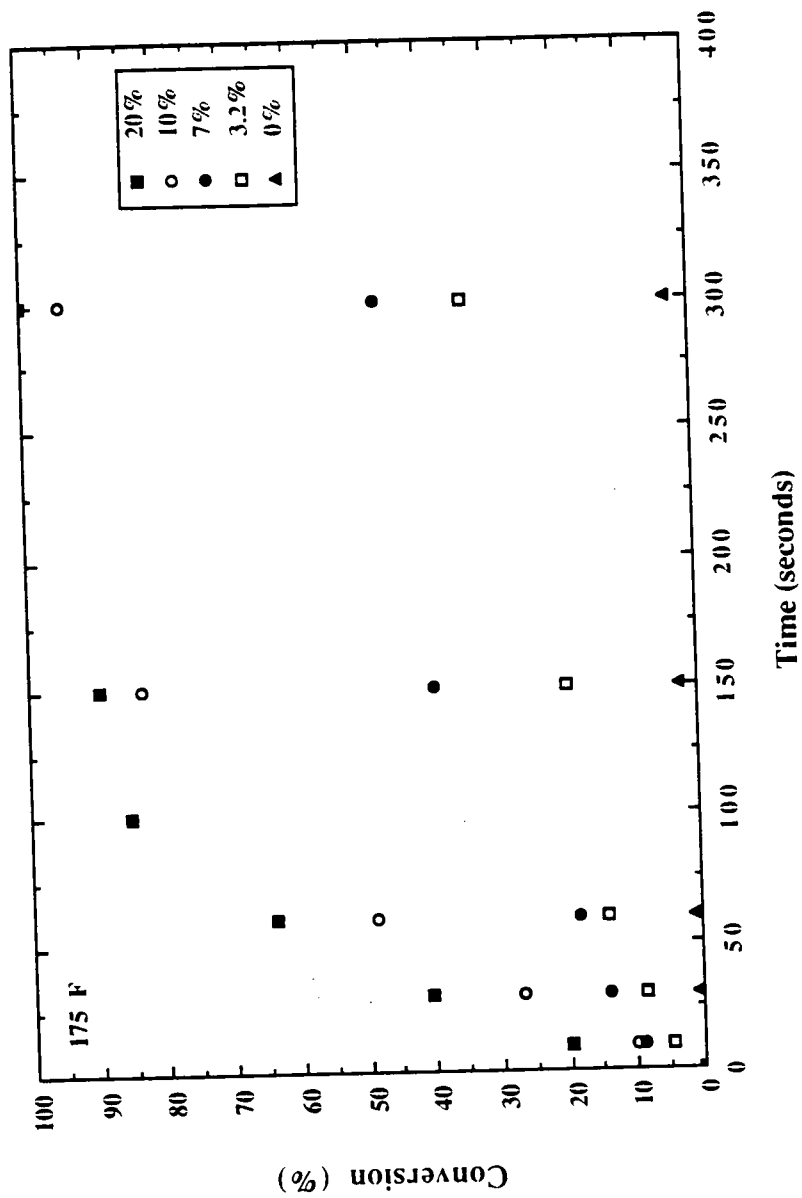


Figure 4.9. Sorbent conversion at 175 F, 1000 ppmv HCl and 0% to 20% moisture.

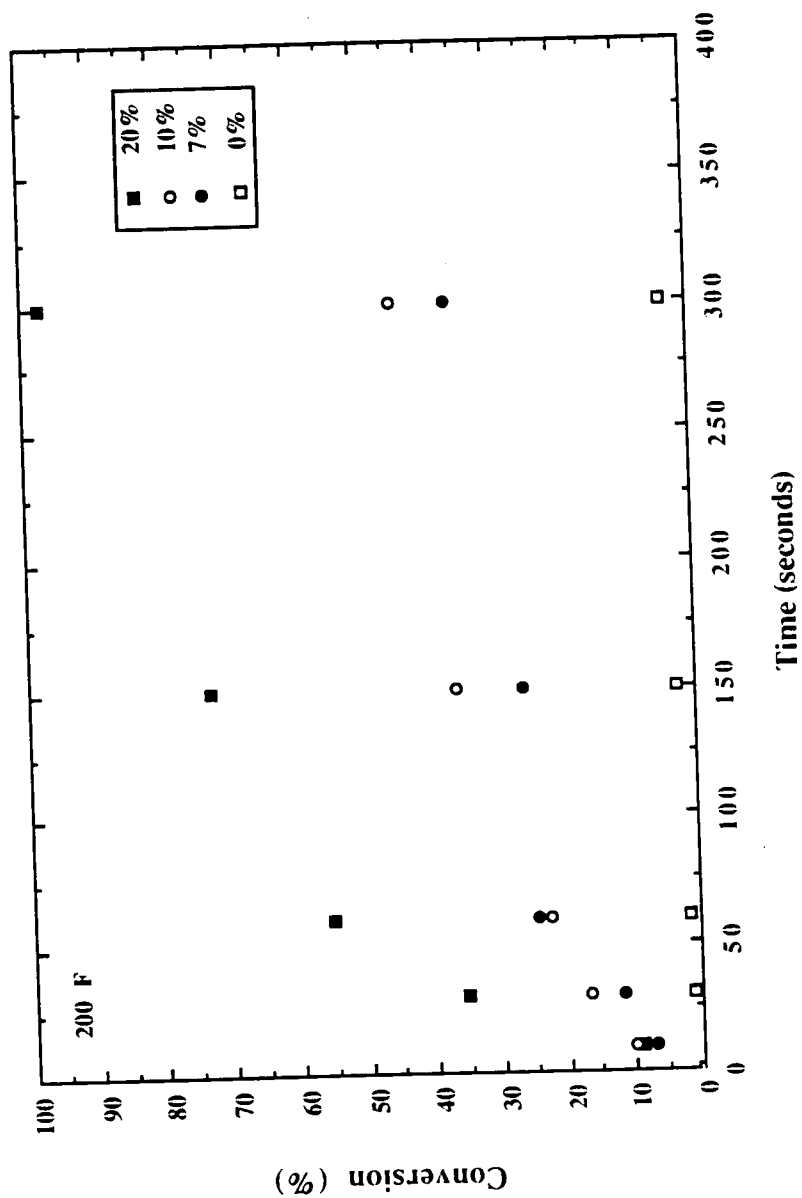


Figure 4.10. Sorbent conversion at 200 F, 1000 ppmv HCl and 0% to 20% moisture.

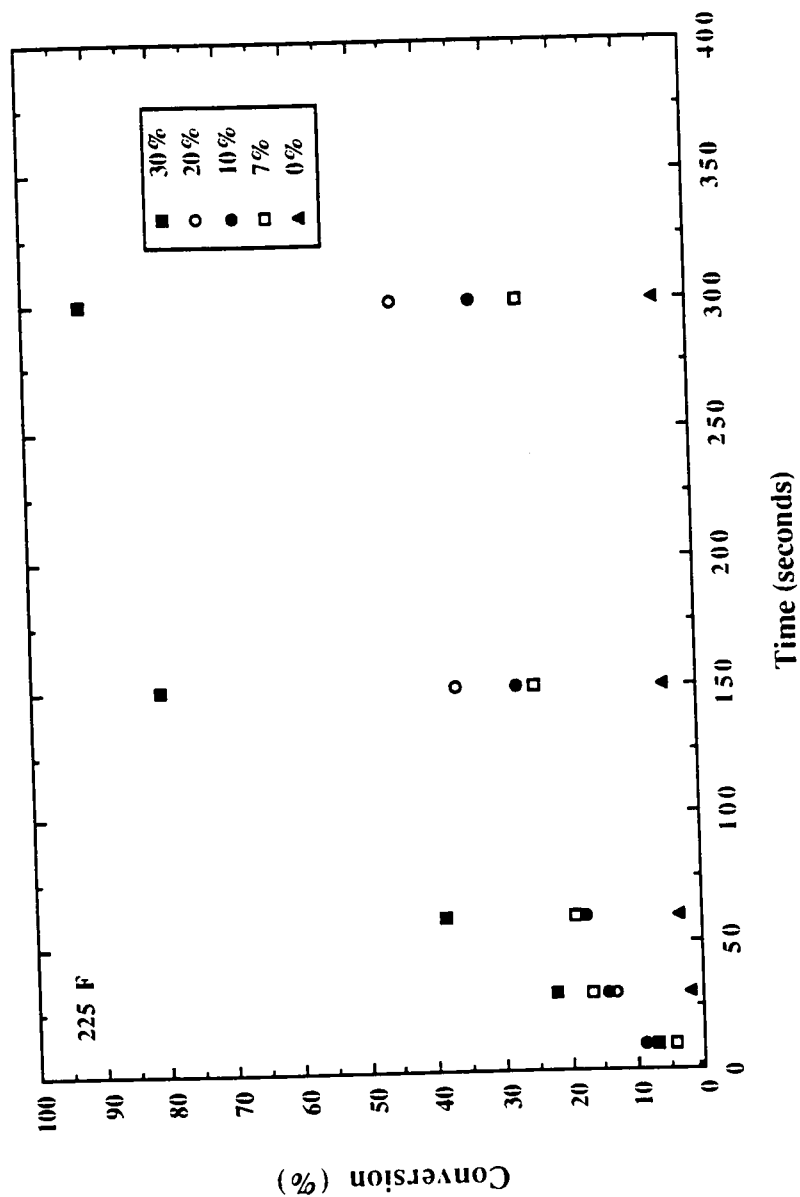


Figure 4.11. Sorbent conversion at 225 F, 1000 ppmv HCl and 0% to 30% moisture.

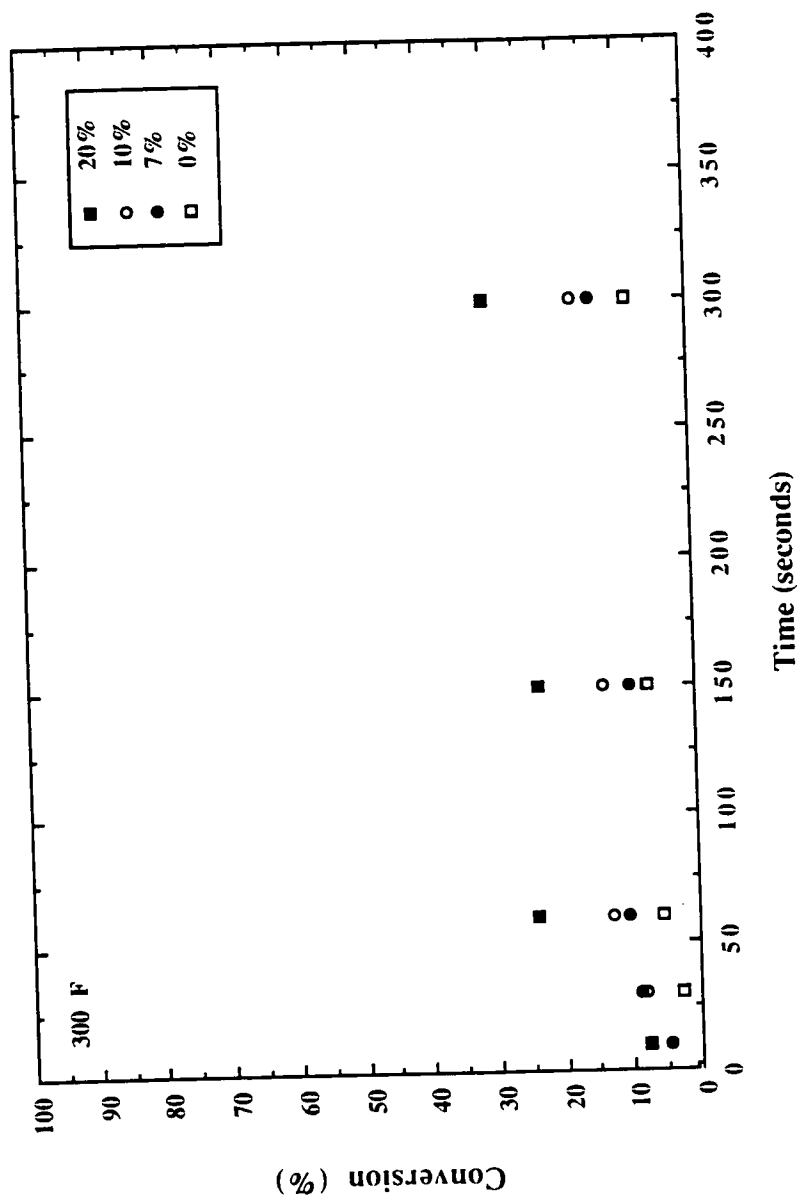


Figure 4.12. Sorbent conversion at 300 F, 1000 ppmv HCl and 0% to 20% moisture.

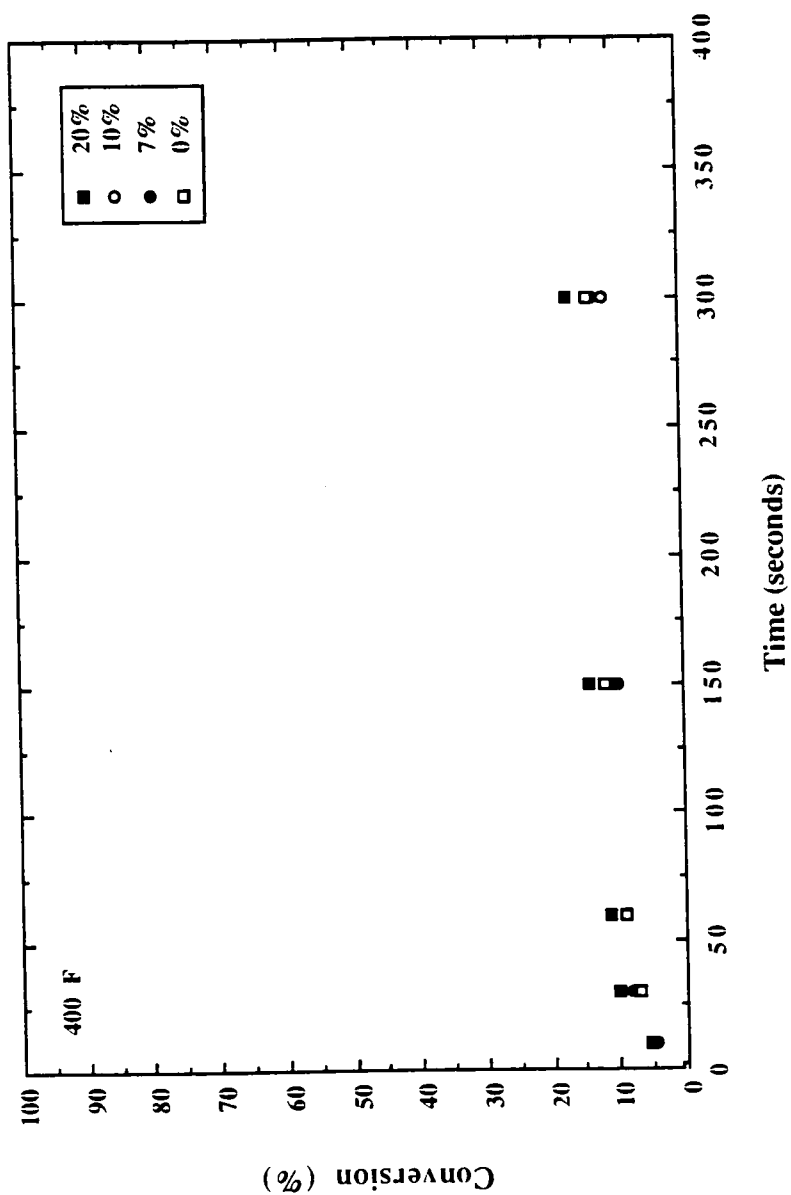


Figure 4.13. Sorbent conversion at 400 F, 1000 ppmv HCl and 0% to 20% moisture.

could be used as a single parameter to describe the conversion without reference to the other.

The temperature and moisture content of a gas are uniquely related by the relative humidity of the gas. The test data were therefore replotted at constant relative humidities irrespective of the temperature or moisture content of the gas, and the results are shown in Figures 4.14 and 4.15. The conversions decreased with lower relative humidity in all the tests. In spite of some scatter in the data, conversions were found to be similar at similar relative humidities, though the test temperatures and moisture content in the test gas differed considerably. Thus, the relative humidity of the test gas was found to be the single parameter which best described the combined effect of moisture and temperature on conversions for these moist hydrogen chloride tests.

Effect of Gas Concentration on Sorbent Conversion

In the next phase of testing, the effect of hydrogen chloride concentration on the conversion of hydrated lime was determined. Ten tests were conducted at a constant moisture content of 10% (v/v) and at temperatures of 175 °F, 200 °F, 225 °F, and 300 °F. Tests were conducted at 500 ppmv and 5000 ppmv of hydrogen chloride at all these temperatures. Additionally, in the case of 300 °F, tests

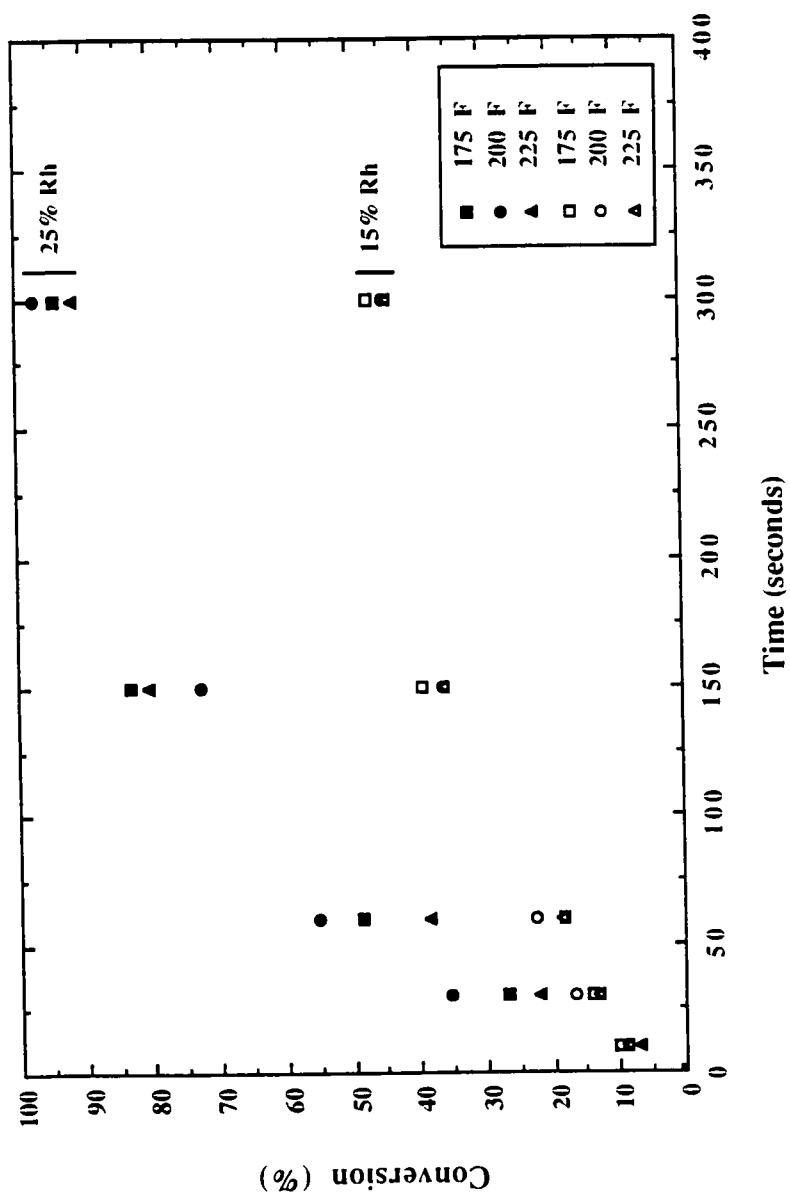


Figure 4.14. Sorbent conversion at 1000 ppmv HCl and relative humidities of 25% and 15%.

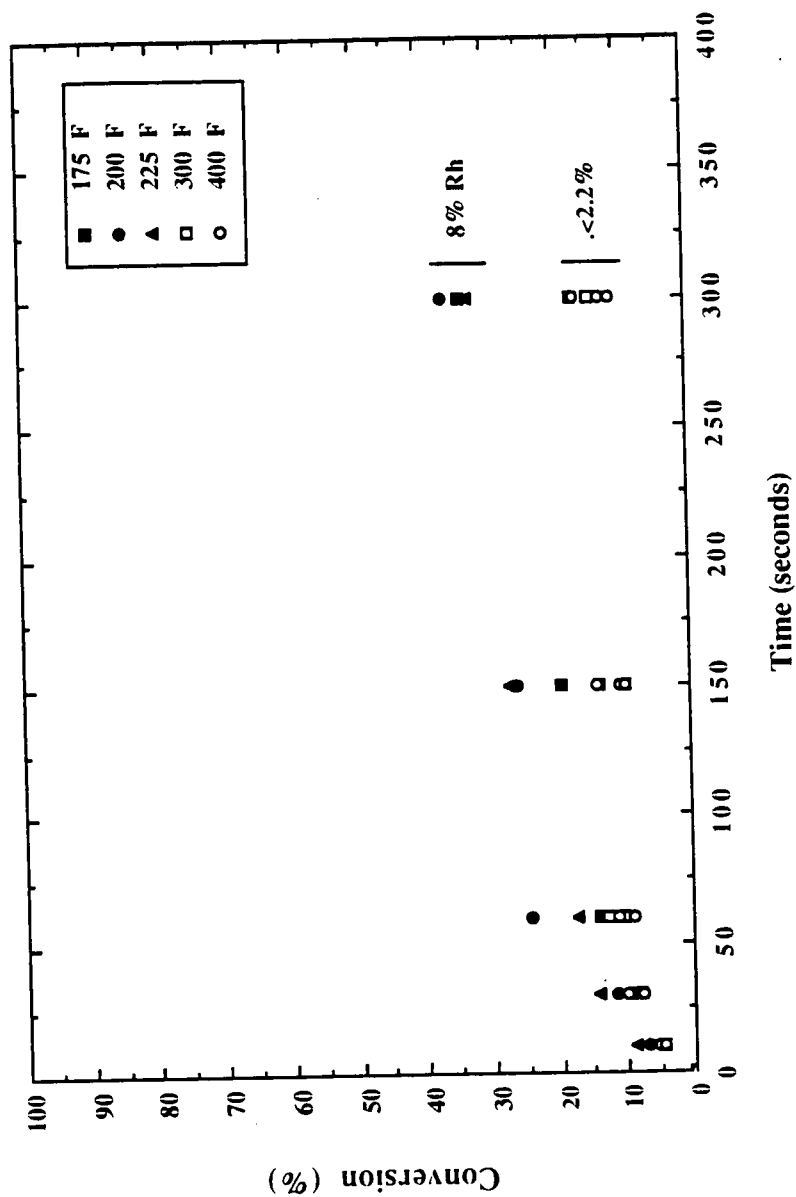


Figure 4.15. Sorbent conversion at 1000 ppmv HCl and relative humidities of 8% and <2.2%.

were also run at 8000 ppmv and 15000 ppmv of hydrogen chloride. The corresponding relative humidities in the test gas were 25%, 15%, 8%, and 2.2% respectively. The results are summarized in Figures 4.16 to 4.19. These figures also include the results of the 1000 ppmv tests described earlier under the moisture tests.

At 175 °F and 25% relative humidity, the hydrated lime achieved complete conversion at all three gas concentrations of 500 ppmv, 1000 ppmv, and 5000 ppmv. However, the time for the complete conversion increased with lower concentration. On the other hand, no significant effect of the gas concentration was observed on the final conversion at 300 °F and 2.2% relative humidity in spite of increasing the gas concentration to 15000 ppmv. A similar trend was observed for the tests at 225 °F between 5000 ppmv and 1000 ppmv gas concentrations. Further, in these lower humidity conditions, most of the conversion occurred within the first 60 seconds of the reaction, after which the reaction seemed to slow down considerably. This is in contrast to the results at 175 °F, 25% RH tests in which the rate of change in conversion was more uniform.

Effect of Lime Surface Area on Conversion

Three tests were run to determine the effect of sorbent surface area on the conversion. Since all three

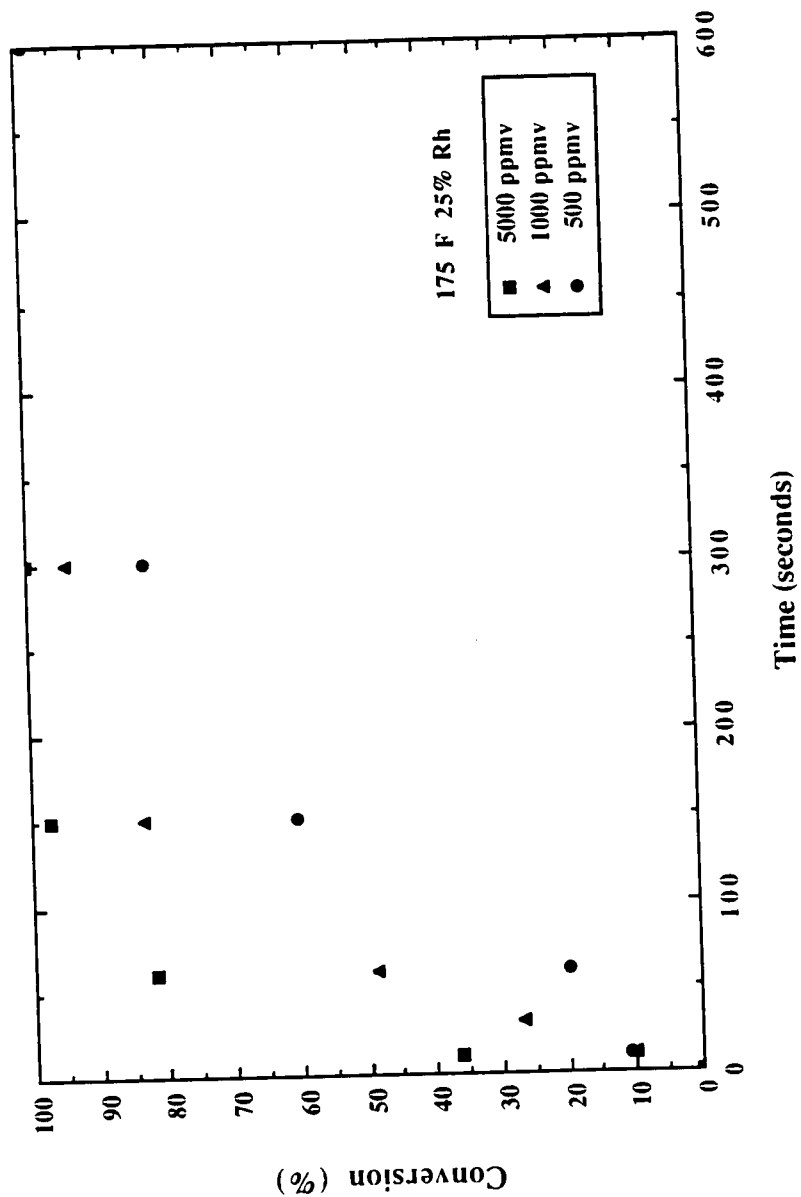


Figure 4.16. Effect of gas concentration on sorbent conversion at 175 F and 25% relative humidity.

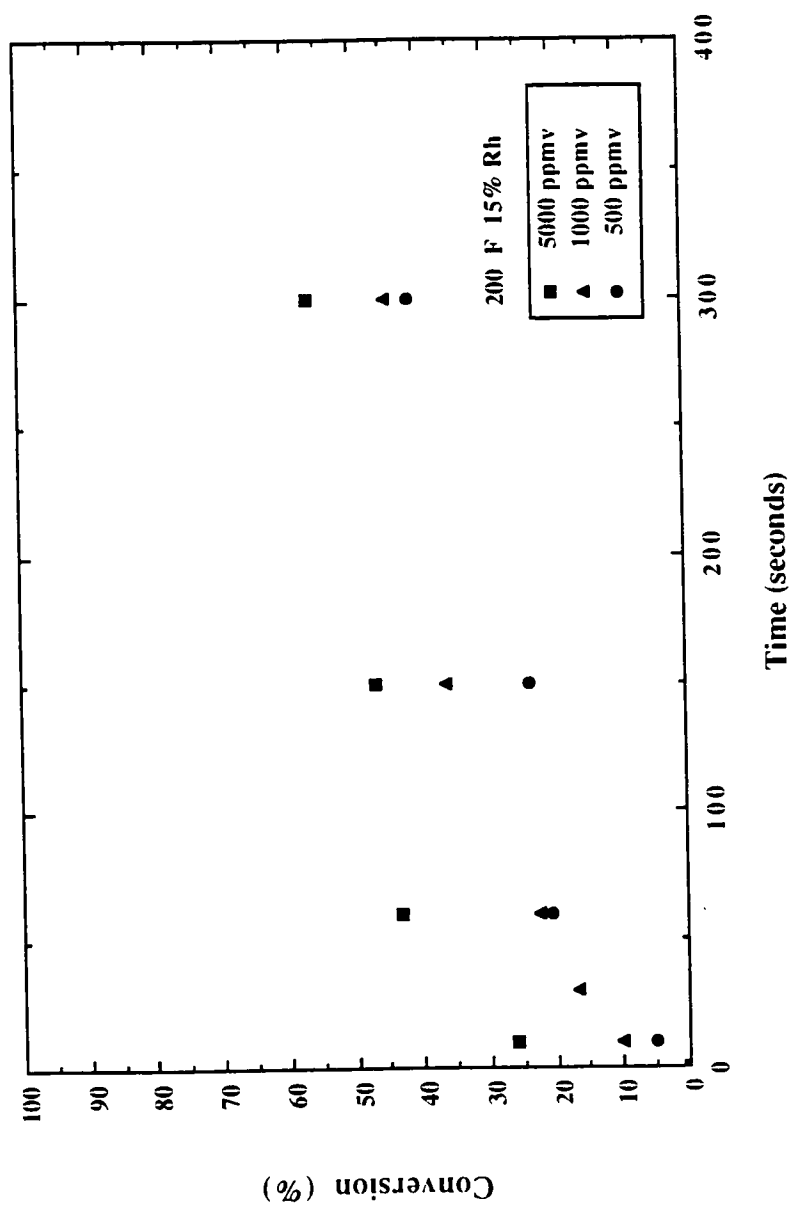


Figure 4.17. Effect of gas concentration on sorbent conversion at 200 F and 15% relative humidity.

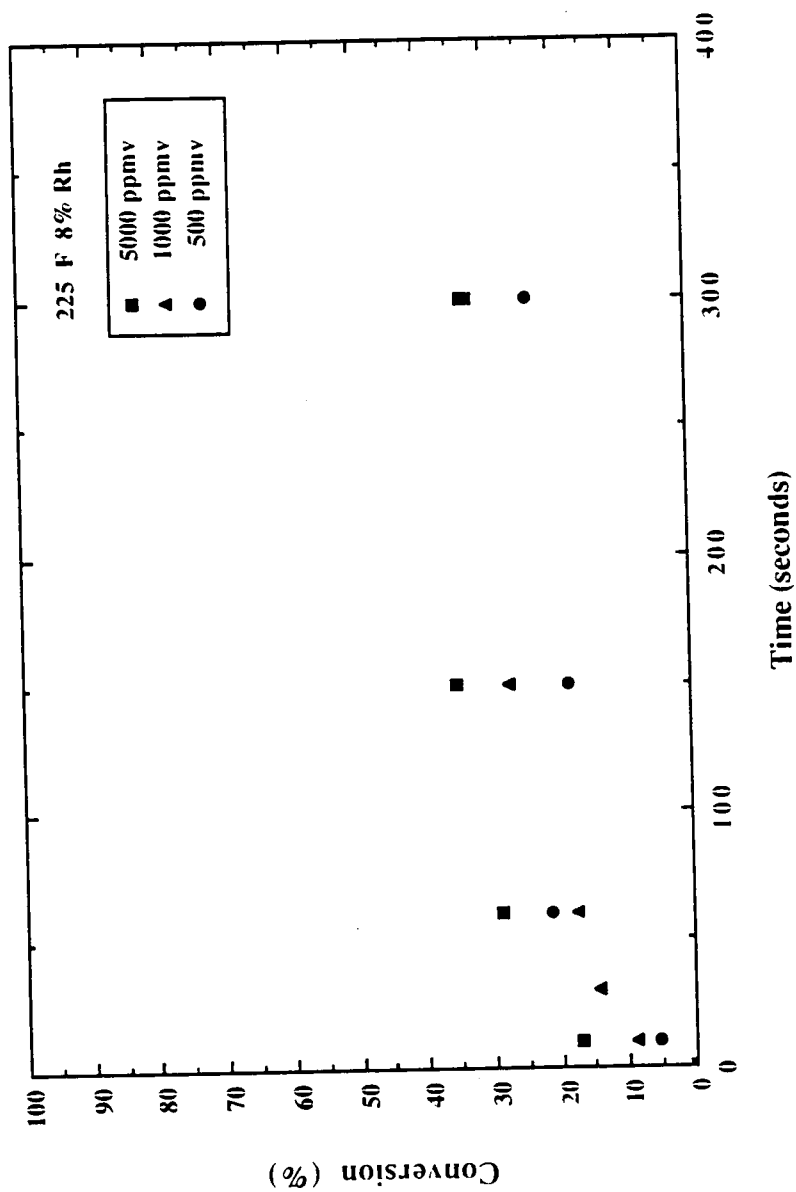


Figure 4.18. Effect of gas concentration on sorbent conversion at 225 F and 8% relative humidity.

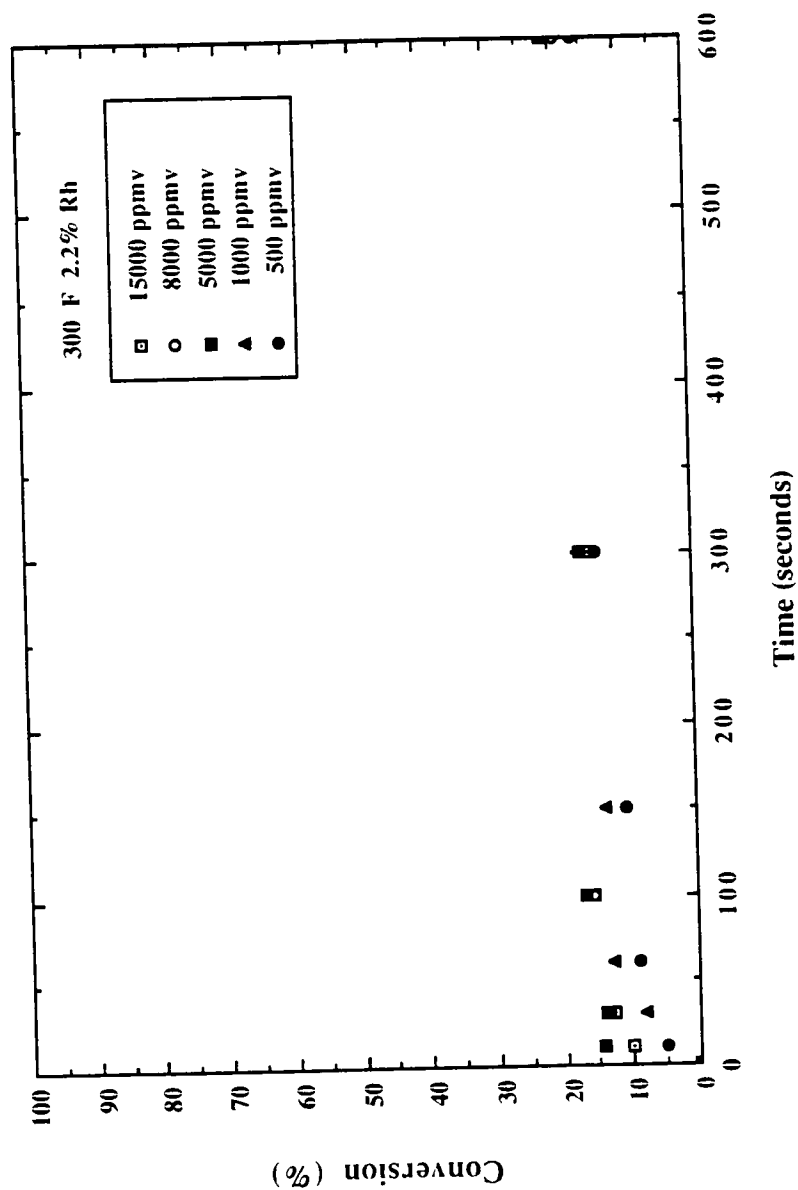


Figure 4.19. Effect of gas concentration on sorbent conversion at 300 F and 2.2% relative humidity.

size fractions of the Tenn Luttrell lime showed similar BET surface area of approximately 18 m²/g, hydrated lime from another source was used to determine the effect of surface area on conversion. This hydrated lime was obtained from "A/S Scansorb". This hydrated lime was expected to have a BET surface area of 35 m²/g as per the manufacturer. However, tests showed that the average BET surface area of this hydrated lime was approximately 26 m²/g.

The tests were run at three conditions: a) 175 °F and 45% relative humidity, b) 225 °F and 8% relative humidity, and c) 400 °F and 0.6% relative humidity. Reaction times were 10 seconds, 30 seconds, 60 seconds, 150 seconds, and 300 seconds. The hydrogen chloride concentration in the gas was 1000 ppmv in all three tests. The results are shown in Figure 4.20, which also includes the results from the tests with Tenn Luttrell hydrated lime for comparison.

With the exception of the highly reactive 175 °F, 45% RH tests, the higher surface area of the scansorb resulted in approximately 15% higher final conversion at both 225 °F and 400 °F. In both these cases, the conversion was not complete and there was a considerable reduction in the rate of conversion after the first 150 seconds of the reaction.

Summary of the Results of the Kinetic Tests

The results of the kinetic tests showed that

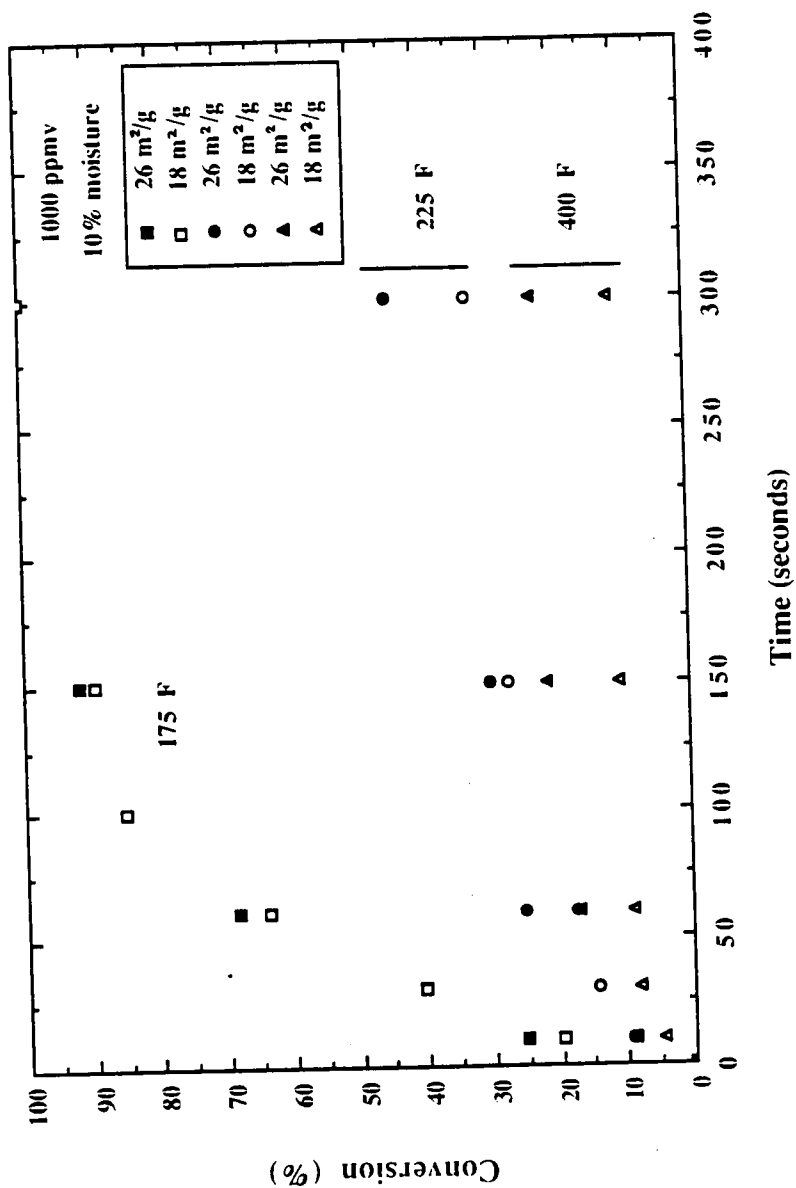


Figure 4.20. Effect of specific surface area on sorbent conversion at 1000 ppmv HCl and 10% moisture.

parameters such as temperature, relative humidity, hydrogen chloride concentration, and lime surface area had different effects on the conversion of the hydrated lime. Increased temperature had a positive effect on conversion in dry hydrogen chloride tests, though the final conversion was low compared to the moist hydrogen chloride tests. Higher relative humidity always resulted in higher conversion of the sorbent at all temperatures. Higher hydrogen chloride concentration increased the conversion significantly at high humidities but practically had no effect on the conversion as the humidity was decreased to approximately 2%. Surface area, on the other hand, significantly increased the final conversion at the lower humidity and higher temperatures but seemed to have no effect at the higher humidity of 45%.

A significant difference was observed also in the rate of change of conversion between high humidity and low humidity tests. In all the high humidity tests, the change in the rate of conversion was gradual with substantial conversion occurring beyond the initial 60 seconds. In the case of low humidity tests, however, a higher percentage of the conversion was achieved during the initial 60 seconds and further conversions were severely limited, thereafter, even at high hydrogen chloride concentrations, resulting in incomplete conversion of the hydrated lime.

4.4 Analysis of the Reaction Product

One of the objectives of this study was to determine the effect of the higher molar volume and hygroscopicity of the reaction product calcium chloride, on the conversion of the sorbent at different test conditions. To meet this objective, seven sorbent conversion tests were carried out. In four of these tests, the pore structure of the reacted sorbent was analyzed to determine the effect of higher molar volume of the calcium chloride on the conversion.

Incomplete conversion of a porous solid reactant can occur due to either pore blockage or high diffusional resistance in the product layer, both of which limit diffusion of the reactant gas to the unreacted core of the solid. Pore blockage can occur if the molar volume of the product is higher than the molar volume of the reactant solid. Depending on the relative rates of chemical reaction and pore diffusion, two forms of pore blockage occur. When the rate of the surface reaction is much higher than the rate of pore diffusion, blockage occurs at the pore mouths openings. In this case, high initial conversion rate is followed by rapid decrease in the rate of conversion and the porosity of the solid reactant. On the other hand, when the rate of pore diffusion is higher than the chemical reaction rate, the reactant gas can penetrate into the depth of the pores and pore blockage occurs in the

whole volume of the pores. The decrease in the initial reaction rate and the porosity of the solid reactant are more gradual in this case. In both cases, the porosity of the reactant solid becomes zero at the time maximum conversion is achieved.

In the case of high rate of pore diffusion, Bhatia and Perlmutter (1981) have noted that the maximum conversion of a porous solid reactant at the time of complete pore blockage can be expressed by

$$X_m = [E_o / (Z-1) (1-E_o)] \quad (4.2)$$

where,

X_m = Maximum conversion of the sorbent

E_o = Initial porosity of the sorbent

Z = Ratio of the molar volume of the
reactant and the product

The reaction between hydrogen chloride and hydrated lime results in the formation of calcium chloride which has a molar volume that is 52% higher than the hydrated lime. Considering an initial porosity of 0.14 for the hydrated lime, as determined from the sorbent characterization tests, the maximum theoretical conversion in case of complete pore blockage should be approximately 32%, based on equation 4.2. Since the low humidity tests showed

maximum conversions close to or less than 32%, it was hypothesized that pore blockage could be the cause of incomplete conversion at these conditions. To check this hypothesis, twelve tests were run in the fixed bed reactor, in which the effects of conversion on the pore structure of the hydrated lime were determined at four different operating conditions. Table 4.4 lists the four operating conditions of these tests. All these tests were run at a hydrogen chloride concentration of 1000 ppmv and at a moisture content of 10% (v/v). The reaction times were selected so that measurable conversion of the sorbent occurred. At least one test was done at each of these four test conditions for sufficiently long time (45 or 60 minutes) to ensure the maximum conversion of the hydrated lime at that test condition.

In these tests, approximately 500 mg of hydrated lime was weighed and then placed on the sample holder over a glass filter bed. This bed of lime was equilibrated at the test conditions for 15 minutes and then exposed to the hydrogen chloride flow for preset times. After these times, the hydrogen chloride flow was stopped, and the hydrated lime without the glass filter was quickly placed inside a preweighed special sample tube which was then weighed and allowed to dry overnight in an oven at 150 °C. The sample was further degassed under vacuum in the surface area analyzer and reweighed. The difference in these two weights

Table 4.4. Brief Operating Conditions of the Product Analyses Tests

Test ID	Temperature (°F)	Moisture content (% v/v)	Relative humidity (%)	Gas concn. (ppmv)	Reaction time (minutes)
TLNM200	200	0	0	1000	10, 20, 60
TL200	200	10	15	1000	10, 20, 60
TL175	175	10	25	1000	5, 15, 45
TL400	400	10	0.6	1000	5, 15, 45
SC200*	200	10	15	1000	10, 20, 60
TLPC200**	200	10	15	1000	10, 60
LICL200	200	10	15	1000	10, 60

- * - Scansorb hydrated lime was used in this test. Tenn Luttrel hydrated lime was used in all other tests.
- ** - The hydrated lime was equilibrated with gas at 50% relative humidity for 15 minutes prior to these tests.
- Detail operating conditions and results are in Appendix 8.1.

was considered as the moisture content of the sample and was expressed as mg of moisture per g of the dry sample. Next the surface area and the pore structure of the reacted sorbent were determined. After these nondestructive analyses, the reacted sorbents were dissolved in 2 liters of IC eluent, filtered, and the filtrates were analyzed for calcium and chloride to determine conversion by the method explained earlier. A summary of the results of these tests is given in Appendix 5.

Figure 4.21 shows the conversion of the sorbent in these tests as a function of time. The results were similar to the results of the earlier kinetic tests and showed higher conversion with higher humidity. The figure shows that in each test condition, the hydrated lime was close to the maximum conversion at the reaction time of 45/60 minutes.

Figure 4.22 shows the maximum conversion of the hydrated lime and the available porosity at this maximum conversion, for different operating conditions. The porosity was calculated from the total pore volume data obtained from the pore size analyzer. The available porosity was defined as the ratio of the porosity of the reacted product to the porosity of the original unreacted hydrated lime, expressed in percentage. The figure shows that in the dry test and low humidity test, a large fraction of the pore volume was still available even when

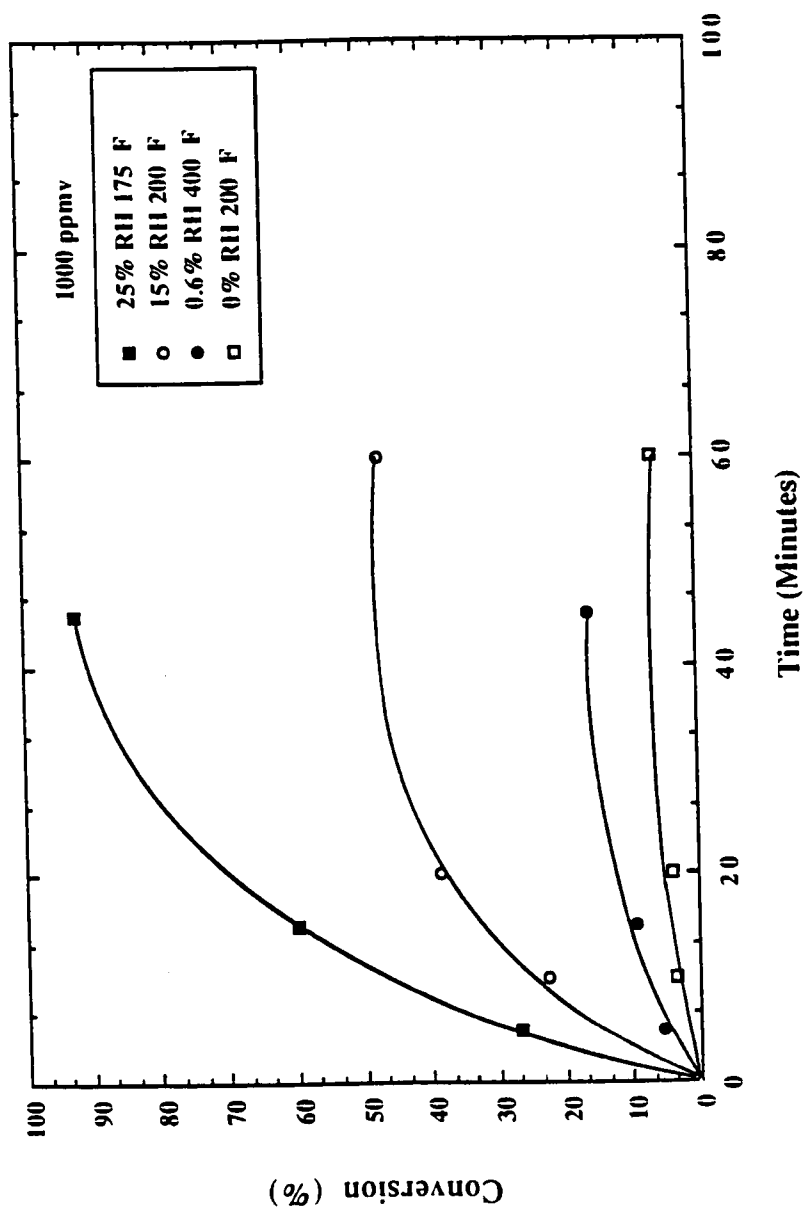


Figure 4.21. Conversion of Hydrated Lime in Product Analysis Tests.

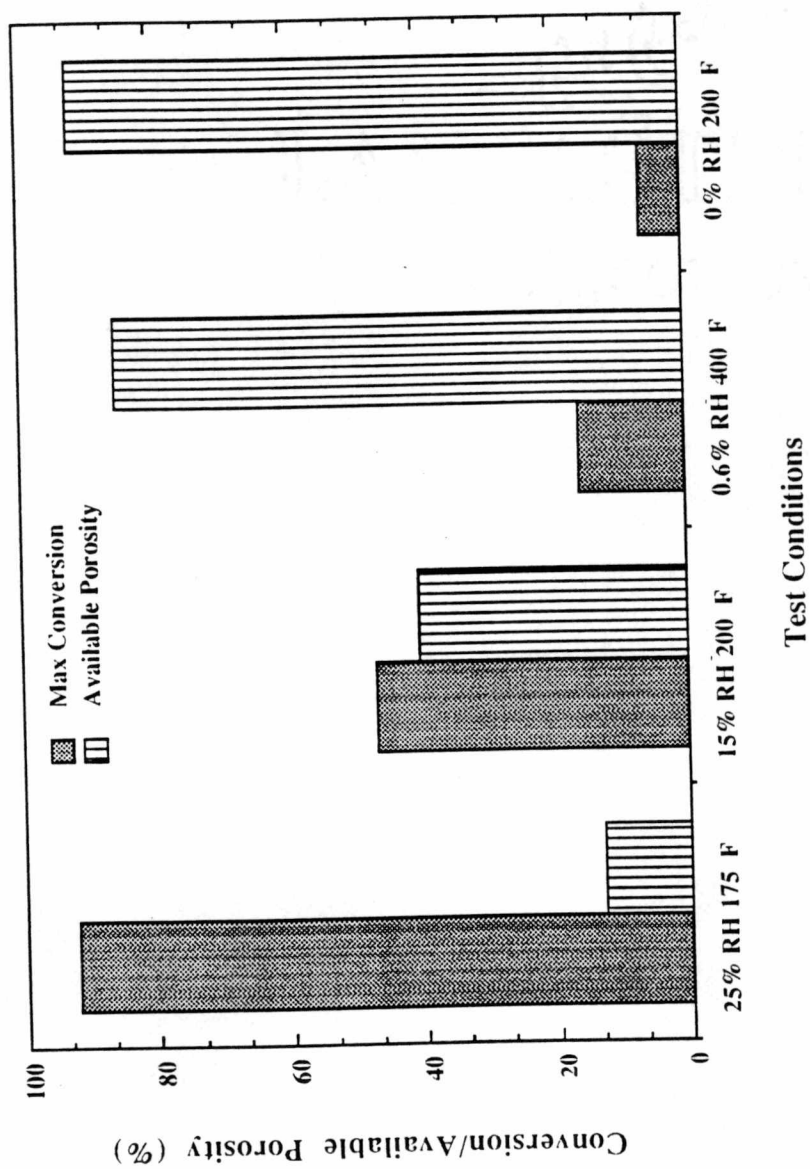


Figure 4.22. Available Porosity at Maximum Conversion.

the final conversions were approached and the reactions was stopped. This suggested that the reaction was not stopped either due to pore mouth closure or pore blockage at these test conditions. One of the possible reasons for incomplete conversion at the low humidity could be the high diffusional resistance of the product layer, which severely restricted the diffusion of the reactant gas to the unreacted core of the solid particles. At the higher humidity of 25%, low porosity occurred at much higher than 32% conversion, the theoretical maximum for the pore blockage hypothesis. Thus, pore blockage did not restrict the conversion at this test condition. At an intermediate relative humidity of 15%, the maximum conversion occurred at approximately 40% residual porosity. Again, pore blockage did not appear to be the primary reason for incomplete conversion.

The change in the pore structure of the hydrated lime with sorbent conversion is also evident in Figures 4.23a and b. These figures show that in both the 25% and 15% relative humidity tests, the pore volume decreased with conversion in all the pore sizes. However, there was preferential filling up of the smaller sized pores, resulting in upward shifts in the average pore diameter.

In the case of pore blockage, the pore area is expected to decrease rapidly with conversion and reduce to nearly zero at the maximum conversion. The effect of

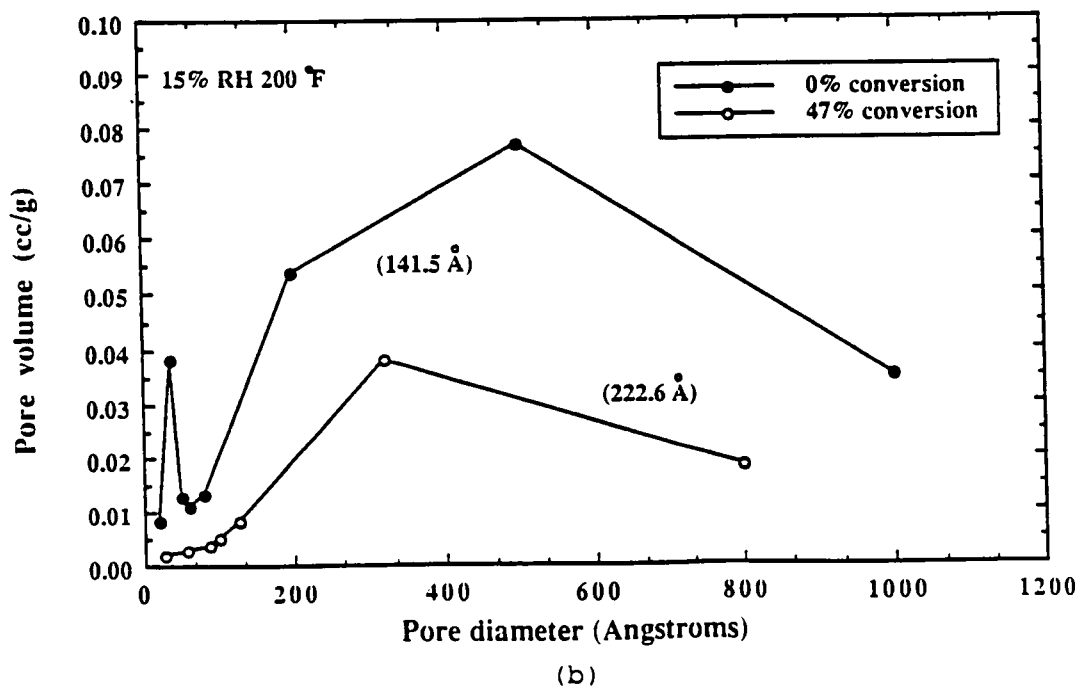
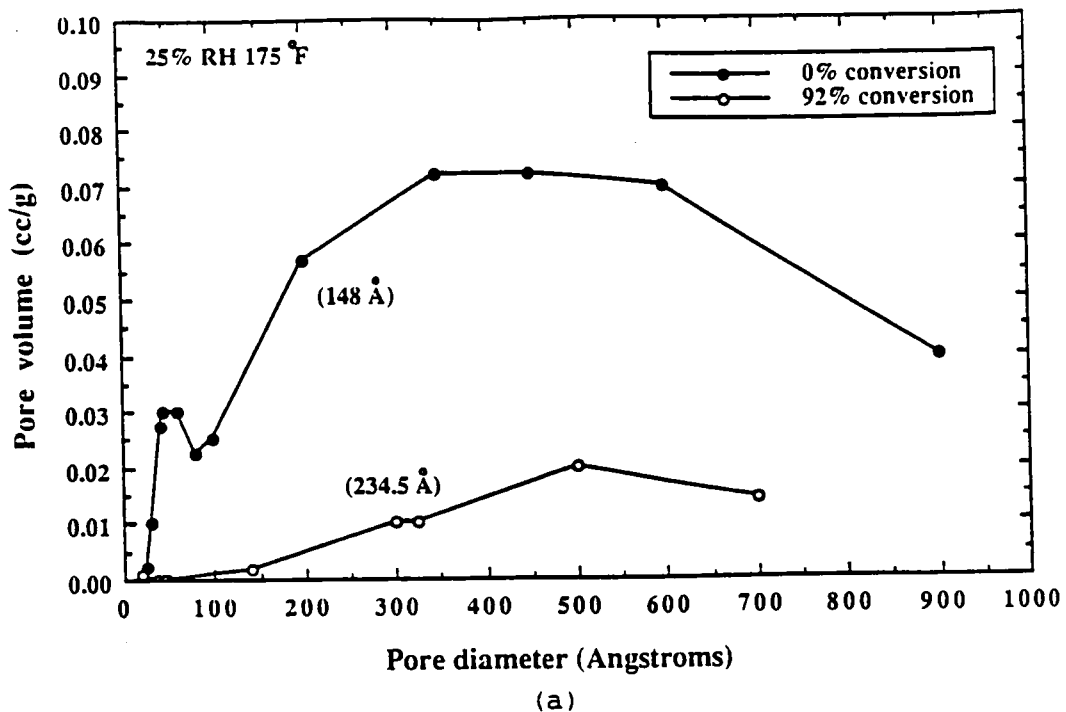


Figure 4.23. Effect of conversion on pore size distribution of hydrated lime at 1000 ppmv HCl.

conversion on the total pore area in these tests was also determined by the Micromeritics surface area and pore size analyzer. The changes in the pore area of the reaction products (determined from the desorption curve by the Brauner Jura and Harkin method) with conversion at different test conditions are shown in Figure 4.24. The available pore areas shown in this figure was the ratio of the pore area of the reaction product to the pore area of the unreacted sample, expressed as a percentage. In the low humidity tests, there was hardly any loss in the pore area at the maximum conversion of sorbent, confirming that pore blockage was not the primary reason for incomplete conversion at these conditions. At higher humidities, there was a significant decrease in available porosity and pore area at higher conversion. However, as mentioned earlier, the conversion in these cases were much higher than the theoretical maximum for the pore blockage hypothesis.

On the basis of these tests, it was concluded that pore blockage was not the primary cause of incomplete conversion of the hydrated lime at any test conditions of this study. Incomplete conversion in the low humidity tests resulted from high diffusional resistance in the calcium chloride product layer. Higher humidity decreased this resistance and at 25% or higher relative humidity, the resistance was decreased to the extent that complete conversion could occur.

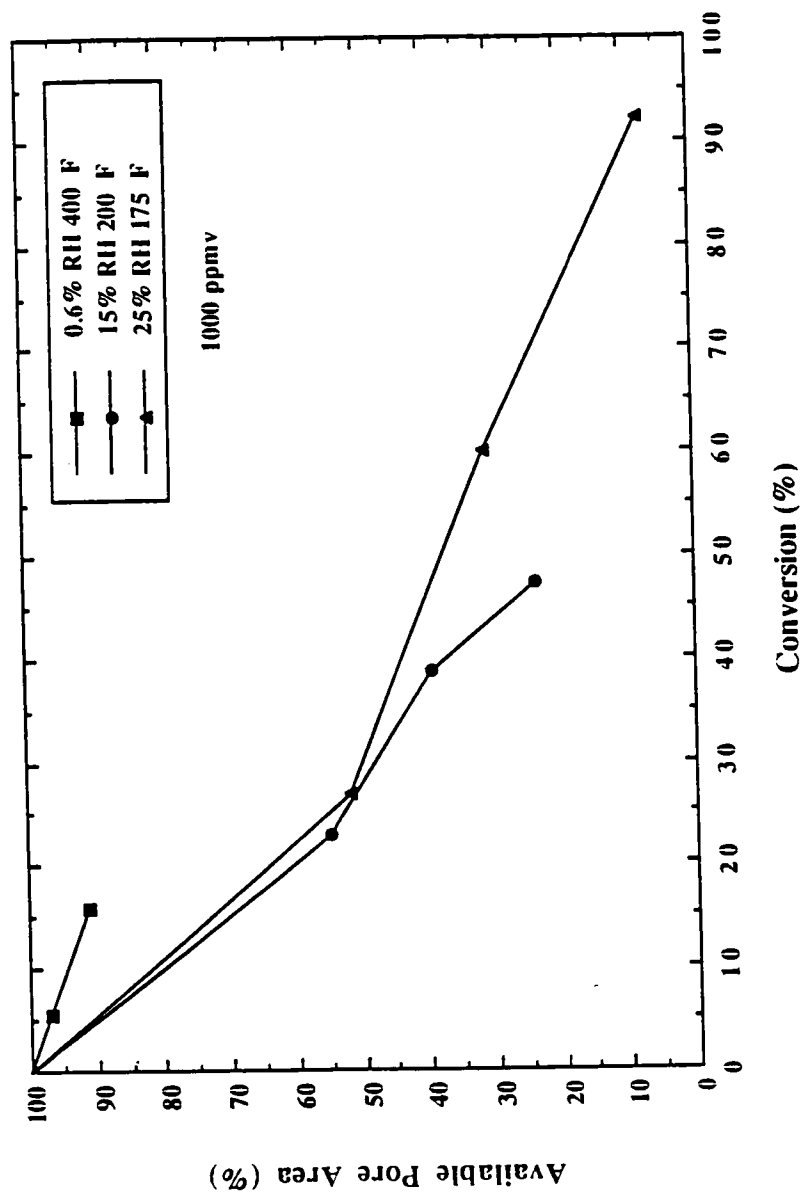
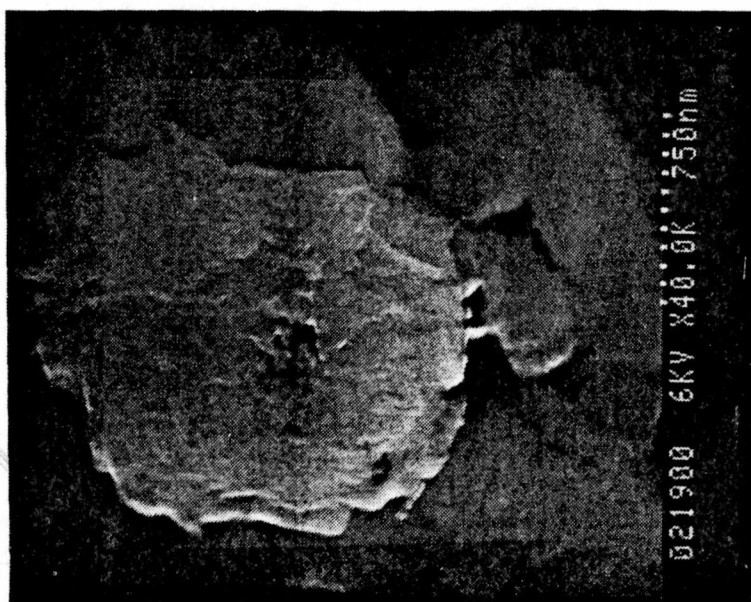


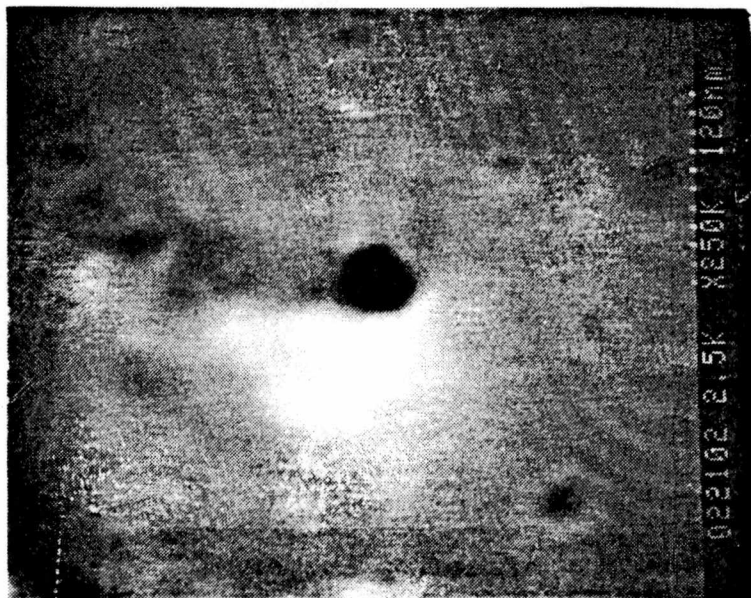
Figure 4.24. Effect of Conversion on Available Pore Area.

The high resistance in the product layer was possibly due to morphological changes occurring during the reaction. This change in surface morphology of the reacted hydrated lime was observed by Scanning Electron Microscopy (SEM). A Hitachi 900 Scanning electron microscope was used for this purpose which allowed magnifications up to 250K. Figures 4.25a and b show two of the typical SEM photographs of the reacted sorbent. These figures clearly show the glass like smooth surface of the product in contrast to the roughness observed in the unreacted product in Figure 4.3. The product also seemed to be more impervious causing the high diffusional resistance mentioned earlier. Figures 4.33 a,b also show some of the unblocked and partially blocked pores in the reaction product.

As shown in Table 2.1, the reaction product i.e. calcium chloride is very hygroscopic and picks up a substantial amount of water from the humid gas. Though data at the test temperatures are not available, calcium chloride is known to be deliquescent at 20% or higher relative humidity at 100 °F (Kirk and Othmer, 1976). It is therefore possible that under the high humidity test conditions in this study, the calcium chloride picked up a substantial amount of water from the humid gas. Both calcium chloride and the reacting hydrogen chloride gas are very soluble in water. Thus, this water in the product layer may affect the morphology of the solid product layer



(a)



(b)

Figure 4.25. SEM Photograph of the Reacted Sorbent.

and enhance the diffusion of the hydrogen chloride to the unreacted core by liquid phase diffusion, which is much faster than the diffusion through the solid phase. This hypothesis would explain the high conversions observed in the high humidity tests in this study.

To check this hypothesis, the moisture content of the unreacted and reacted sorbent were measured by the method mentioned earlier in the description of the product analysis tests. The free moisture content of hydrated lime is estimated to be 1% or lower (Boynton, 1976), which corresponds to 10 mg/g of hydrated lime. The loss in weight of the unreacted and unequilibrated hydrated lime before and after degassing was found to range between 19.3 and 20.2 mg/g. This slightly higher than expected weight loss indicated that the high temperature vacuum degassing might have also removed either some of the bound moisture or other adsorbed materials from the hydrated lime surface. The difference however was considered small compared to the water uptake of the reacted lime as shown later and so, no further corrections were made.

To obtain a baseline, the moisture content of the unreacted, but equilibrated, hydrated lime was determined for all the test conditions. The moisture content of the equilibrated hydrated lime samples was measured in the same manner described above. However, the test gas contained nitrogen and moisture only and no hydrogen chloride. There

was a definite trend of higher moisture in the equilibrated hydrated lime as the humidity in the test gas increased. These moisture contents (measured as the weight loss before and after degassing), are given in Table 4.5 for quick reference. The table also includes the results obtained with unequilibrated, unreacted hydrated lime for comparison.

Figure 4.26 shows the results of the water uptake tests at the various test conditions and conversions. Even from these limited data a clear trend is discernible. At the lowest humidity, there was initially a loss of water as the surface moisture possibly dried during equilibration. Thereafter, there was practically no change in the water content of the sorbent suggesting no uptake of water by the reaction product. The reaction product was therefore very dry at this condition. On the other extreme, at the 25% relative humidity test, there was a significant increase in the water content of the reacted sorbent with conversion and at the maximum conversion of 92%, the water content of the reacted sorbent was approximately 25% by weight. It is possible that the water content of the reacted product at this conversion was even higher than 25%, since complete removal of the reacted sorbent from the glass filter bed could not be achieved due to stickiness of the product. Figure 4.26 also shows that the water content of the sorbent at all stages of conversion was much higher in the

Table 4.5. Moisture Content of Tenn Luttrell Hydrated
Lime at Various Equilibration Conditions

Test condition	Water content (mg/g of sorbent)
Unequilibrated	19.3 - 20.2
Equilibrated	
- at 175 °F, 25% Rh	26.05
- at 200 °F, 50% Rh	32.45
- at 200 °F, 15% Rh	20.30
- at 200 °F, 0% Rh	10.52
- at 400 °F, 0.6% Rh	9.12

- Notes :
1. All equilibrations were for 15 minutes.
 2. Water content was calculated based on weight loss before and after degassing.

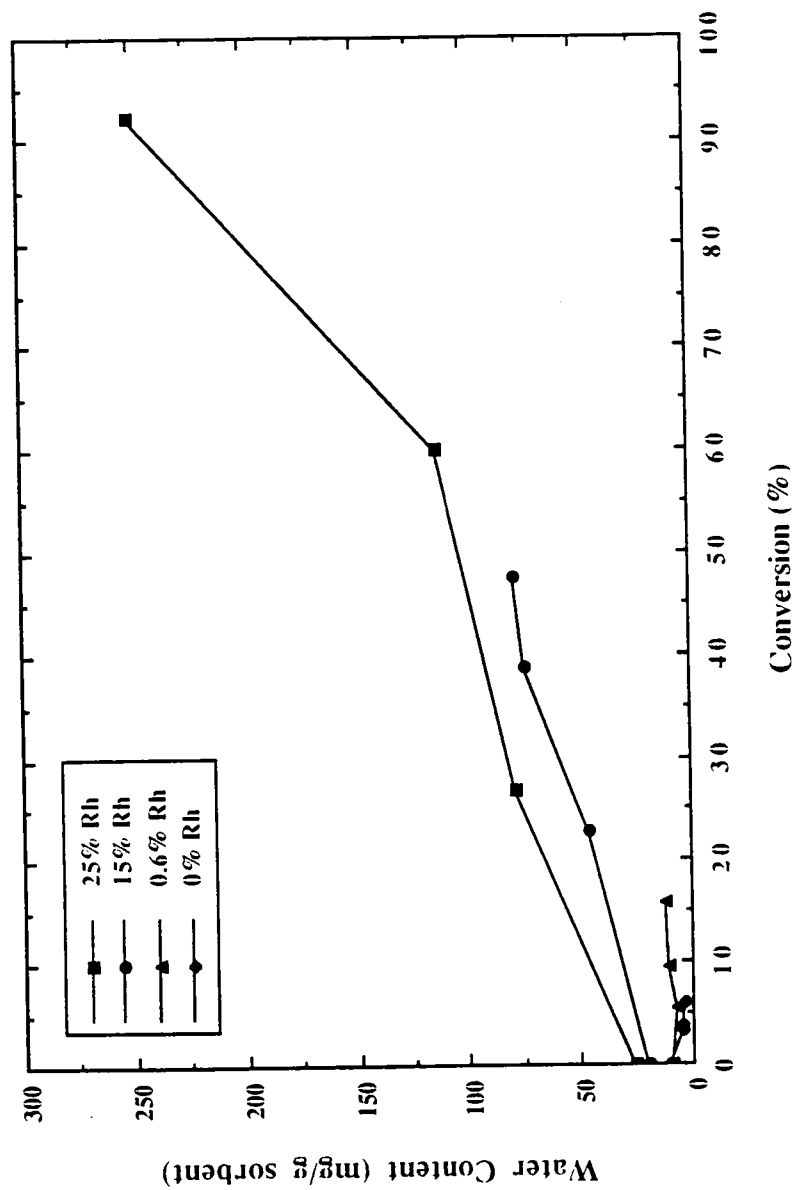


Figure 4.26. Water Content of the Reacted Sorbent at Various Test Conditions.

high humidity test than in the low humidity test.

Based on the above results it can be concluded that the water content of the hygroscopic product layer increases as the humidity of the gas is increased. It is hypothesized that this water alters the morphology of the product layer, and at higher relative humidities in the gas, the diffusion of the hydrogen chloride to the unreacted core takes place through this water phase instead of solid phase. Since the diffusion through the water phase is much faster than through dry solid phase, complete conversion of the sorbent is observed at these higher humidity conditions.

The effect of higher initial moisture content on the rate and extent of conversion was investigated in two additional tests. In one case, preconditioning of the hydrated lime was done by equilibrating the lime with test gas at 50% relative humidity for fifteen minutes to increase the amount of adsorbed water on the external surface. Then the relative humidity of the test gas was quickly (in about 1/2 minute) reduced to the test condition of 15% and hydrogen chloride flow was started to initiate the reaction. In the second case, the hydrated lime was mixed with 20% by weight of lithium chloride. Being highly hygroscopic, lithium chloride was expected to increase the water content in the sorbent even higher, by adsorption from the humid gas. Both these conversion tests were run at

200 °F and 15% relative humidity, and at two reaction times of 10 and 60 minutes. These results were compared with one other method of increasing the conversion i.e. providing increased surface area of sorbent without any preconditioning. For this test, scansorb with BET area of approximately 24-28 m²/g was used.

The results of these tests are shown in Figure 4.27. In the case of the lithium chloride test, the chloride contribution of the lithium chloride was adjusted in the chloride analyses to calculate the actual conversion of hydrated lime. Figure 4.27 also includes the results of similar test run with the Tenn Luttrell hydrated lime without preconditioning (shown earlier in Figure 4.21) for comparison. The initial moisture contents of the sorbents in the different tests are shown within parenthesis in this figure.

The initial conversion at 10 minutes was highest for the scansorb, showing a significant effect of the higher surface area, at this test condition. The lithium chloride also enhanced the initial conversion to some extent. Preconditioning with 50% relative humidity did not result in any substantial improvement in the initial conversion, possibly due to the fact that the additional surface moisture evaporated rapidly when the sorbent was exposed to the test gas at the lower humidity of 15%. This preconditioned hydrated lime also showed no improvement in

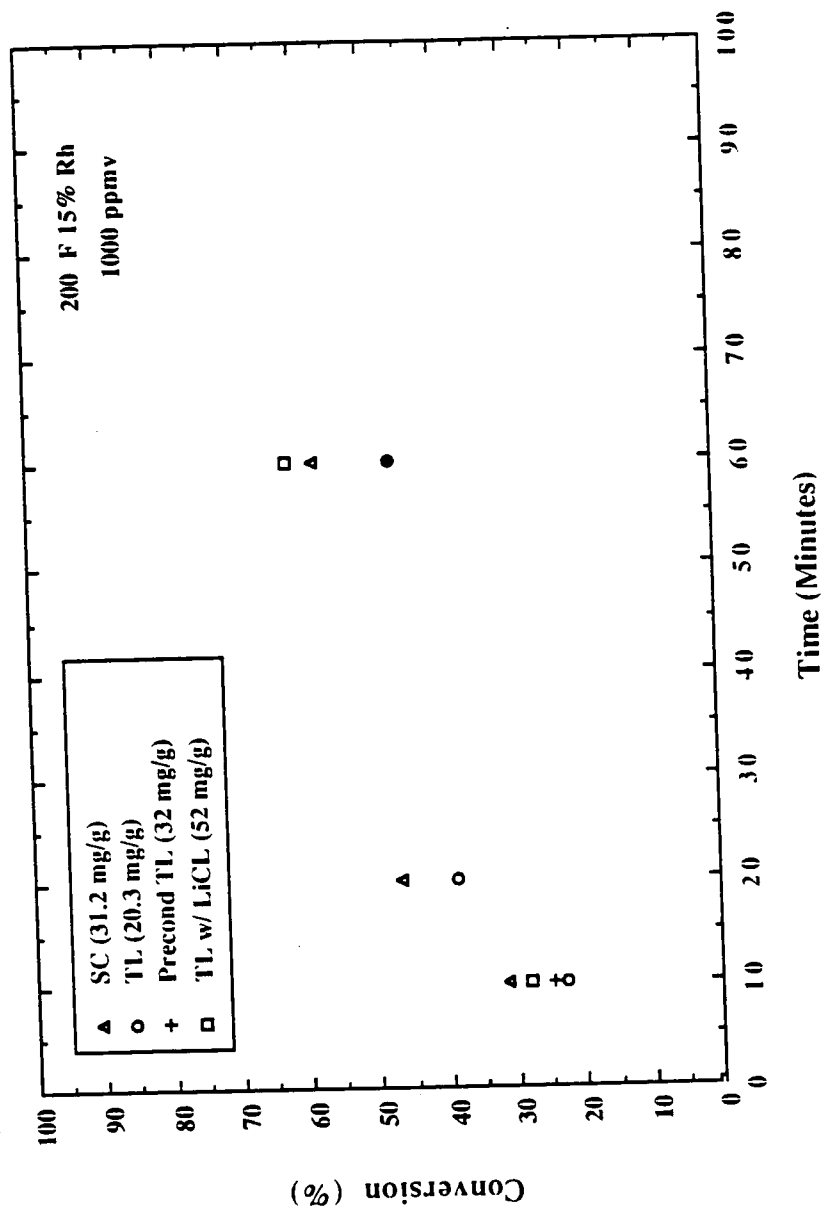


Figure 4.27. Effect of Preconditioning of Hydrated Lime on Conversion.

the final conversion over the regular hydrated lime. The highest final conversion was achieved with the lithium chloride additive. The final conversion of the scansorb was also higher than the regular lime. The data suggested that either a higher surface area or a hygroscopic additive might increase the conversion significantly at this test condition. The effect of preconditioning however, may be different at other temperatures and humidities which needs to be determined through separate tests.

4.5 Application of Gas-solid Reaction Models

The results of this study suggest that resistance of the product layer rather than pore plugging, was the primary reason for the observed incomplete conversions of hydrated lime at lower than 25% relative humidity. None of the pore plugging models currently available, considers the effect of relative humidity of the gas. Moreover, most of the pore plugging models are derived based on cylindrical geometry of the pores. As shown earlier in subsection 4.2, the majority of the pores for hydrated lime are parallel plates or slits, violating the basic assumptions of these models. Thus, the existing pore plugging models can not be used to explain the results of the tests in this study.

One of the more widely used models in gas-solid reactions is the shrinking unreacted core model mentioned

in Section 2 (Literature Survey). Though this model is more appropriate for nonporous spherical particles, it has also been used to model agglomerates of porous particles also, e.g. in the case sulfation of lime and limestone. It was therefore decided to determine the suitability of the shrinking unreacted core model to interpret the results of this study.

The Shrinking Unreacted Core (SUC) model is described in detail in a standard text on gas solid reactions (Levenspiel, 1962, Szekelly et al., 1976). Figure 4.28 shows the basic elements of this conceptual model. The reacting solid is visualized to be comprised of spherical particles, in which the reaction occurs first at the outer surface. With the progress of reaction, the reaction surface moves radially towards the center of the particle, leaving behind a product layer. Thus, at any time during the reaction, there is an unreacted core of material which shrinks in size with the progress of the reaction.

The overall resistance to the reaction at any time is assumed to be comprised of three separate resistances namely, a) the resistance of the gas film on the external surface of the solid limiting the flow of reactant gas from the bulk gas stream to the external surface of the solid, b) the resistance of the solid product layer on the surface of the solid reactant, and c) the resistance to the chemical reaction at the surface of the unreacted solid.

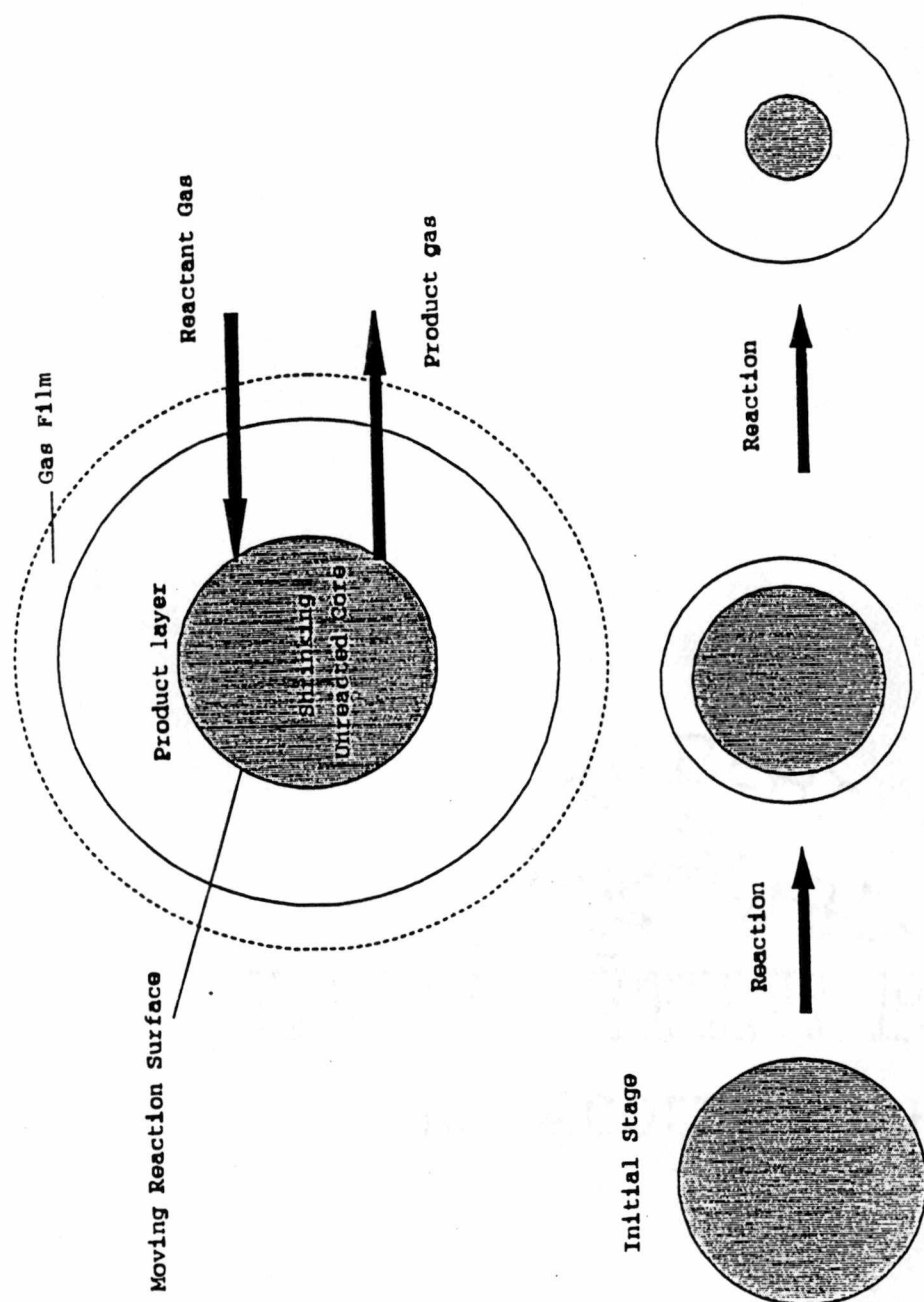


Figure 4.28. Conceptual Model of the Shrinking Unreacted Core.

Kinetic expressions, based on a mass balance, have been derived when one or the other of these resistances control the overall rate of reaction. Gas phase diffusional resistances are not considered to be the rate limiting mechanism in this study due to the high gas velocity and small particle sizes used. Further, Itaya (1989) showed that the chemical kinetics was not the rate determining step in this reaction at temperatures between 340 °F and 450 °F and relative humidities of 4.2% and 1.2%. At lower temperatures and higher humidities, the rate of the reaction is greatly enhanced as observed from the results of this study, further reducing the possibility that the reaction was being controlled by chemical kinetics. Based on the above, the results of this study were checked with the predictions of the shrinking unreacted core model in which the product layer diffusion controlled the overall rate of reaction.

The expressions relating the conversion with reaction time for this condition (Levenspiel, 1962), are as follows:

$$[1 - 3(1 - X)^{(2/3)} + 2(1 - X)] = \tau_d t \quad (4.3)$$

$$\tau_d = 6bD_e C_g / (\rho_b R_p^2) \quad (4.4)$$

where,

t = Reaction time (seconds)

X = Conversion of sorbent

ρ_B = Molal density of sorbent (moles/m³)

R_p = Radius of the sorbent particle (m)

b = Moles of sorbent consumed per mole of the
gaseous reactant as per the stoichiometry of
the reaction

D_e = Effective diffusivity of the reactant gas in
the sorbent (m²/sec)

C_g = Molal concentration of reactant gas
(moles/m³)

The appropriateness of the model for a particular gas-solid reaction is determined by plotting the left hand side of the Equation 4.3 calculated from experimentally determined conversion "X" with reaction time "t". A straight line plot suggests a perfect fit of the model. The values of τ_a is obtained from the slope of this line. The effective diffusivity " D_e " can then be estimated using equation 4.4, since values of other parameters are known. The shrinking core model assumes that this effective diffusivity " D_e " remains constant at all times during the reaction.

Figures 4.29 shows the such a plot for the tests at relative humidity of 25%. The experimental data in this test show some deviation from a straight line suggesting that the effective diffusivity may be changing as the reaction progresses. As seen in this figure, the slope is

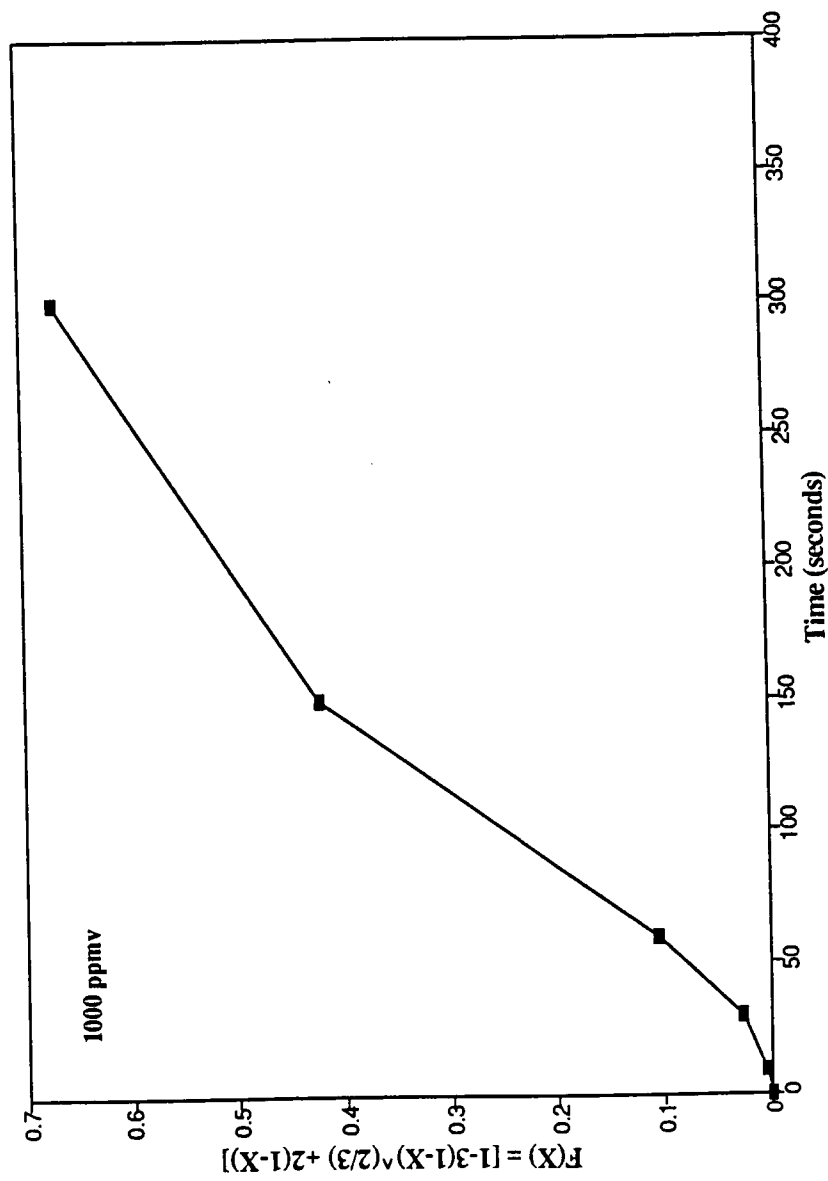


Figure 4.29. $F(X)$ versus Time Plot at Relative Humidity of 25% and 175 F.

initially small and then increases significantly between 30 and 150 seconds. From equation 4.4, and assuming the shrinking core model to be valid, the slope of the curve at any point is a measure of the effective diffusivity of the product layer at that time. Thus in the 25% relative humidity, the diffusivity of the product layer initially increases with the progress of the reaction. This trend in the data can be explained by the hygroscopic nature of the reaction product. With the progress of the reaction, the hygroscopic calcium chloride adsorbs water from the humid gas and as mentioned earlier, the diffusion of the hydrogen chloride to the unreacted core takes place through this wet phase, which results in higher effective diffusivity of the product layer. Figure 4.30 shows the predictions of the shrinking core model and the experimental conversion at the test condition of 25% relative humidity. The model prediction was based on an average effective diffusivity " $(D_e)_{AVG}$ ", considered to be constant at all the reaction times for this test condition. This effective diffusivity was estimated from the slope of the best fit straight line thorough the experimental data shown in Figure 4.29. The effective diffusivity calculated in this manner for this test condition was found to be $4.22E-13 \text{ m}^2/\text{sec}$. Figure 4.30 shows that in spite of the changes in the effective diffusivity with reaction time, the model predicted the experimental conversions reasonably well.

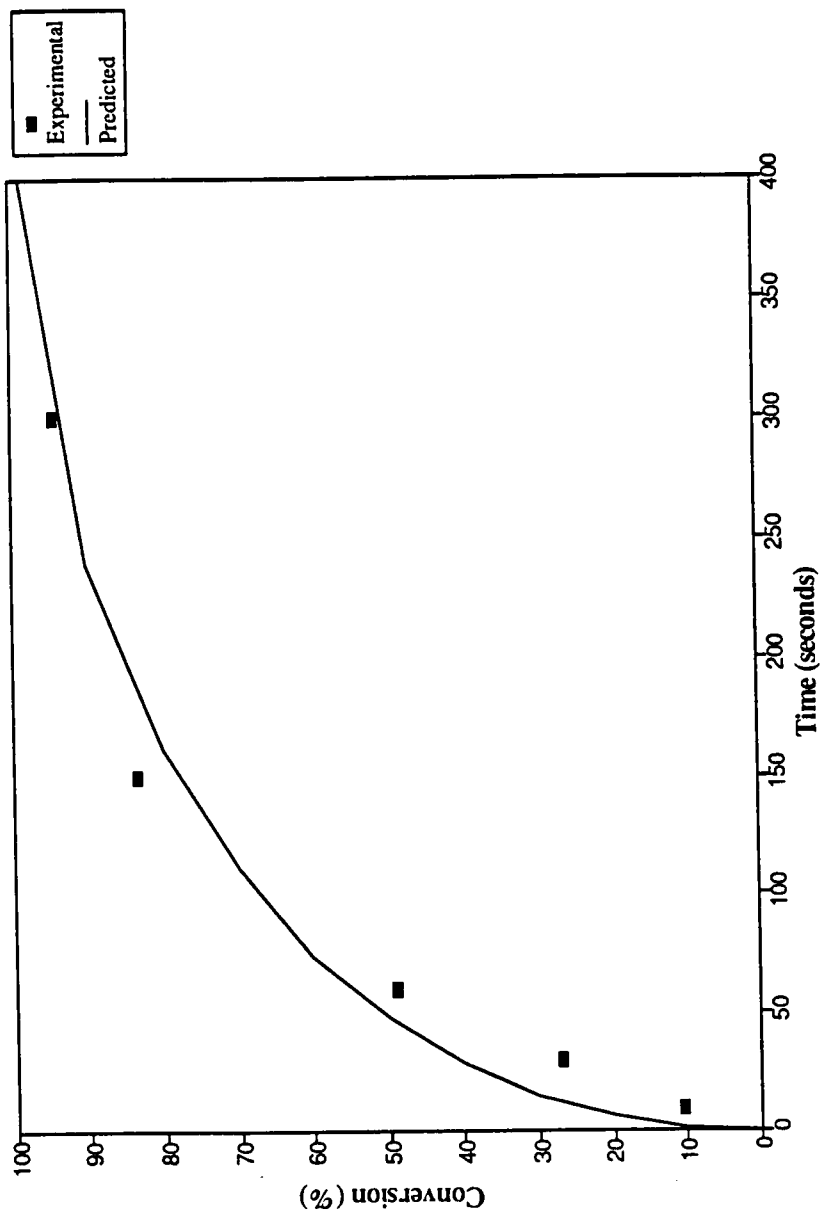


Figure 4.30. Shrinking Core Model Predicted Conversions and Experimental Conversions at 25% Relative Humidity and 175 F.

One significant drawback in applying this model to the results of the tests below 25% relative humidity is the inability of the shrinking unreacted core model to account the incomplete conversion of the sorbent. The model assumes that reaction progresses until the conversion of the solid reactant is complete. Theoretically, all sorbents will finally achieve complete conversion after an infinite reaction time, regardless of the value of the effective diffusivity. However, within practical time limits, the results of this study show that the conversion of the sorbent will be incomplete for the tests below 25% relative humidity. Jozewicz (1990) showed similar incomplete conversion after one hour of reaction time. Karlsson (1981) showed such incomplete conversion in some tests even after 10 hours of reaction times. This incomplete conversion of the sorbent indicates that the effective diffusivity of the sorbent decreases with conversion and a stage is reached when the solid state resistance is high enough to prevent transport of the reactant gas to the unreacted core. This aspect of the reaction is not accounted for by the shrinking core model which assumes constant effective diffusivity throughout the reaction time.

This limitation of the model is further illustrated in Figure 4.31, which shows the plot of $[1 - 3(1 - X)^{(2/3)} + 2(1 - X)]$ versus the reaction time "t", for the test condition of 0.6% relative humidity at 400 °F. The slope of the plot

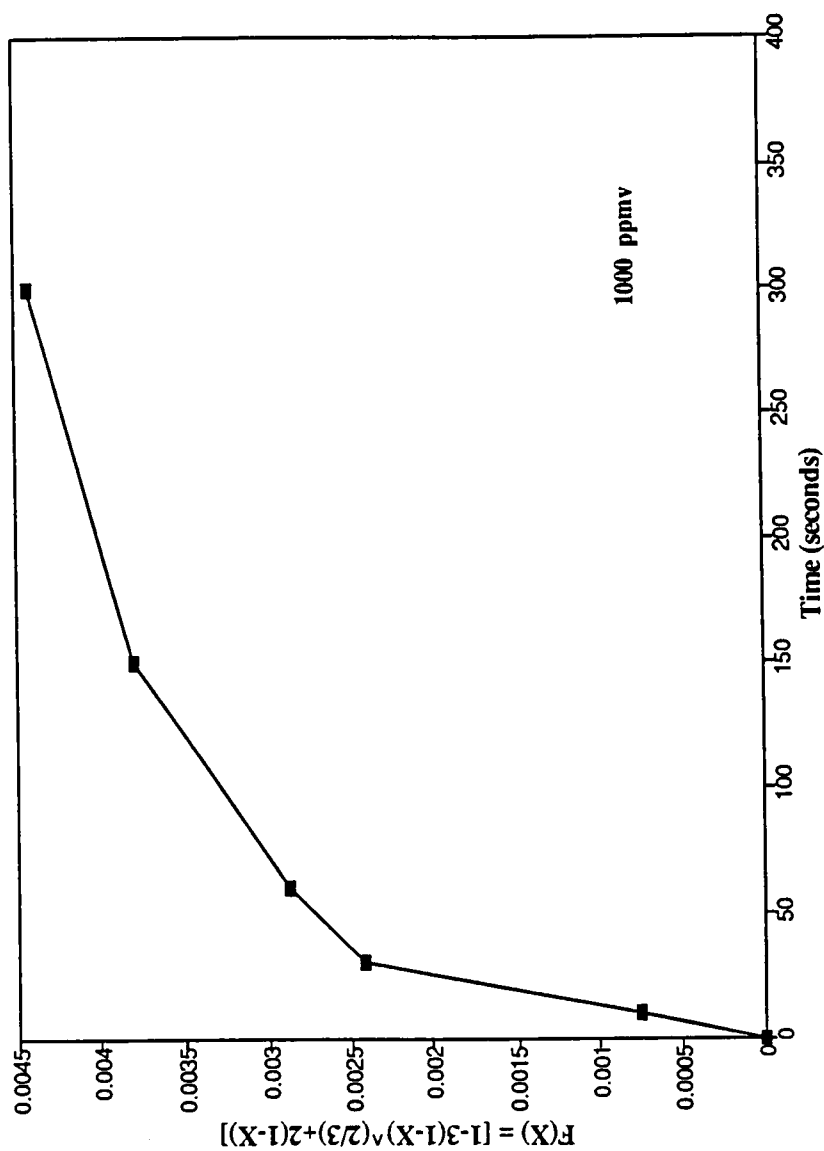


Figure 4.31. F(X) versus Time Plot at 0.6% Relative Humidity and 400 F.

and thus the effective diffusivity is high in the initial stage of the reaction and rapidly decreases to a very low value as the reaction progress, possibly due to structural changes occurring in the product layer. One possible reason for this structural change is the expansion of the particle due to higher molar volume of the product. The impervious structure of the dry calcium chloride is probably the other reason for this low diffusivity. Thus in this case, as shown in Figure 4.32., the predictions of the model (based on a constant average diffusivity as mentioned earlier) is poor compared to the predictions at the test condition of 25% relative humidity. In the case of the tests showing incomplete conversion, i.e. tests at relative humidities of less than 25%, the model predictions become worse with longer reaction times. This is evident from Figure 4.33, which shows the conversions predicted by the model and expected conversions based on extrapolation of experimental data for the tests at less than 25% relative humidity and at one hour reaction time. The above analysis clearly suggests that while the shrinking unreacted core model may be applicable for tests which showed complete conversion, it is not appropriate for the tests in which incomplete conversion of the sorbent was observed.

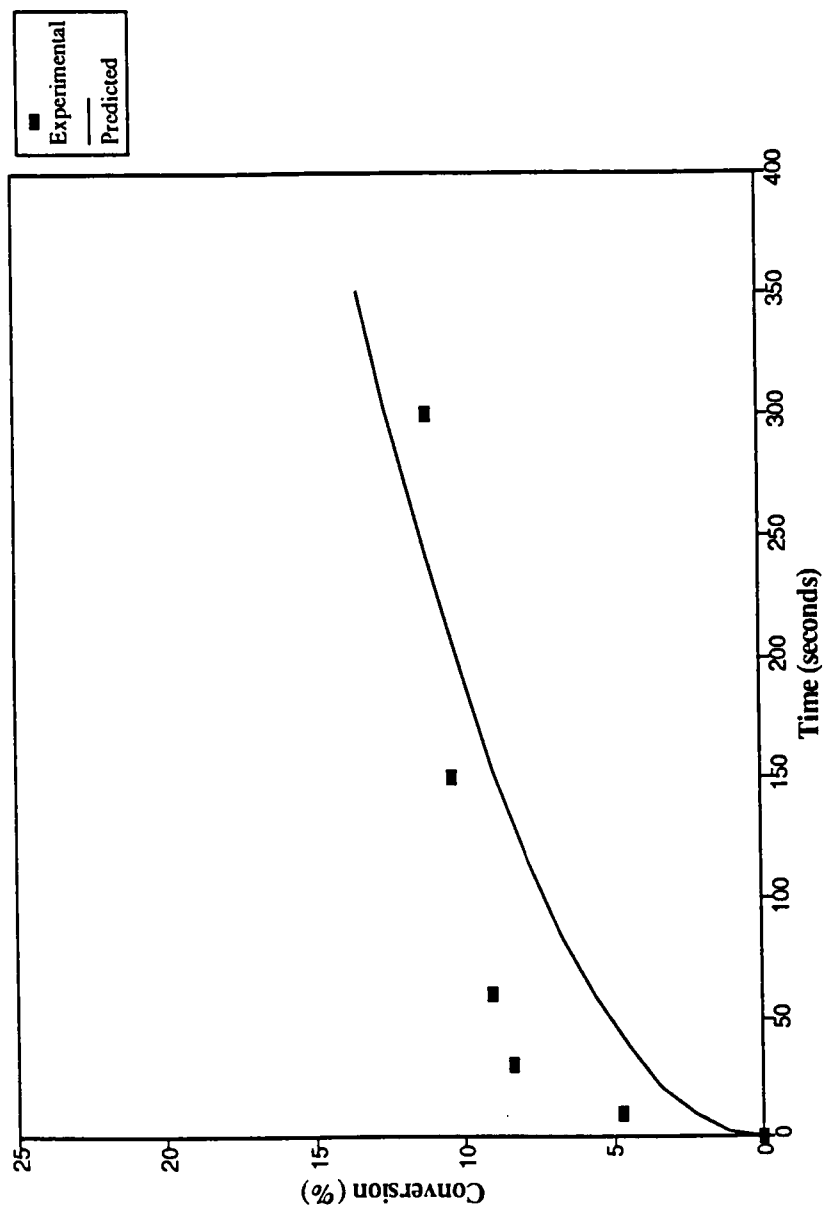


Figure 4.32. Shrinking Core Model Predicted Conversions and Experimental Conversions at 0.6% RH and 400 F.

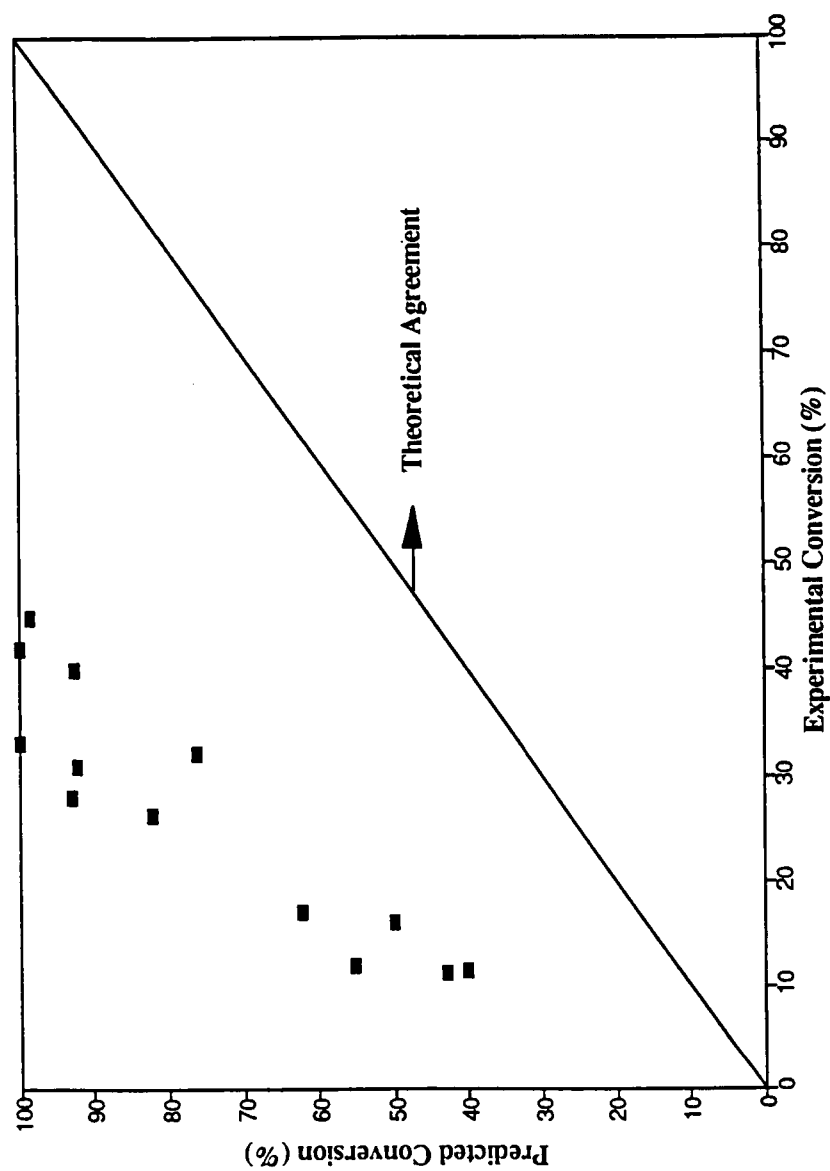


Figure 4.33. Comparison of Experimental Conversion with Conversion Predicted by Shrinking Core Model for Tests at < 25% Relative Humidity.

CHAPTER 5

DEVELOPMENT OF AN EMPIRICAL MODEL

The foregoing discussions showed that existing gas solid reaction models could not be applied directly to this particular reaction, since these models did not account for either the effect of relative humidity of the gas on the rate of conversion of the sorbent or the incomplete conversion of the sorbent. Therefore, a first generation empirical model was developed based on the experimental data of this study. The model was based on a simplified rate equation for gas solid reaction. The key parameters of this rate equation were then correlated with the relative humidity of the gas by empirical equations derived from non linear curve fit of the experimental data.

5.1 Conceptual Model

The reaction was assumed to be initiated on the external surface of the reacting particle. At that time the rate of the reaction was assumed to be determined by the chemical kinetics, since no product layer existed. This initial rate of reaction based on the external surface area of the solid can be expressed as (Levenspiel, 1976)

$$r_a(o) = (1/S_e) d(N_a) / dt = KC_g^n \quad (5.1)$$

where,

$r_a(o)$ = Initial rate of reaction (moles/m²-sec)

S_e = External surface area of the hydrated
lime (m²)

N_a = Moles of hydrogen chloride consumed
(moles)

t = Time (sec)

K = Reaction rate constant

C_g = Gas phase concentration of the hydrogen
chloride (moles/m³)

n = Order of the reaction

The reaction rate constant "K" can be expressed by an Arrhenius type equation as follows :

$$K = A_o[\exp(-E/RT)] \quad (5.2)$$

where,

A_o = Frequency factor

E = Activation energy of the reaction (cal/mole)

R = Universal gas constant (cal/mole-°K)

T = Reaction temperature (°K)

With the progress of the reaction, the diffusion

through the solid product layer was assumed to become the controlling mechanism for the reaction. This resistance through the product layer progressively decreased the initial reaction rate and after a certain time the reaction rate was practically zero thereby stopping further conversion. This was reflected by the experimental conversion versus time plots shown in Figures 4.5 to 4.8, which showed that the maximum conversion was achieved at or before reaction time of 300 seconds.

In this model, this effect of the product layer on the rate of reaction is empirically expressed as an exponential decay term related to the initial reaction rate as follows:

$$r_a(t) = r_a(0) \cdot \exp(-t/t_c) \quad (5.3)$$

where,

$r_a(t)$ = Reaction rate at any time "t"

$r_a(0)$ = Initial reaction rate i.e. at "t" = 0

t = Reaction time (seconds)

t_c = An empirical time constant describing the decrease in the rate of reaction for the particular test condition (seconds)

Lee and Georgakis (1981), and Ronblaad (1984) used similar expressions to model the experimentally observed decrease in reaction rate for sulfation of lime.

Combining equations 5.1, 5.2 and 5.3, the rate of reaction at any time can be expressed as

$$r_a(t) = [A_o \cdot \exp(-E/RT) \cdot C_g^n] \cdot [\exp(-t/t_c)] \quad (5.4)$$

The key parameters describing the reaction rate in this equation are " A_o ", " E ", " n ", and " t_c ". The experimental data were used to derive empirical equations correlating these parameters with the relative humidity of the tests. The reaction rate at any time " t " was obtained from the experimental data on conversion of the sorbent. The moles of hydrogen chloride reacted at any time was related to the conversion at that time by the stoichiometry of the reaction. Thus,

$$N_a = bXN_{Ca(OH)_2} \quad (5.5)$$

where,

N_a = Moles of hydrogen chloride consumed in the reaction at time " t " (moles)

X = Conversion of hydrated lime at time " t "

b = Moles of hydrogen Chloride reacted per mole of hydrated lime i.e. stoichiometry of the reaction (2 for this reaction).

$N_{Ca(OH)_2}$ = Moles of hydrated lime used in the test

Therefore, the rate of reaction at time "t" was related to the rate of conversion by the following equation

$$\begin{aligned} r_a(t) &= [(1/S_e) (dN_a/dt)_t] \\ &= [(1/S_e) (dX/dt)_t bN_{Ca(OH)_2}] \end{aligned} \quad (5.6)$$

The rate of conversion at any time was obtained by determining the time derivative of the best fit empirical equations of experimental kinetic test data, mentioned in section 4.3 earlier. Since the amount of the hydrated lime used, and the surface area of the hydrated lime were known, the reaction rate at any time, " $r_a(t)$ ", was determined by equation 5.6. The initial reaction rate was calculated by using the value of the initial conversion rate " $(dX/dt)_0$ ".

Reaction Order

The effect of the relative humidity on the order of the reaction was first determined. The experimental data for gas concentrations of 500 ppmv, 1000 ppmv, and 5000 ppmv at 25%, 15%, 8% and 2.2% relative humidities were used for this purpose. Taking natural log on both sides of equation 5.1,

$$\ln[(r_a(0))] = \ln(K) + n \ln(C_g) \quad (5.7)$$

Thus, the order of the reaction was obtained from the slope of the linear regression line at the different relative humidities. Figure 5.1 shows the effect of the relative humidity on the order of the reaction. The best fit equation describing the effect of the relative humidity on the order of the reaction from a nonlinear curve fit of the data was

$$n = 0.2 + 0.7[1 - \exp(-RH/11)] \quad (5.8)$$

Frequency Factor and Activation Energy

In the next step, the effect of relative humidity on the frequency factor and the activation energy were determined. Using the values of reaction order "n" from equation 5.8, and the initial reaction rate, the reaction rate constant "K" for any test condition was determined by rearranging equation 5.1,

$$K = [(r_a(o)/C_g^n)] \quad (5.9)$$

Taking the natural log of equation 5.2,

$$\ln(K) = \ln(A_o) + (-E/R) (1/T) \quad (5.10)$$

The natural log of "K" was plotted with the inverse of the temperature. The frequency factor "A_o" and the

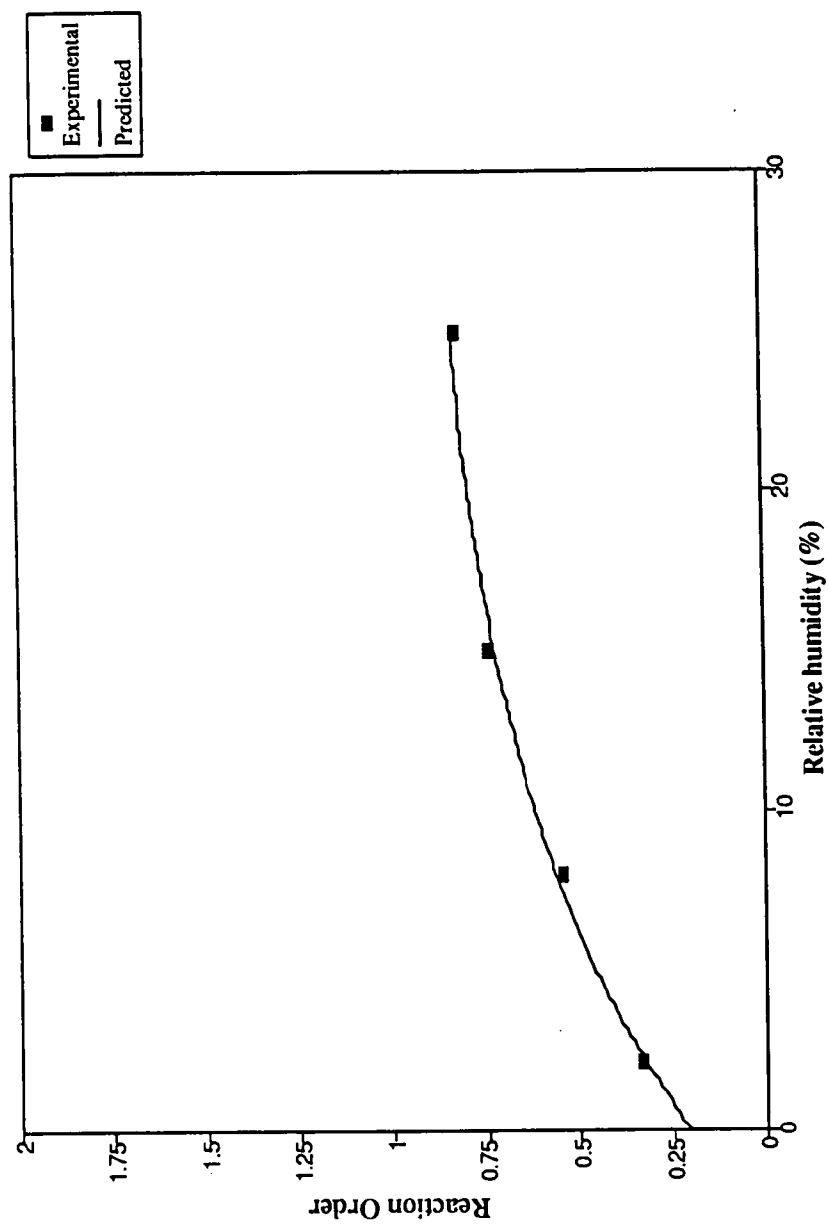


Figure 5.1. Effect of Relative Humidity on Reaction Order

activation energy "E" of the reaction were then determined from the intercept and the slope of the linear regression line. Table 5.1 shows the results of the linear regression lines at relative humidities of 25%, 15%, 8%. Figures 5.2 and 5.3 shows the effect of relative humidity on the frequency factor and the activation energy. The best fit equation describing these effects were found to be

$$A_0 = (-0.004) + 5.45e-3[\exp(-24253RH)] + 8.61e-2[\exp(-0.12RH)] \quad (5.11)$$

$$E = 5648.6 - 77RH - 5.18RH^2 \quad (5.12)$$

It was found that the empirical equation for the activation energy could not be adequately extrapolated to the lower humidities. The extrapolated value of activation energy at 0% relative humidity from the equation was found to be 5650 cal/mole as compared to the experimentally obtained value of 8602 cal/mole. It is believed that the effect of relative humidity on the conversion at these high temperature, low humidity conditions is different than at higher humidities due to the hygroscopic nature of the product. Thus a different relationship between relative humidity and activation energy was sought for these higher temperature lower humidity conditions.

For those tests below 5% relative humidity, a

Table 5.1. Frequency Factor " A_0 " and Activation Energy " E " obtained from the Initial Reaction Rate Constant and Temperature.

RH (%)	$\ln(A_0)$	A_0	E/R	E (cal/mole)	r
25	-7.5494	$5.3e-4$	245.0	486.8	0.953
15	-4.5407	$106e-4$	1674.9	3328.0	0.997
8	-3.5227	$295e-4$	2366.2	4701.7	0.979
0	-2.4353	$876e-4$	4329.3	8602.3	0.910

Notes :

1. The frequency factor and the activation energy were determined from the linear regression of initial reaction rate constant " $\ln(K)$ " and inverse of absolute temperature " $(1/T)$ ".
2. Value of Universal gas constant " R " was taken as 1.987 cal/mole.
3. " r " gives the values of regression coefficient.

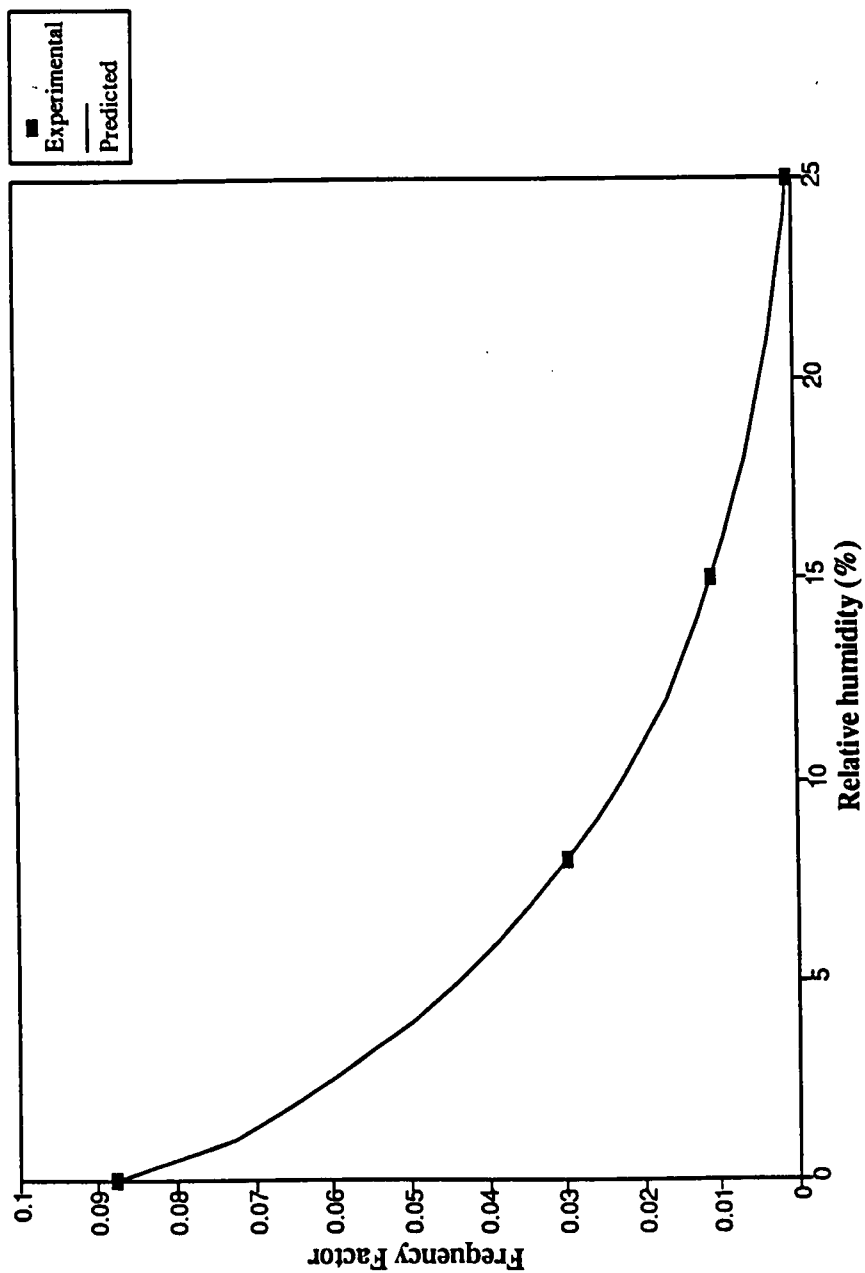


Figure 5.2. Effect of Relative Humidity on Frequency Factor.

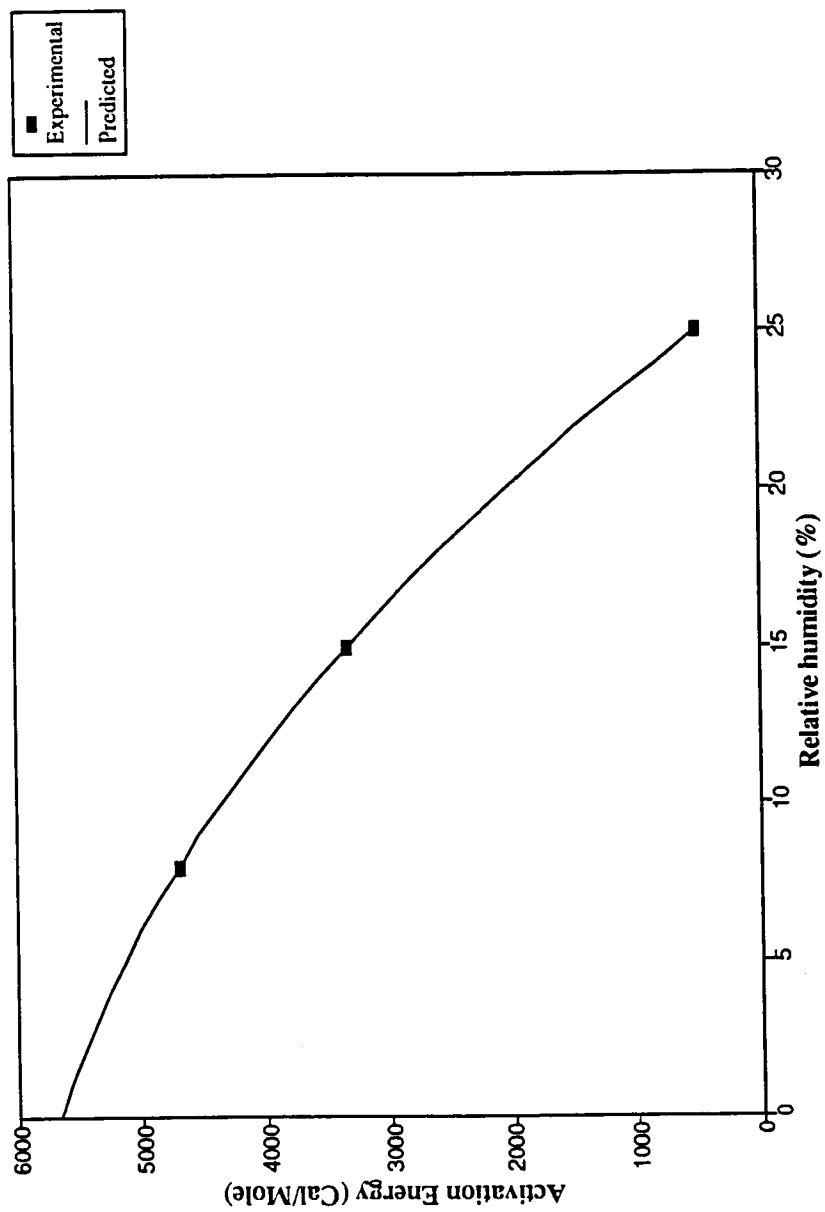


Figure 5.3. Effect of Relative Humidity on Activation Energy in >5% Relative Humidity Tests.

different approach was used to determine the correlation between relative humidity and the activation energy, since enough test data were not available to pursue the above approach. In these cases, the values of "K" and "A_o" were first determined from equations 5.9 and 5.11. The activation energy "E" was then calculated using equation 5.2 for each test condition. Figure 5.4 shows the effect of relative humidity on the activation energy at these test conditions. The best fit equation is

$$E = 8797 - 966RH + 814RH^2 \quad (5.13)$$

Time Constant

The correlation of "t_c" with the relative humidity was next determined. Taking the natural log of equation 5.3 , then

$$\ln[r_a(t)] = \ln[r_a(o)] - t/t_c \quad (5.14)$$

For a particular test, the value of the reaction rate "r_a(t)" at any time "t" was determined from the best fit equation to the experimental conversion data as described above. The value of the "t_c" for that particular test was then determined from the slope of the plot of "ln[r_a(t)]" and "t". Table 5.2 gives the experimentally obtained values of "r_a(o)" and "t_c" for all the test conditions.

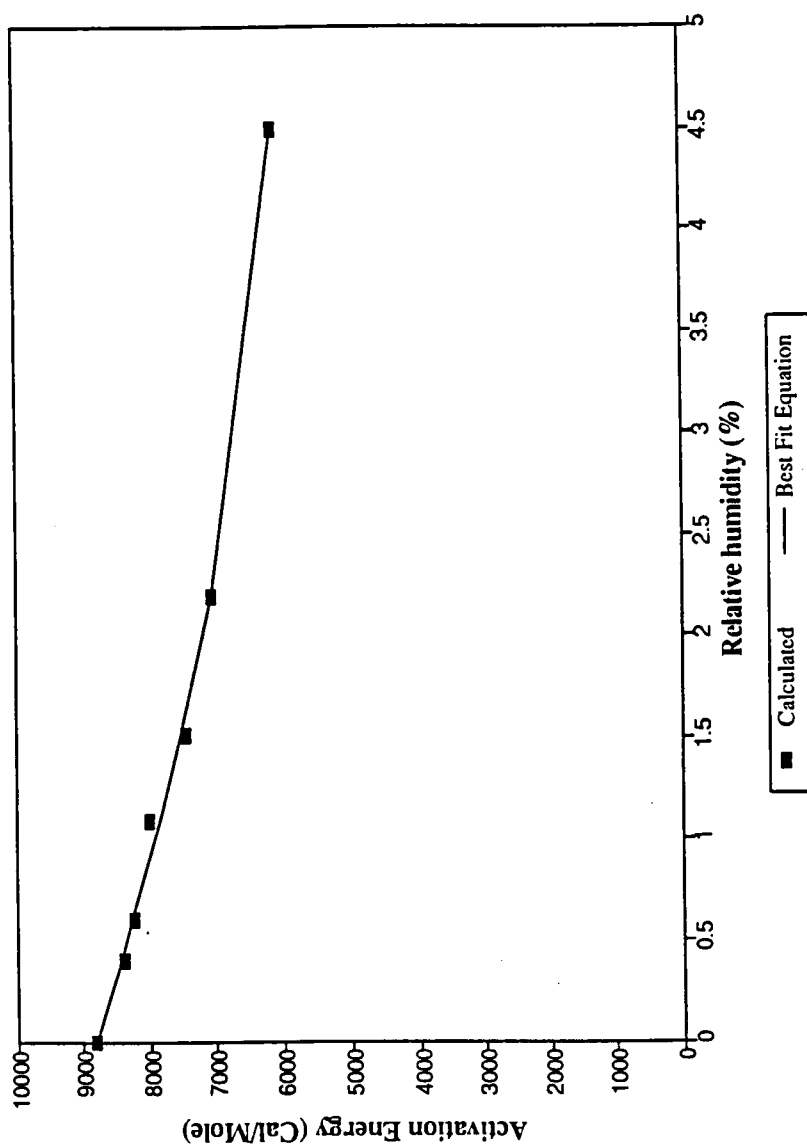


Figure 5.4. Effect of Relative Humidity on Activation Energy in <5% Relative Humidity Tests.

Table 5.2. Initial Reaction Rate " $r_a(o)$ " and time Constant " t_c " at Different Test Conditions.

Test ID	GC (ppmv)	RH (%)	RXT (°F)	$r_a(o)$ (moles/m ² -sec)	t_c (sec)
T11	1000	25	225	1.59e-05	97
T12	1000	25	200	1.63e-05	83
T13	1000	25	175	1.61e-05	93
T14	1000	15	175	8.12e-06	61
T15	1000	8	175	5.61e-06	75
T16	1000	15	200	1.09e-05	88
T17	1000	15	200	9.65e-06	70
T18	1000	8	200	6.49e-06	88
T19	1000	8	225	8.78e-06	53
T20	1000	6	225	8.55e-06	46
T21	1000	4.5	300	6.86e-06	70
T22	1000	2.2	300	4.35e-06	57
T23	1000	1.5	300	3.40e-06	53
T24	1000	1.1	400	6.01e-06	40
T26	1000	0.6	400	5.61e-06	30
T27	1000	0.4	400	4.93e-06	25
M13	500	25	175	8.83e-06	165
M17	500	15	200	4.86e-06	140
M19	500	8	225	6.13e-06	60
M22	500	2.2	300	4.56e-06	50
H13	5000	25	175	5.89e-05	25
H17	5000	15	200	2.79e-05	28
H19	5000	8	225	2.13e-05	23
H22_3	5000	2.2	300	1.02e-05	25

RH - Relative Humidity
GC - Gas Concentration
 t_c - Time Constant

RXT - Reaction Temperature
 $r_a(o)$ - Initial Reaction Rate

Since the time constant would also be affected by the hygroscopicity of the product, a correlation with relative humidity was obtained by using different equations for a) 8% to 25% RH and b) <5% RH as follows:

$$a) \quad t_c = 61 + 1.1RH \quad (5.15)$$

$$b) \quad t_c = 15.1 + 27.6RH - 3.45RH^2 \quad (5.16)$$

Figures 5.5 and 5.6 show the effect of relative humidity on the time constant at the various humidities.

The gas concentration affected the time constant differently depending on the relative humidity of the test. Between the gas concentration of 500 ppmv to 5000 ppmv, the following empirical equation was found to correlate reasonably well the effect of gas concentration on the time constant :

$$t_c = K_c \cdot C_g^{-n} \quad (5.17)$$

where,

K_c = An arbitrary constant

n = Reaction Order

C_g = Gas concentration

Similar expression was used by Lee and Georgakis (1981) to describe the effect of gas concentration on the time constant for the sulfation of lime.

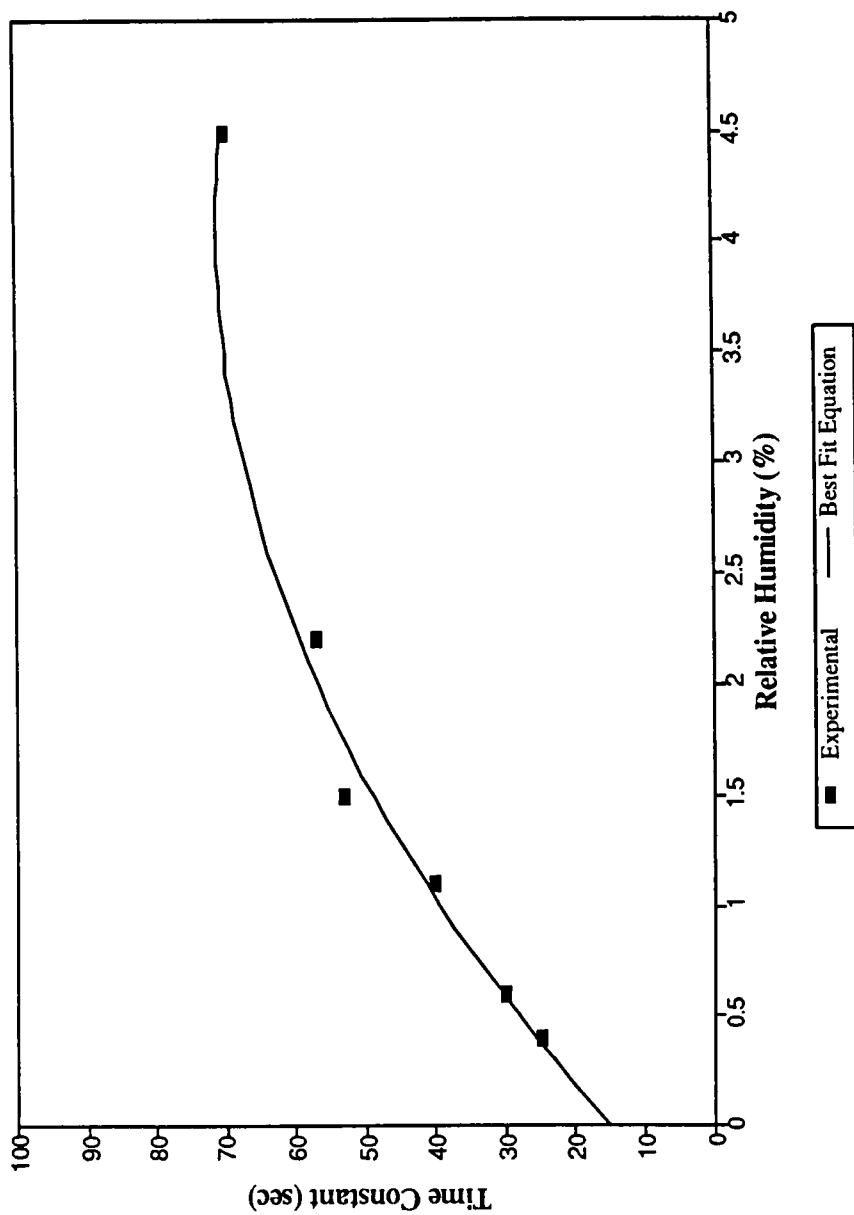


Figure 5.5. Effect of Relative Humidity on Time Constant in <5% Relative Humidity Tests.

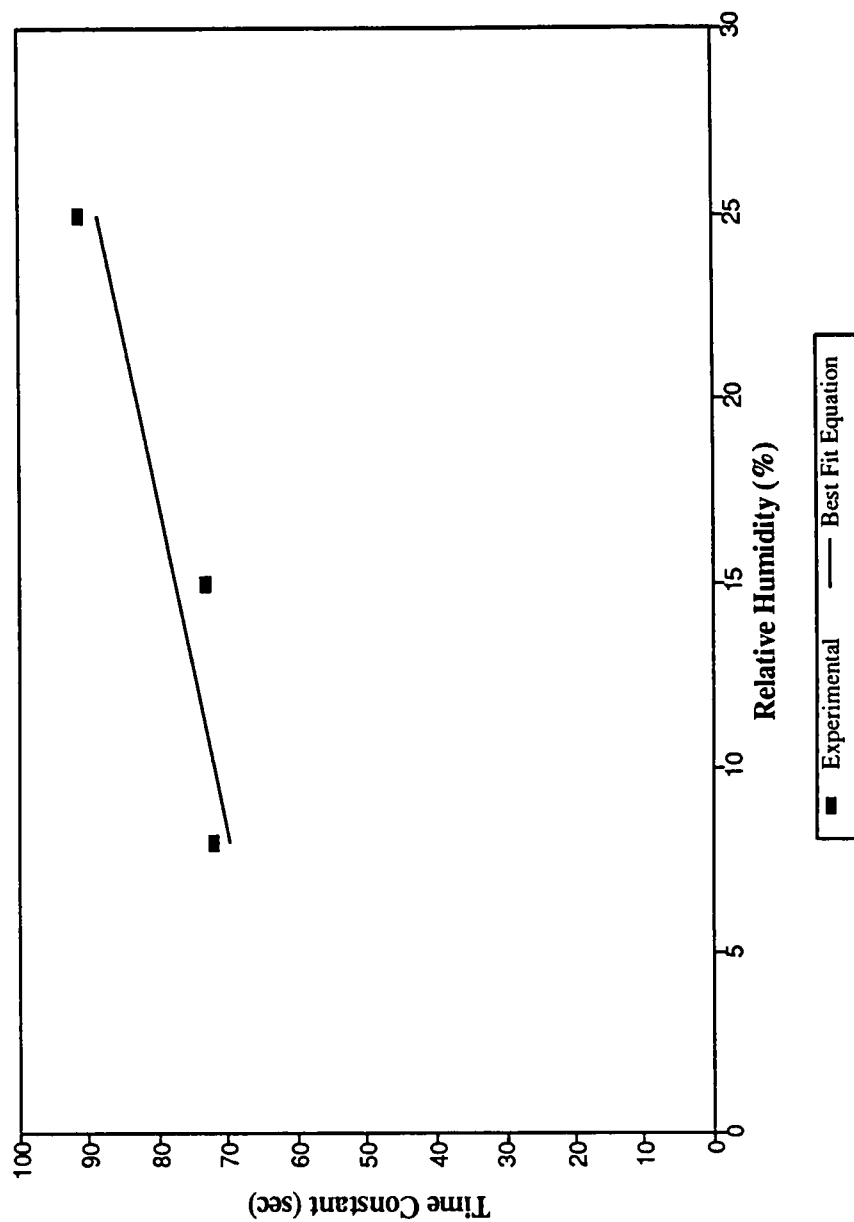


Figure 5.6. Effect of Relative Humidity on Time Constant in >5% Relative Humidity Tests.

Thus, the values of the time constant obtained at 1000 ppmv gas concentration were used to determine the time constant at a different gas concentration by

$$t_c = t_{c1000} (C_g/1000)^{-n} \quad (5.18)$$

Thus, all the parameters in the rate equation 5.4 are expressed in terms of the relative humidity of the tests. Therefore, knowing the operating conditions of a test such as temperature, gas concentration, and the relative humidity, the reaction rate at any reaction time can be calculated for the range of test conditions conducted in this study. Table 5.3 lists these empirical correlations for a quick review.

5.2 Prediction of Conversion by Empirical Model

The model predicted reaction rates were used to calculate the model predicted conversion for all the test conditions and reaction times tested in this study. The objective was to determine how well the correlations could predict the experimental conversions in the tests of this study, when all of the correlations were incorporated into the calculation of the conversion.

The predicted conversion of the hydrated lime at any time was calculated from the reaction rate as follows.

Table 5.3. Summary of Correlations Used in the Empirical Model.

1.	Reaction Order "n" (Eqn 5.8)	
	$n = 0.2 + 0.7[1 - \exp(-RH/11)]$	
2.	Frequency Factor "A _o " (Eqn 5.11)	
	$A_o = (-0.004) + 5.45e-3[\exp(-24253RH)] + 8.61e-2[\exp(-0.12RH)]$	
3.	Activation Energy "E" (Eqn 5.12 and 5.13)	
	$E = 5648.6 - 77RH - 5.18RH^2$	$8\% \leq RH \leq 25\%$
	$E = 8797 - 966RH + 81.4RH^2$	$RH \leq 5\%$
4.	Time Constant "t _c " (Eqn 5.15, 5.16, 5.18)	
	$t_c = 61.0 + 1.1RH$	$8\% \leq RH \leq 25\%$
	$t_c = 15.1 + 27.6RH - 3.45RH^2$	$RH \leq 5\%$
	$t_{c(cg)} = t_{c1000} \cdot (Cg/1000)^{-n}$	For gas concentrations other than 1000 ppmv

RH - Relative Humidity (%)

Rearranging equation 5.1 and combining with equation 5.3, we have

$$d(N_a)/dt = S_e \cdot r_a(t) = S_e \cdot r_a(o) \cdot \exp(-t/t_c) \quad (5.19)$$

Integrating between time "t" = 0 and t, the total moles of hydrogen chloride consumed in the hydrated lime sorbent during this time is given by

$$N_a(t) = [S_e \cdot r_a(o) / (-t_c)] \cdot \exp(-t/t_c) + C \quad (5.20)$$

where C is the integration constant. The value of C was calculated as follows. At

$$t = 0, N_a(t) = 0$$

Therefore, from Equation 5.20,

$$C = [S_e \cdot r_a(o) / (t_c)] \quad (5.21)$$

Finally, the conversion at time "t" was related to the moles of hydrogen chloride consumed by rearranging equation 5.5 i.e.

$$X = N_a(t) / (b \cdot N_{Ca(OH)_2}) \quad (5.22)$$

Equations 5.21, 5.22, and 5.22 were used to determine the predicted conversion of the sorbent at any time "t" based on the empirical relationships developed from the experimental data of this study. Figures 5.7 to 5.10 show the experimental and predicted conversions for four test conditions of 25%, 15%, 8%, and 0.6% relative humidities. Figure 5.11 shows a comparison of the predicted conversion versus measured conversion for all of the data illustrating the ability of the empirical model to simulate the observed data. The predicted conversion and the measured conversions for individual tests are in Appendix 6.

The empirical model predicted the experimental conversions within reasonable limits at all test conditions, and certainly better than the previously discussed shrinking unreacted core model in the case of the tests showing incomplete conversion. Further, this empirical model predicted the observed incomplete conversions of the sorbent at some of the test conditions more realistically than the shrinking unreacted core model. It may be noted that this is a first generation model based on the experimental data of this study only. Due to the empirical nature of these correlations, this model applies only within the range of test conditions covered in this study. The approach shows that, like the other operating parameters such as temperature and gas concentration, the relative humidity of the gas should also be considered in

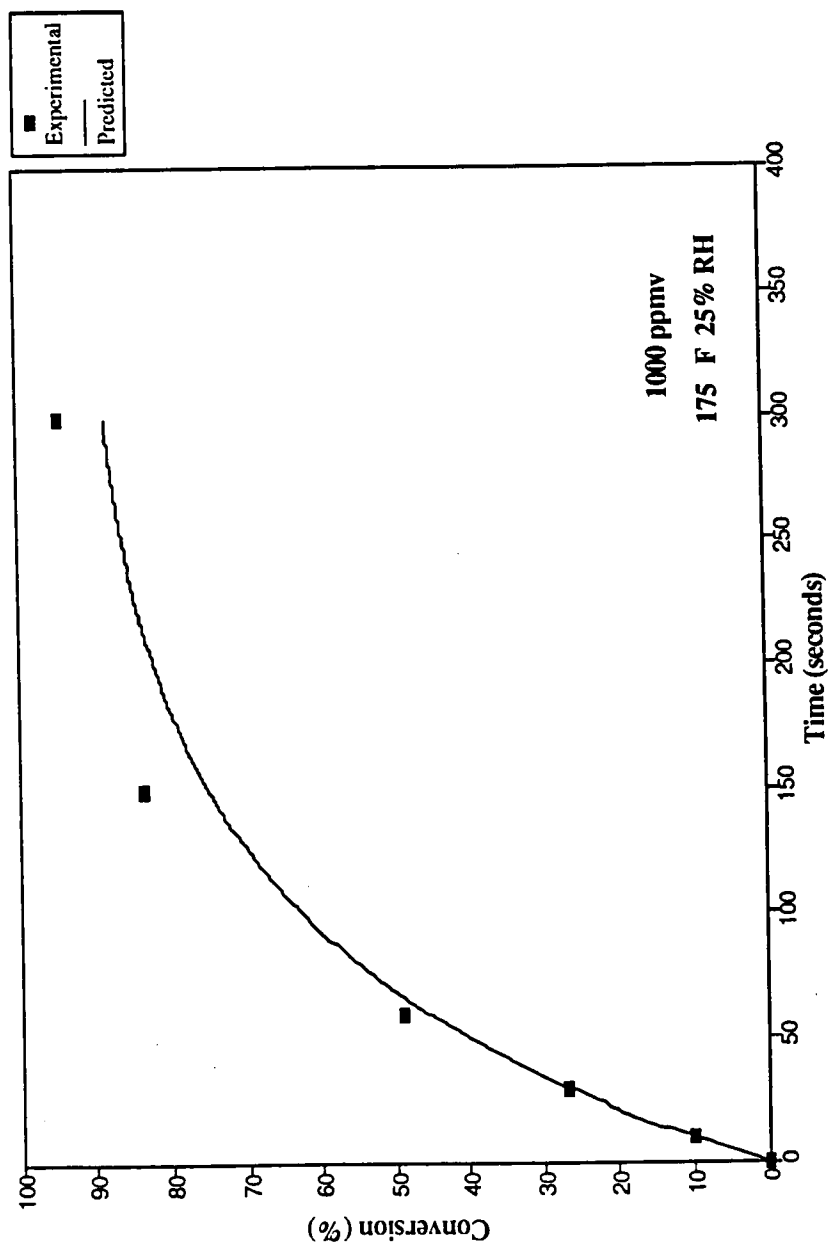


Figure 5.7. Conversion Predicted by the Empirical Model at 175 F and 25% Relative Humidity.

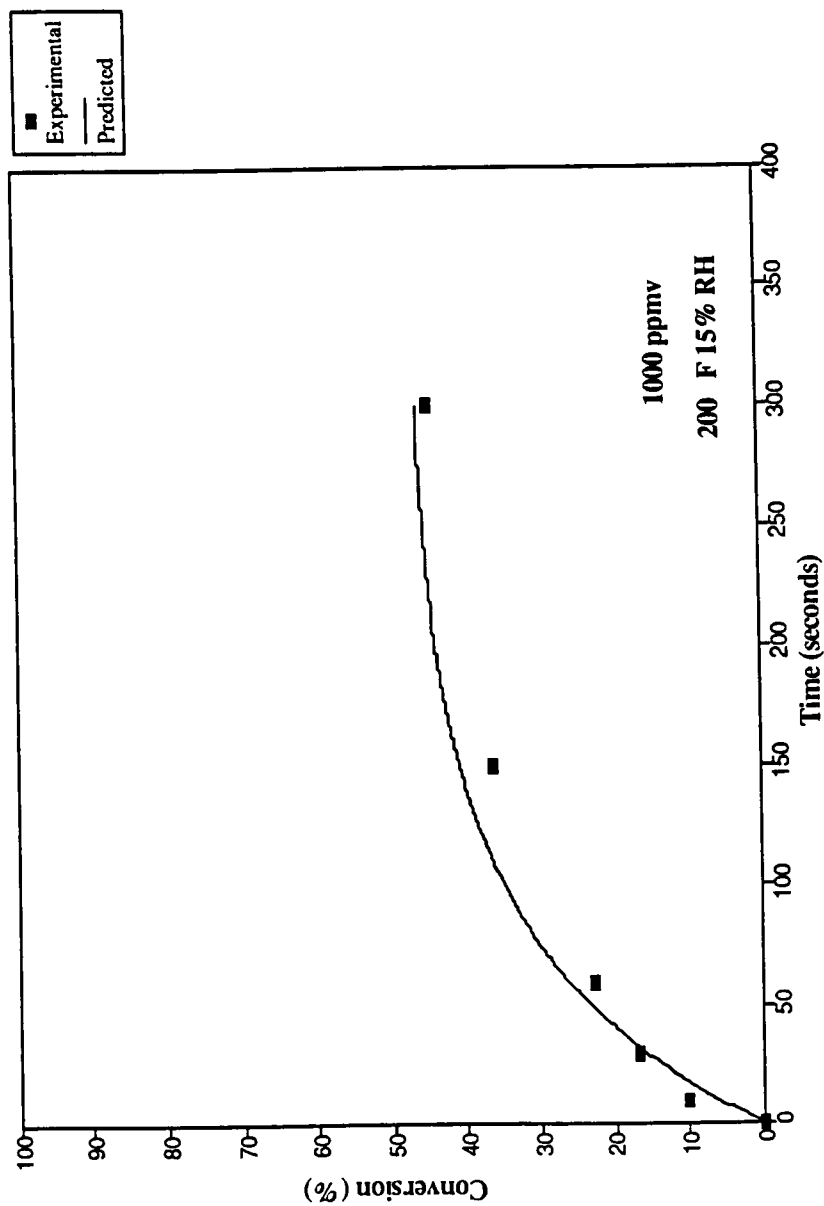


Figure 5.8. Conversion Predicted by Empirical Model at 200 F and 15% Relative Humidity.

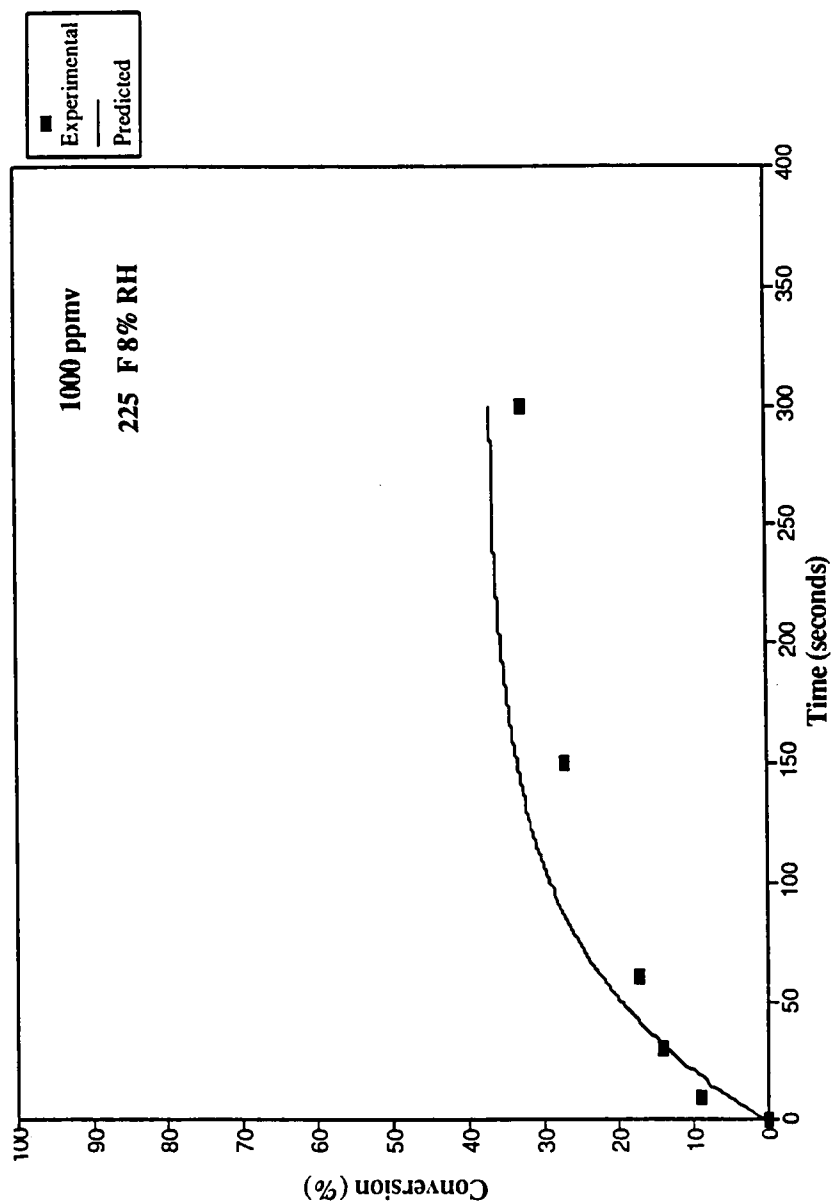


Figure 5.9. Conversion Predicted by the Empirical Model at 225 F and 8% Relative Humidity.

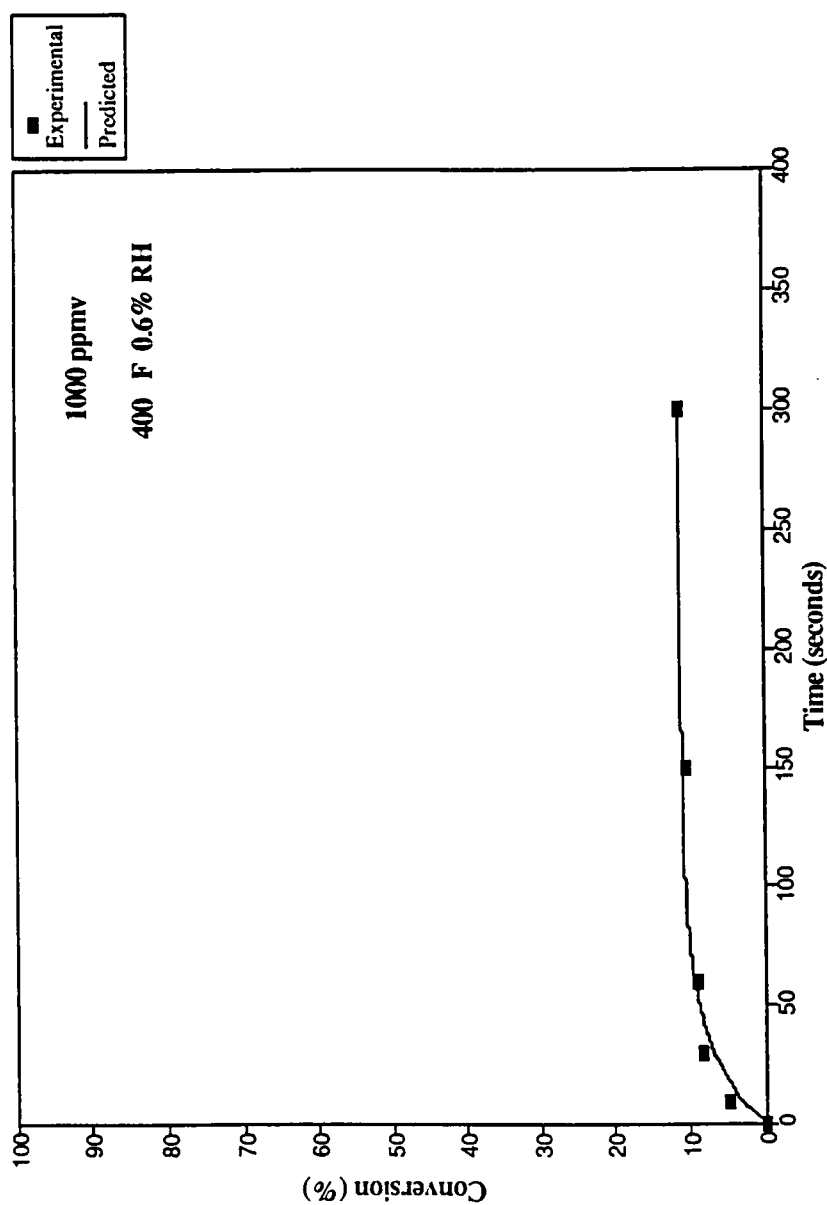


Figure 5.10. Conversion Predicted by the Empirical Model at 400 F and 0.6% Relative Humidity.

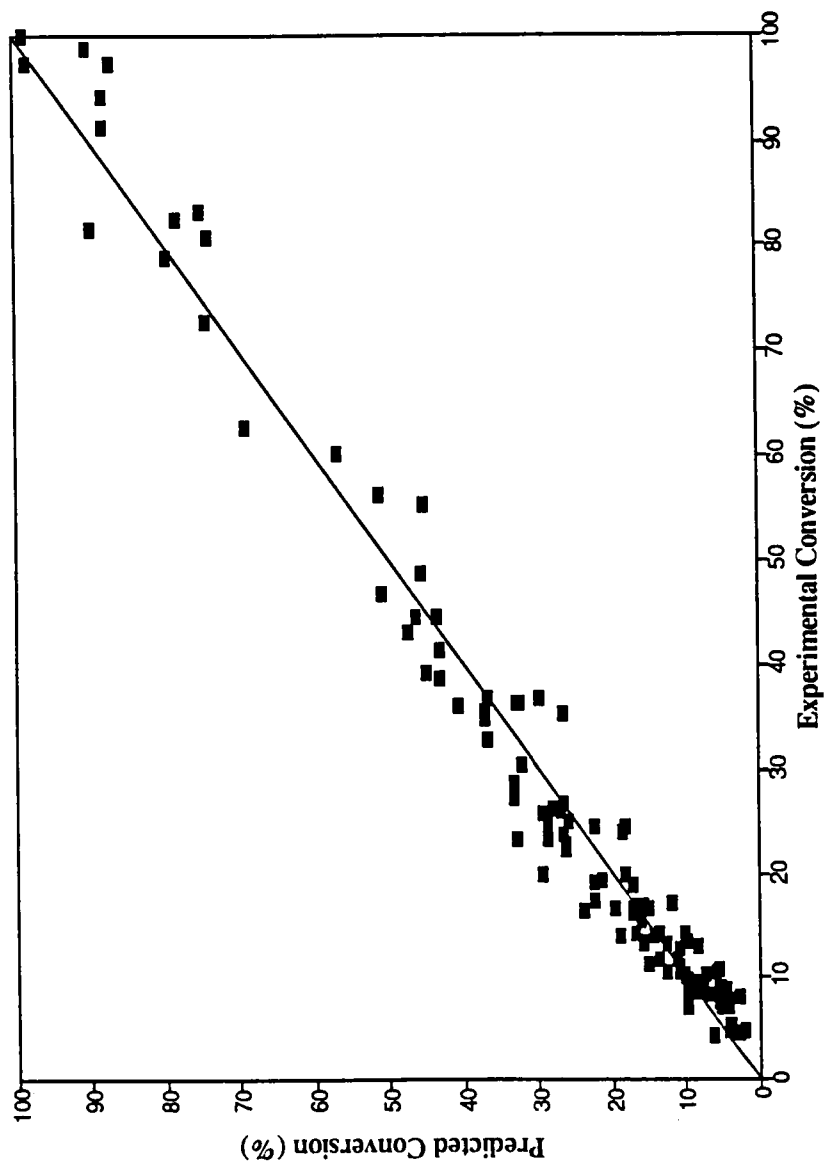


Figure 5.11. Conversion Predicted by the Empirical Model for All Tests between 500 ppmv and 5000 ppmv HCl concentration.

determining the conversion of the sorbent through empirical relationships. As more data are accumulated on this reaction from future studies, more appropriate empirical relationships can be developed to account for the effect of relative humidity on the sorbent conversion.

5.3 Comparison of Model with Reported Experimental Data

As mentioned in Section 2 (Literature Survey), complete data on operating conditions are not available from existing full scale plants. Many of the pilot scale and bench scale studies were conducted at test conditions outside the range of this study and thus could not be used for comparison with the model predictions. In fact, the lack of complete data had been one of the reasons for the unavailability of a model for this reaction.

Based on a literature search, the tests reported by Karlsson (1981), Itaya (1989), Jozewicz (1990) mentioned in Section 2 (Literature Survey), were selected for comparison with the model predictions. The operating conditions of these studies were reasonably close to those used in the present study and are summarized in Table 5.4 for quick reference.

Figure 5.12 compares the empirical model predicted conversion with the experimental sorbent conversion reported in these studies. The figure also includes the

Table 5.4. Summary of Operating Conditions and Results of Selected Pilot Scale and Bench Scale Studies for Comparison with Empirical Model

Reference	GC (ppmv)	RXT (°F)	MC (%)	RH (%)	SC ⁽¹⁾ (%)	Comments
Karlsson (1981)	630	300	10.0	2.4	12.0	Bench scale integral reactor 1 g hydrated lime w/ 40 g sand
	630	400	10.0	0.65	17.0	
Itaya (1989)	400	340	32.5	4.2	30.0	Injection before bag filter
	400	340	32.5	4.2	31.0	
	400	400	32.5	2.0	31.0	
	400	400	32.5	2.0	29.0	
	400	450	32.5	1.2	31.0	
	400	450	32.5	1.2	37.0	
	850	340	32.5	4.2	33.0	
	850	450	32.5	1.2	42.0	
	850	450	32.5	1.2	34.0	
	850	450	32.5	1.2	34.0	

Table 5.4. Summary of Operating Conditions and Results of Selected Pilot Scale and Bench Scale Studies for Comparison with Empirical Model (cont.)

Reference	GC (ppmv)	RXT (°F)	MC (%)	RH (%)	SC ⁽¹⁾ (%)	Comments
Jozewicz	1000	350	10.0 ⁽²⁾	1.5	19.0	Bench scale
(1990)	1000	305	10.0 ⁽²⁾	2.9	22.0	integral
	1000	225	10.0 ⁽²⁾	11.5	37.0	reactor
						1 g hydrated lime w/ 40 g sand

Notes :

1. Sorbent Conversions are approximate values obtained from figures in the cited references. The sorbent conversions were reported for a reaction time of 1 hour.
2. These moisture contents have been reported on mass basis. All other moisture contents are on volume (or mole) basis.

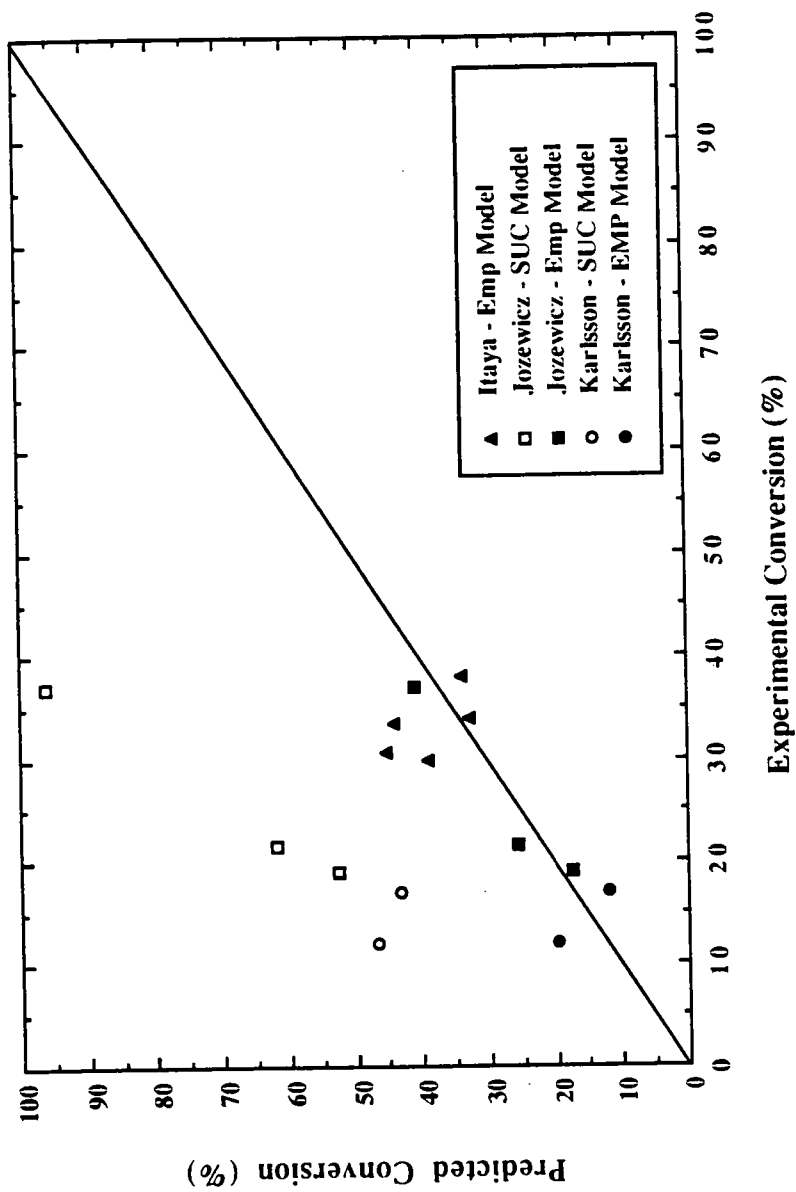


Figure 5.12. Comparison of Predictions of the Empirical Model and the Shrinking Core Model with Reported Experimental Data.

predicted conversion of the earlier described shrinking unreacted core model for comparison. The experimental conversion was found to be better predicted by the empirical model than the shrinking unreacted core model further confirming the suitability of the model over this wide range of test conditions. All these studies were conducted in integral reactors i.e. the concentration of the hydrogen chloride in the gas phase was decreasing as the gas flowed over the sorbent bed. In the present study on the other hand, the gas concentration was approximately constant throughout the sorbent bed at all times due to the small quantity of the lime used and high gas flow. This may explain why the empirical model tended to overpredict in some conditions. The difference in the reactivity of the hydrated lime used may be one of the other reasons for the deviations in the predicted and reported conversion in these studies. More pilot scale and field data are needed to determine the suitability of the empirical model at other test conditions.

CHAPTER 6

CONCLUSIONS

The reaction between hydrogen chloride gas and hydrated lime powders was studied in a bench scale fixed bed reactor, at test conditions representative of low temperature dry sorbent injection (DSI) process. The effects of the operating parameters such as, temperature, moisture, gas concentration and lime surface area on the progress of the reaction, were investigated. Physical properties of the sorbent were determined to understand their implications on the reaction. The change in the physical properties of the reacted sorbent with progressive conversions were determined to understand the mechanism of the reaction. Based on the results of this study, the following conclusions can be drawn regarding the reaction between hydrogen chloride and hydrated lime powders in a fixed bed.

1. In tests with dry hydrogen chloride, a higher reaction temperature increased both the initial rate of conversion and the final conversion. However, the final conversion was only 11.2% at 400 °F and 300 seconds reaction time. Very little additional conversion was expected with increased reaction time.

High resistance to gas diffusion in the solid product layer, rather than pore plugging, was determined to be the rate limiting mechanism for this reaction.

2. Moisture in the reacting gas enhanced both the rate of conversion and the final conversion significantly. The enhancement was found to increase with increase in moisture content at all temperatures, however, the degree of enhancement was higher at lower temperatures. Thus, neither the temperature nor the moisture content of the gas could be used as a single parameter to correlate to the conversion rate. Instead, the combined effect of these two parameters, expressed as the relative humidity of the gas was found to be correlated with the conversion at all test conditions.
3. All of the tests showed a reduction in the rate of conversion with increasing reaction time. The final conversion (i.e. the conversion after which further conversion practically ceased) depended on the operating conditions such as relative humidity, gas concentration, and sorbent surface area. These tests showed that complete conversion of the hydrated lime could be achieved at relative humidities of 25% or higher in the test gas.

4. The porosity and the pore area of the reacted sorbent decreased with higher conversions and preferential filling of smaller pores was observed. However, the incomplete conversions observed in tests at <25% relative humidities were considered to be due to high resistance to gas diffusion in the solid product layer rather than pore mouth closure or pore blockage. Thus, available pore plugging models were not considered to be appropriate for this reaction at the test conditions of the study.
5. Increasing the relative humidity of the gas increased the surface moisture of the unreacted sorbent and also the water content of the reacted sorbent. Analyses of the reacted sorbent showed that the moisture in the sorbent played a very important part in the reaction. Higher water in the sorbent increased both the initial rate of reaction, and the effective diffusivity through the solid product layer, resulting in higher final conversions. Though the exact mechanism for this increase in the effective diffusivity by the water in the sorbent could not be determined from the results of these limited number of tests, it was believed to be linked to the high solubility of hydrogen chloride and calcium chloride, in water.

6. Increasing the gas concentration increased the rate of conversion significantly at >25% relative humidity. The effect was less significant at the lower humidities. At approximately 2.2% relative humidity and 300 °F, the gas concentration had little effect on the rate of conversion or the final conversion. These results once again underscored the importance of the water content of the sorbent in this reaction.
7. Increasing the surface area of the hydrated lime increased both the rate of conversion and the final conversion at all test conditions, though the effect seemed to be more significant at the lower humidities. More tests were needed to confirm this effect.
8. A shrinking unreacted core model with product layer diffusion as the rate limiting step, seemed to fit the experimental data quite well at humidities of 25% or higher. The model predictions were less accurate at lower humidities, and at less than 2% humidity, this model was found to be unsuitable. The main limitations of the shrinking core model were the inability to account for the change in effective diffusivity of the reacted product layer with progressive conversion and the resulting incomplete conversion of the sorbent.

9. A mathematical model was developed to predict the sorbent conversions based on fundamental equations of gas solid reactions and empirical correlations of the parameters with the relative humidities of the tests. The empirical correlations were developed from the experimental test data of this study and were expected to be valid for similar test conditions only. The model predictions matched well with the experimental data of this study. The model predictions were checked with sorbent conversions of hydrated lime in three studies reported in the literature. The model predicted these reported sorbent conversions within reasonable limits.

CHAPTER 7

RECOMMENDATIONS FOR FURTHER STUDY

This study has generated preliminary kinetic data for the reaction between hydrogen chloride and hydrated lime powders. The effects of the operating parameters have been determined and insight into the possible mechanisms of the process have been gained. In addition, the following studies are recommended to fully characterize the process of removal of acid gases in DSI processes :

1. Water in the sorbent was found to have a significant impact on the conversion. The uptake of water by the sorbent should be monitored more precisely, preferably by online Thermogravimetric Analyses (TGA), and at different operating conditions. Water uptake by pure calcium chloride should also be determined in the same manner. Such data are not available at present and would be useful in understanding the role of water in the reaction.
2. More kinetic tests at all operating conditions need to be done both at shorter and longer reaction times than used in this study. These data will provide more accurate information on the initial reaction rates and the final conversions.
3. Kinetic data at lower gas concentrations are needed at

all operating conditions in order to derive expressions relating the changing gas concentration on the rate of conversion. These data would be useful in developing mathematical models for full scale plants in which the gas phase concentration changes with conversion of the sorbent.

4. Research on new sorbents with higher surface area and water holding capacities than hydrated lime, should be pursued. These sorbents would be especially useful at the low humidity, high temperature operating conditions.
5. Kinetic studies should be done with gas containing various concentrations of both hydrogen chloride and sulfur dioxide, to determine the interaction of these two acid gases in a DSI process.
6. The role of water in enhancing the reaction needs to be investigated in more detail. Though water was not necessary to achieve a reaction between calcium hydroxide and hydrogen chloride, it's presence in the gas was found to accelerate the reaction. The removal of hydrogen chloride may have been enhanced due to complex interactions between the calcium hydroxide, calcium chloride, hydrogen chloride, and water. These interactions may have included diffusion of water vapor into the solids, condensation and diffusion of water into the solids, dissolution of the calcium

based solids into the condensed water, absorption of hydrogen chloride into the condensed water, followed by reaction. The role of water formed in the actual reaction has to be also accounted for in these interactions.

This concept suggests that the extent and rate of reaction could be limited by the availability of condensed water at the reacting surface. In turn, that will depend on the rate of diffusion of water through the product layer and the rate of condensation at the reacting surface. These aspects of the reaction mechanism need to be investigated in more detail.

LIST OF REFERENCES

1. Batarseh K. I., Swaney, G.P., and Stiller, A. H., "A Mathematical Model for Heterogenous Reactions with a Moving Boundary," AICHE Journal, Vol 35, No. 4, p 625, 1989.
2. Bhatia, S. K., and Perlmutter, D. D., "Unified Treatment of Structural Effects in Gas-Solid Reactions," AICHE Journal, Vol 9, No. , p 108 ,1983.
3. Brna, T. G., "Toxic Metal Emissions from MWCs and Their Control," Proceedings of the Second International Speciality Conference, Tampa, FL, p 145, 1991.
4. Boynton, R. S., "Chemistry and Technology of Limestone," John Wiley and Sons, 2nd. Ed., p 340, 1980.
5. Chang, J. C. S., Brna, T. G., and Sedman, C. B., "Pilot Evaluation of Sorbents for Simultaneous Removal of HCl and SO₂ from MSW Incinerator Flue Gas by Dry Injection Process," Proceedings of the International Speciality Conference, Tampa, FL, p 8C-59, 1989.
6. Christman, P. G., and Edgar, T. F., "Distributed Pore Size Model for Sulfation of Limestone," AICHE Journal, Vol 29, No. 3, p 388, 1983.
7. Darcy, M., and Beutner, H.P., "Operating Experience and Performance of a Dry Scrubbing System on a Municipal Waste Incinerator," Paper presented at the Air and

Waste Management Association Annual Conference,
Anaheim, CA, 1989.

8. Dennis, J. S., and Hayhurst, A. N., "A Simplified Analytical Model for the Rate of Reaction of SO₂ with Limestone Particles," Chemical Engineering Science, Vol 41, No. 1, p 25, 1986. 1986
9. Department of Energy, "Theoretical Approach for Enhanced Mass Transfer Effects in In-Duct Flue Gas Desulfurization Processes," Annual Technical Progress Report, Prepared by Acurex Corporation and University of Texas, Austin, 1990.
10. Donnelly, J., R., "Overview of Air Pollution Controls for Municipal Waste Combustors", Proceedings of the Second International Speciality Conference, Tampa, FL, p 125, 1991.
11. Environment Canada, "The National Incinerator Testing and Evaluation Program: Air Pollution Control Technology," Report EPS 3/UP/2, 1986.
12. Felsvang, K. S., " Results of Full Scale Dry Injection Tests at MSW-Incinerators Using a New Active Sorbent," Proceedings of the Second International Speciality Conference, Tampa, FL, p 542, 1991.
13. Foster, John T. et al., "Design and Start-up of a Dry Scrubbing System for Solid Particulate and Acid Gas Control on a Municipal Refuse Fired Incinerator," Paper presented in APCA Speciality Conference on Thermal

Treatment of Municipal Industrial and Hospital Wastes,
Pittsburgh, PA, 1987.

14. Frame, G. B., "A comparison of Air Pollution Control Systems for Municipal Solid Waste Incinerators," JAPCA, vol 38, No. 8, p 1081, 1988.
15. Georgakis, C., Chang, C. W., and Szekely, J., Chemical Engineering Science, Vol 34, p 1072, 1979.
16. Gregg, S. J., and Sing, K. S. W., "Adsorption, Surface Area and Porosity," Academic Press, 2nd. Ed., p 111, 1982.
17. Gullet, B. K., Bruce, K. R., and Beach, L. O., "Formation Mechanism of Chlorinated Organics and Impacts of Sorbent Injection," Proceedings of the International Speciality Conference, Tampa, FL, p 8C-1, 1989.
18. Hartman, M., and Coughlin, R. W., "Reaction of Sulfur Dioxide with Limestone and the Grain Model," AIChE Journal, Vol 22, No. 3, 1976.
19. "Incineration and Treatment of Hazardous Waste," Proceedings of the Eleventh Annual Research Symposium, Cincinnati, 1985.
20. Itaya, M., et al., "Removal of Hydrogen Chloride Gas from MSW Fluidized Bed Incinerator Using Bag Filter," Proceedings of the International Speciality Conference, Tampa, FL, p 8C-45, 1989.
21. JAWMA, Vol 41, No 3, March 1991.

22. Jozewicz, W., Chang, J. C. S., and Sedman, C. B., "Bench-Scale Evaluation of Calcium Sorbents for Acid Gas Emission Control," Environmental Progress, Vol 9, No. 3, p 137, 1990.
23. Jozewicz, W., "A Novel Calcium Based Sorbent for the Removal of Flue Gas HCl by Dry Injection," Proceedings of the Second International Speciality Conference, Tampa, FL, p 523, 1991.
24. Karlsson, H. T., Klingspor, J, Bjerle, I., "Adsorption of Hydrochloric Acid on Solid Slaked Lime for Flue Gas Cleanup," JAPCA, Vol 31, No. 5, p 1177, 1981.
25. Keener, T. C., "Thermal Decomposition of Sodium Bicarbonate and It's Effect on the Reaction of Sodium Dioxide in a Simulated Flue Gas," Ph.D. Dissertation, The University of Tennessee, 1982.
26. Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Ed., Vol 4, p 11, 1978.
27. Klingspor, J., et, al., "Similarities Between Lime and Limestone in Wet-Dry Scrubbing," Chemical Engineering Progress, Vol 16, p 239, 1984.
28. Klingspor, J. S., Roberts, D. L., and Jefcoat, I. A., "Acid Gas Emissions: Results of Spray Dry Scrubbing Pilot Plant Study," Proceedings of the International Speciality Conference, Tampa, FL, p 9C-1, 1989.
29. Lee, D. C., and Georgakis, C., "A Single, Particle-Size Model for Sulfur Retention in Fluidized Bed Coal

- Combustors," AICHE Journal, Vol 27, No. 3, p 472, 1981.
30. Levenspiel, O, "Chemical Reaction Engineering," John Wiley and Sons, p 338, 1962.
 31. Linder, B. and Simonsson, D., "Comparisons of Structural Models for Gas-Solid Reactions in Porous Solids Undergoing Structural Changes," Chemical Engineering Science, Vol 36, No. 9, p 1519, 1981.
 32. McClanahan, D., Licata, A., and Buschman, J.C., "Operating Experience with Three APC Designs on Municipal Incinerators," Proceedings of the International Speciality Conference, Tampa, FL, p 8C-1, 1989.
 33. Petersen, E. E., "Reaction of Porous Solids," AICHE Journal, Vol 3, No. 4, p 443, 1957. (1957).
 34. Ramachandran, P. A., and Smith, J. M., "A Single Pore Model for Gas-Solid Noncatalytic Reactions," AICHE Journal, Vol 23, No 3, p 353, 1977.
 35. Ronblaad, S., and Ahlbeck, J. R., "Removal of Sulfur Dioxide in a Fabric Filter," JAPCA, Vol 41, No. 3, 1983.
 36. Sherwood T. K., Pigford, R. L., and Wilke, C. R., "Mass Transfer", McGraw Hill, New York, p 561, 1975.
 37. Szekely J., Evans, J. W., "A structural Model for Gas-solid Reactions with a Moving Boundary," Chemical Engineering Science, Vol 25, p 1091, 1970.
 38. Szekely, J., Evans, J. W., and Sohn, H. Y., "Gas-Solid

- Reactions," Academic Press, New York, 1976.
39. Yu, H. C., Sotirchos, S. V., "A Generalized Pore Model for Gas-Solid Reactions Exhibiting Pore Closure," AICHE Journal, Vol 33, No. 3, p 382, 1987.
 40. White, D. M., and Vancil, M. A., "Review of Dry Injection Technology for Reducing Emissions from Municipal Waste Combustors," Proceedings of the International Speciality Conference, Tampa, FL, p 10C-31, 1989.
 41. Zmuda, Jan T., and Smith, Peter V, "Retrofit Acid Gas Emission Control for Municipal Waste Incineration: An Application of Dry Sorbent Injection, " Proceedings of the Second International Speciality Conference, Tampa, FL, p 797, 1991.

APPENDIXES

APPENDIX - 1



PRODUCT DATA

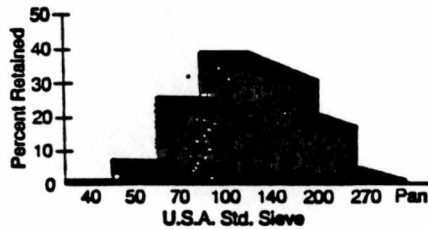
F-75

Mine: Ottawa, Illinois

Form Number: 5022

Date: June, 1987

TYPICAL SIZE ANALYSIS:



U.S.A. Std. Sieve	Millimeter Designation	% Retained On Sieve		% Retained Cumulative	% Passing
		Mean	Range	Mean	Mean
40	.425	0.3	0-1	0.3	99.7
50	.300	6.0	3-9	6.3	93.7
70	.212	25.4	20-30	31.7	68.3
100	.150	39.9	35-45	71.6	28.4
140	.106	22.0	17-27	93.6	6.4
200	.075	5.6	3-9	99.2	0.8
270	.053	0.8	0-2	100.0	0
Pan		T	0-0.5	T	

TYPICAL PHYSICAL PROPERTIES:

Mineral	Quartz	Melting Point	3100°F
Color	White	Theoretical Surface Area (cm ² /gm)	138
Grain Shape	Rounded	Actual Surface Area (cm ² /gm)	162
Sphericity (Krumbein)	.8/7	Coefficient of Area	1.17
Roundness (Krumbein)	.8/7	Base Permeability	71
Hardness (Moh)	7.0	Moisture Content Dry (Max.)	<1
Specific Gravity	2.65	Acid Demand (pH-7)	<1
Bulk Density — Compacted (lbs/ft ³)	104	AFS Grain Fineness (Range)	71-79
Uncompacted (lbs/ft ³)	92	pH	Neutral

APPENDIX - 2

COULTER(R) Multisizer AccuComp(R) Rev. 1.00 Wed Jun 05 21:19:58 1991.

ARIJITDI.033

Filename: ARIJITDI.033 Sample Number: 0
Group ID: ARIJIT DISSERTATION
Sample ID: GREAT THAN 53 MICRON - 70 MICRON ORFC
Comments: DRY HYDRATED LIME SAMPLE - PDKT #1 TENN LUTTRELL
Operator: ARIJIT
Electrolyte: ISOTONE
Dispersant:
Aperture Size: 70 μm Aperture Current: 1600 μA
Channels: 256 Kd: 677.00
Full Data Linear Diameter Gain: 2
Control Method: Manual
Raw Count: 442532 Variable 1: 0.000000
Coinc. Corr. Count: 1 Variable 2: 0.000000
Acquired at: 18:42 Fri May 24 1991

ARIJITDI.033

Volume Statistics (Geometric)

Calculations from 1.62 μm^3 to 40.02 μm^3
Volume 19.39*10⁶ μm^3 Coinc. Corrected: 1 μm
Mean: 5.573 μm 95% Conf. Limits: 5.572-5.573
Median: 5.839 μm Std. Dev.: 0.091
Mean/Median Ratio: 0.954 Variance: 0.0083
Mode: 6.191 μm Coef. Var.: 12.22 %
Skewness: -1.485e+000 Left skewed
Kurtosis: 3.316e+000 Leptokurtic

% >	10.00	25.00	50.00	75.00	90.00
Size μm	6.861	6.412	5.839	5.124	4.235

COULTER(R) Multisizer AccuComp (R) Rev. 1.00 Wed Jun 05 21:25:10 1991.
 ARIJITDI.035

Filename: ARIJITDI.035 Sample Number: 0
 Group ID: ARIJIT DISSERTATION
 Sample ID: GREAT THAN 53 MICRON - 70 MICRON ORFC
 Comments: DRY HYDRATED LIME SAMPLE - PDKT #1 TENN LUTTRELL
 Operator: ARIJIT
 Electrolyte: ISOTONE
 Dispersant:
 Aperture Size: 70 um Aperture Current: 1600 uA
 Channels: 256 Kd: 677.00
 Full Data Linear Diameter Gain: 2
 Control Method: Manual
 Raw Count: 664263
 Coinc. Corr. Count: 1 Variable 1: 0.000000
 Variable 2: 0.000000
 Acquired at: 18:51 Fri May 24 1991

Volume Statistics (Geometric) ARIJITDI.035

Calculations from 1.62 um³ to 40.02 um³
 Volume 16.03*10⁶ um³ Coinc. Corrected: 1 um
 Mean: 4.485 um 95% Conf. Limits: 4.484-4.485
 Median: 4.578 um Std. Dev.: 0.091
 Mean/Median Ratio: 0.980 Variance: 0.0083
 Mode: 4.576 um Coef. Var.: 14.00 %
 Skewness: -7.037e-001 Left skewed
 Kurtosis: 9.488e-001 Leptokurtic

% >	10.00	25.00	50.00	75.00	90.00
Size um	5.752	5.197	4.578	3.970	3.423

COULTER(R) Multisizer AccuComp(R) Rev. 1.00 Wed Jun 05 21:21:51 1991.
 ARIJITDI.032

Filename: ARIJITDI.032 Sample Number: 0
 Group ID: ARIJIT DISSERTATION
 Sample ID: GREAT THAN 53 MICRON - 70 MICRON ORFC
 Comments: DRY HYDRATED LIME SAMPLE - PDKT #1 TENN LUTTRELL
 Operator: ARIJIT
 Electrolyte: ISOTONE
 Dispersant:
 Aperture Size: 70 um Aperture Current: 1600 uA
 Channels: 256 Kd: 677.00
 Full Data Linear Diameter Gain: 2
 Control Method: Manual
 Raw Count: 897603
 Coinc. Corr. Count: 1 Variable 1: 0.000000
 Variable 2: 0.000000
 Acquired at: 18:41 Fri May 24 1991

Volume Statistics (Geometric) ARIJITDI.032

Calculations from 1.62 um³ to 40.02 um³
 Volume 17.01*10⁶ um³ Coinc. Corrected: 1
 Mean: 4.272 um 95% Conf. Limits: 4.271-4.272
 Median: 4.326 um Std. Dev.: 0.110
 Mean/Median Ratio: 0.987 Variance: 0.012
 Mode: 4.038 um Coef. Var.: 17.50 %
 Skewness: 6.051e-002 Right skewed
 Kurtosis: 1.812e+000 Leptokurtic

% >	Size um	50.00	75.00	90.00
10.00	25.00	50.00	75.00	90.00
5.756	5.129	4.326	3.611	3.079

COULTER(R) Multisizer AccuComp(R) Rev. 1.00 Wed Jun 05 21:32:30 1991.
 ARIJITDI.021

Filename: ARIJITDI.021 Sample Number: 0
 Group ID: ARIJIT DISSERTATION
 Sample ID: 45 TO 53 MICRONS
 Comments: DRY HYDRATED LIME SAMPLE - PDKT #1 TENN LUTTRELL
 Operator: ARIJIT
 Electrolyte: ISOTONE
 Dispersant:
 Aperture Size: 70 um Aperture Current: 1600 uA
 Channels: 256 Kd: 677.00
 Full Data Linear Diameter Gain: 2
 Control Method: Manual
 Raw Count: 22219
 Coinc. Corr. Count: 24156 Variable 1: 0.000000
 Variable 2: 0.000000
 Acquired at: 17:29 Fri May 24 1991

Volume Statistics (Geometric) ARIJITDI.021

Calculations from 1.62 um³ to 40.02 um³
 Volume 556.1*10³ um³ Coinc. Corrected: 24156 um
 Mean: 6.975 um 95% Conf. Limits: 6.962-6.989
 Median: 7.483 um Std. Dev.: 0.313
 Mean/Median Ratio: 0.932
 Mode: 3.141 um
 Variance: 0.098
 Coef. Var.: 37.09 %
 Skewness: -1.690e-001 Left skewed
 Kurtosis: -1.042e+000 Platykurtic

%	10.00	25.00	50.00	75.00	90.00
Size um	17.68	12.97	7.483	3.844	2.503

OULTER(R) Multisizer AccuComp(R) Rev. 1.00 Wed Jun 05 21:39:20 1991.
 ARIJITDI.025

Filename: ARIJITDI.025 Sample Number: 0
 Group ID: arijit dissertation
 Sample ID: TENN LUTTRELL PKT #1 - 45-53 MICRON
 Comments: dried sample
 Operator: arijit
 Electrolyte: isotone
 Dispersant:
 Aperture Size: 70 μm Aperture Current: 1600 μA
 Channels: 256 Kd: 677.00
 Full Data Linear Diameter Gain: 2
 Control Method: Manual
 Raw Count: 69139
 Coinc. Corr. Count: 1 Variable 1: 0.000000
 Variable 2: 0.000000
 Acquired at: 12:48 Sun Jun 02 1991

Volume Statistics (Geometric) ARIJITDI.025

Calculations from 1.62 μm^3 to 40.02 μm^3
 Volume 1.320*10⁶ μm^3 Coinc. Corrected: 1 μm
 Mean: 6.269 μm 95% Conf. Limits: 6.260-6.277 μm
 Median: 5.523 μm Std. Dev.: 0.343
 Mean/Median Ratio: 1.135 Variance: 0.118
 Mode: 2.782 μm Coef. Var.: 43.03 %
 Skewness: 3.300e-001 Right skewed
 Kurtosis: -9.475e-001 Platykurtic

% >	10.00	25.00	50.00	75.00	90.00
Size μm	21.55	11.69	5.523	3.351	2.344

COULTER(R) Multisizer AccuComp(R) Rev. 1.00 Wed Jun 05 21:34:29 1991.
 ARIJITDI.022

Filename: ARIJITDI.022 Sample Number: 0
 Group ID: ARIJIT DISSERTATION
 Sample ID: 45 TO 53 MICRONS
 Comments: DRY HYDRATED LIME SAMPLE - PDKT #1 TENN LUTTRELL
 Operator: ARIJIT
 Electrolyte: ISOTONE
 Dispersant:
 Aperture Size: 70 um Aperture Current: 1600 uA
 Channels: 256 Kd: 677.00
 Full Data Linear Diameter Manual Gain: 2
 Control Method:
 Raw Count: 130455
 Coinc. Corr. Count: 1 Variable 1: 0.000000
 Variable 2: 0.000000
 Acquired at: 17:51 Fri May 24 1991

Volume Statistics (Geometric) ARIJITDI.022

Calculations from 1.62 um³ to 40.02 um³
 Volume 3.008*10⁶ um³ Coinc. Corrected: 1 um
 Mean: 8.375 um 95% Conf. Limits: 8.366-8.383
 Median: 7.976 um Std. Dev.: 0.380
 Mean/Median Ratio: 1.050 Variance: 0.145
 Mode: 1.705 um Coef. Var.: 41.20 %
 Skewness: -5.671e-002 Left skewed
 Kurtosis: -1.042e+000 Platykurtic

% >	10.00	25.00	50.00	75.00	90.00
Size um	28.46	17.99	7.976	4.295	2.408

COULTER (R) Multisizer AccuComp (R) Rev. 1.00 Wed Jun 05 21:02:57 1991.
 ARIJITDI.011

Filename: ARIJITDI.011 Sample Number: 0
 Group ID: ARIJIT DISSERTATION
 Sample ID: LESS THAN 45 MICRON
 Comments: DRY HYDRATED LIME SAMPLE - PKT #1 TENN LUTTRELL
 Operator: ARIJIT
 Electrolyte: ISOTONE
 Dispersant:
 Aperture Size: 70 μm Aperture Current: 1600 μA
 Channels: 256 Kd: 677.00
 Full Data Linear Diameter Gain: 2
 Control Method: Manual
 Raw Count: 278763
 Coinc. Corr. Count: 1 Variable 1: 0.000000
 Variable 2: 0.000000
 Acquired at: 16:46 Fri May 24 1991

Volume Statistics (Geometric) ARIJITDI.011

Calculations from 0.00 μm^3 to 45.94 μm^3
 Volume 4.802*10⁶ μm^3 Coinc. Corrected: 1
 Mean: 4.572 μm 95% Conf. Limits: 4.570-4.574 μm
 Median: 4.426 μm Std. Dev.: 0.213
 Mean/Median Ratio: 1.033 Variance: 0.045
 Mode: 4.397 μm Coef. Var.: 32.21 %
 Skewness: 6.254e-001 Right skewed
 Kurtosis: 6.591e-001 Leptokurtic

% >	10.00	25.00	50.00	75.00	90.00
Size μm	9.484	5.511	4.426	3.457	2.505

COULTER(R) Multisizer AccuComp(R) Rev. 1.00 Wed Jun 05 21:04:54 1991.
ARIJITDI.012

Filename: ARIJITDI.012 Sample Number: 0
Group ID: ARIJIT DISSERTATION
Sample ID: LESS THAN 45 MICRON
Comments: DRY HYDRATED LIME SAMPLE - PDKT #1 TENN LUTTRELL
Operator: ARIJIT
Electrolyte: ISOTONE
Dispersant:
Aperture Size: 70 um Aperture Current: 1600 uA
Channels: 256 Kd: 677.00
Full Data Linear Diameter Gain: 2
Control Method: Manual
Raw Count: 89183
Coinc. Corr. Count: 1 Variable 1: 0.000000
Acquired at: 17:11 Fri May 24 1991 Variable 2: 0.000000

Volume Statistics (Geometric) ARIJITDI.012

Calculations from 1.62 μm^3 to 40.02 μm^3
Volume 2.429*10⁶ μm^3 Coinc. Corrected: 1
Mean: 7.630 um 95% Conf. Limits: 7.622-7.638 um
Median: 6.471 um Std. Dev.: 0.368
Mean/Median Ratio: 1.179 Variance: 0.136
Mode: 3.320 um Coef. Var.: 41.72 %
Skewness: 2.951e-001 Right skewed
Kurtosis: -1.037e+000 Platykurtic

% >	10.00	25.00	50.00	75.00	90.00
Size um	27.56	15.93	6.471	3.878	2.708

COULTER(R) Multisizer AccuComp (R) Rev. 1.00 Wed Jun 05 21:06:10 1991.
 ARIJITDI.013

Filename: ARIJITDI.013 Sample Number: 0
 Group ID: ARIJIT DISSERTATION
 Sample ID: LESS THAN 45 MICRON
 Comments: DRY HYDRATED LIME SAMPLE - PKT #1 TENN LUTTRELL
 Operator: ARIJIT
 Electrolyte: ISOTONE
 Dispersant:
 Aperture Size: 70 μm Aperture Current: 1600 μA
 Channels: 256 Kd: 677.00
 Full Data Linear Diameter Gain: 2
 Control Method: Manual
 Raw Count: 71186
 Coinc. Corr. Count: 1 Variable 1: 0.000000
 Variable 2: 0.000000
 Acquired at: 17:15 Fri May 24 1991

Volume Statistics (Geometric) ARIJITDI.013

Calculations from 1.62 μm^3 to 40.02 μm^3

Volume	1.711 $\times 10^6$ μm^3	Coinc. Corrected:	1	
Mean:	6.628 μm	95% Conf. Limits:	6.620-6.635	μm
Median:	5.810 μm	Std. Dev.:	0.335	
Mean/Median Ratio:	1.141	Variance:	0.112	
Mode:	3.858 μm	Coef. Var.:	40.81	%
		Skewness:	4.267e-001	Right skewed
		Kurtosis:	-6.718e-001	Platykurtic

% >	10.00	25.00	50.00	75.00	90.00
Size μm	21.00	11.24	5.810	3.714	2.611

ASAP 2000 V1.04

Micromeritics Instrument Corporation

PAGE 26

SAMPLE DIRECTORY/NUMBER: DATA1 /103
SAMPLE ID: TENN LUTTREL PDKT#1 >53um
SUBMITTER: ARIJIT
OPERATOR:
UNIT NUMBER: 1
ANALYSIS GAS: Nitrogen

START 09:33:57 06/10/91
COMPL 14:41:26 06/10/91
REPT 17:25:54 06/10/91
SAMPLE WT: 1.6086 g
FREE SPACE: 51.8645 cc
EQUIL INTRVL: 5 sec

SUMMARY REPORT

AREA

BET SURFACE AREA:	18.0913	sq. m/g
LANGMUIR SURFACE AREA:	25.6919	sq. m/g
SINGLE POINT SURFACE AREA AT P/Po 0.2147:	17.3157	sq. m/g
BJH CUMULATIVE ADSORPTION SURFACE AREA OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	21.4226	sq. m/g
BJH CUMULATIVE DESORPTION SURFACE AREA OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	26.8293	sq. m/g
MICROPORE AREA:	0.9704	sq. m/g

VOLUME

SINGLE POINT TOTAL PORE VOLUME OF PORES LESS THAN 917.8568 A DIAMETER AT P/Po 0.9786:	0.075332	cc/g
BJH CUMULATIVE ADSORPTION PORE VOLUME OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	0.082183	cc/g
BJH CUMULATIVE DESORPTION PORE VOLUME OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	0.086693	cc/g
MICROPORE VOLUME:	0.000210	cc/g

PORE SIZE

AVERAGE PORE DIAMETER (4V/A BY BET):	166.5598	A
BJH ADSORPTION AVERAGE PORE DIAMETER (4V/A):	153.4506	A
BJH DESORPTION AVERAGE PORE DIAMETER (4V/A):	129.2517	A

Micromeritics Instrument Corporation

ASAP 2000 V1.04

PAGE 25

SAMPLE DIRECTORY/NUMBER: DATA1 /102	START 11:47:39 06/08/91
SAMPLE ID: TENN LUTTRELL PDKT01 - 45-53uN	COMPL 16:23:36 06/08/91
SUBMITTER: ARIJIT	REPT 16:23:37 06/08/91
OPERATOR:	SAMPLE WT: 1.2395 g
UNIT NUMBER: 1	FREE SPACE: 52.3339 cc
ANALYSIS GAS: Nitrogen	EQUIL INTRVL: 5 sec

SUMMARY REPORT

AREA

BET SURFACE AREA:	18.6984 sq. m/g
LANGMUIR SURFACE AREA:	26.7241 sq. m/g
SINGLE POINT SURFACE AREA AT P/P ₀ 0.2156:	17.8660 sq. m/g
BJH CUMULATIVE ADSORPTION SURFACE AREA OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	22.1766 sq. m/g
BJH CUMULATIVE DESORPTION SURFACE AREA OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	28.4109 sq. m/g
MICROPORE AREA:	0.6896 sq. m/g

VOLUME

SINGLE POINT TOTAL PORE VOLUME OF PORES LESS THAN 912.8271 A DIAMETER AT P/P ₀ 0.9785:	0.071145 cc/g
BJH CUMULATIVE ADSORPTION PORE VOLUME OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	0.077118 cc/g
BJH CUMULATIVE DESORPTION PORE VOLUME OF PORES BETWEEN 17.0000 AND 3000.0000 A DIAMETER:	0.081071 cc/g
MICROPORE VOLUME:	0.000058 cc/g

PORE SIZE

AVERAGE PORE DIAMETER (4V/A BY BET):	152.1947 A
BJH ADSORPTION AVERAGE PORE DIAMETER (4V/A):	139.0984 A
BJH DESORPTION AVERAGE PORE DIAMETER (4V/A):	114.1402 A

APPENDIX - 3

Appendix 3

Operating Conditions and Sorbent Conversions in Kinetic Tests

Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (°F)	GC (PPMV)	RT (SEC)	CNV (%)
NM175-1	175	5	NA	NA	NA	1015	30	0.75
NM175-2	175	5	NA	NA	NA	1015	60	1.14
NM175-3	175	5	NA	NA	NA	1015	150	2.73
NM175-4	175	5	NA	NA	NA	1015	300	3.61
NM200-1	200	6	NA	NA	NA	1030	30	1.01
NM200-2	200	6	NA	NA	NA	1030	60	1.58
NM200-3	200	6	NA	NA	NA	1030	150	2.87
NM200-4	200	6	NA	NA	NA	1030	300	4.05
NM225-1	225	10	NA	NA	NA	1030	30	2.09
NM225-2	225	10	NA	NA	NA	1030	60	3.46
NM225-3	225	10	NA	NA	NA	1030	150	5.20
NM225-4	225	10	NA	NA	NA	1030	300	5.16
NM300-1	300	10	NA	NA	NA	1030	30	2.54
NM300-2	300	10	NA	NA	NA	1030	60	5.52

Appendix 3 (cont.)

Operating Conditions and Sorbent Conversions in Kinetic Tests

Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (°F)	GC (PPMV)	RT (SEC)	CNV (%)
NM300-3	300	10	NA	NA	NA	1030	150	7.03
NM300-4	300	10	NA	NA	NA	1030	300	8.8
NM400-1	400	5	NA	NA	NA	1020	30	7.03
NM400-2	400	5	NA	NA	NA	1020	60	9.02
NM400-3	400	5	NA	NA	NA	1020	150	11.57
NM400-4	400	5	NA	NA	NA	1020	300	13.75
T15-1	175	10	3.13	8	80	1030	10	4.80
T15-2	175	10	3.13	8	80	1030	30	8.66
T15-3	175	10	3.13	8	80	1030	60	13.97
T15-4	175	10	3.13	8	80	1030	150	19.52
T15-5	175	10	3.13	8	80	1030	300	33.76
T14-1	175	5	7.1	15	103	1020	10	9.06
T14-2	175	5	7.1	15	103	1020	30	13.96

Appendix 3 (cont.)

Operating Conditions and Sorbent Conversions in Kinetic Tests

Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (°F)	GC (PPMV)	RT (SEC)	CNV (%)
T14-3	175	5	7.1	15	103	1020	60	18.25
T14-4	175	5	7.1	15	103	1020	150	39.27
T14-5	175	5	7.1	15	103	1020	300	46.96
T18-1	200	5	7.07	15	103	1015	10	7.18
T18-2	200	5	7.07	15	103	1015	30	11.85
T18-3	200	5	7.07	15	103	1015	60	24.57
T18-4	200	5	7.07	15	103	1015	150	25.94
T18-5	200	5	7.07	15	103	1015	300	36.68
T20-1	225	10	6.97	6	102	1025	10	4.39
T20-2	225	10	6.97	6	102	1025	30	16.85
T20-3	225	10	6.97	6	102	1025	60	19.10
T20-4	225	10	6.97	6	102	1025	150	24.70
T20-5	225	10	6.97	6	102	1025	300	25.77

Appendix 3 (cont.)

Operating Conditions and Sorbent Conversions in Kinetic Tests

Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (°F)	GC (PPMV)	RT (SEC)	CNV (%)
T23-1	300	5	7.07	1.5	103	1015	10	4.85
T23-2	300	5	7.07	1.5	103	1015	30	8.82
T23-3	300	5	7.07	1.5	103	1015	60	10.38
T23-4	300	5	7.07	1.5	103	1015	150	9.75
T23-5	300	5	7.07	1.5	103	1015	300	14.33
T27-1	400	10	6.95	0.40	102	1045	10	4.76
T27-2	400	10	6.95	0.40	102	1045	30	7.65
T27-3	400	10	6.95	0.40	102	1045	60	8.90
T27-4	400	10	6.95	0.40	102	1045	150	9.65
T27-5	400	10	6.95	0.40	102	1045	300	12.98
T13-1	175	10	9.9	25	115	1030	10	10.22
T13-2	175	10	9.9	25	115	1030	30	26.76
T13-3	175	10	9.9	25	115	1030	60	48.82

Appendix 3 (cont.)

Operating Conditions and Sorbent Conversions in Kinetic Tests

Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (°F)	GC (PPMV)	RT (SEC)	CNV (%)
T13-4	175	10	9.9	25	115	1030	150	83.30
T13-5	175	10	9.9	25	115	1030	300	94.2
T17-1	200	6	9.81	15	115	1035	10	10.02
T17-2	200	6	9.81	15	115	1035	30	16.91
T17-3	200	6	9.81	15	115	1035	60	22.7
T17-4	200	6	9.81	15	115	1035	150	36.16
T17-5	200	6	9.81	15	115	1035	300	44.70
T19-1	225	10	10.05	8	116	1024	10	8.94
T19-2	225	10	10.05	8	116	1024	30	14.34
T19-3	225	10	10.05	8	116	1024	60	17.44
T19-4	225	10	10.05	8	116	1024	150	27.15
T19-5	225	10	10.05	8	116	1024	300	32.76
T22-1	300	5	9.63	2.2	114	1010	10	-

Appendix 3 (cont.)

Operating Conditions and Sorbent Conversions in Kinetic Tests

Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (°F)	GC (PPMV)	RT (SEC)	CNV (%)
T22-2	300	5	9.63	2.2	114	1010	30	8.13
T22-3	300	5	9.63	2.2	114	1010	60	12.82
T22-4	300	5	9.63	2.2	114	1010	150	13.51
T22-5	300	5	9.63	2.2	114	1010	300	17.10
T26-1	400	10	10.33	0.6	117	1020	10	4.70
T26-2	400	10	10.33	0.6	117	1020	30	8.35
T26-3	400	10	10.33	0.6	117	1020	60	9.08
T26-4	400	10	10.33	0.6	117	1020	150	10.38
T26-5	400	10	10.33	0.6	117	1020	300	11.19
T12SP-1	175	5	19.57	45	141	1070	10	20.03
T12SP-2	175	5	19.57	45	141	1070	30	40.48
T12SP-3	175	5	19.57	45	141	1070	60	63.89
T12SP-4	175	5	19.57	45	141	1070	100	85.18

Appendix 3 (cont.)

Operating Conditions and Sorbent Conversions in Kinetic Tests

Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (°F)	GC (PPMV)	RT (SEC)	CNV (%)
T12SP-4	175	5	19.57	45	141	1070	150	89.58
T12SP-5	175	5	19.57	45	141	1070	300	100.0
T12-1	200	6	19.4	15	139	1025	10	8.96
T12-2	200	6	19.4	15	139	1025	30	35.26
T12-3	200	6	19.4	15	139	1025	60	55.3
T12-4	200	6	19.4	15	139	1025	150	72.89
T12-5	200	6	19.4	15	139	1025	300	97.3
T16-1	225	6	19.57	15	141	1030	10	8.88
T16-2	225	6	19.57	15	141	1030	30	13.40
T16-3	225	6	19.57	15	141	1030	60	18.8
T16-4	225	6	19.57	15	141	1030	150	36.34
T16-5	225	6	19.57	15	141	1030	300	44.52
T21-1	300	10	19.24	4.5	140	1040	10	7.77
T21-2	300	10	19.24	4.5	140	1040	30	

Appendix 3 (cont.)

Operating Conditions and Sorbent Conversions in Kinetic Tests

Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (°F)	GC (PPMV)	RT (SEC)	CNV (%)
T21-3	300	10	19.24	4.5	140	1040	60	24.01
T21-4	300	10	19.24	4.5	140	1040	150	23.3
T21-5	300	10	19.24	4.5	140	1040	300	30.31
T24-1	400	6	19.3	1.1	140	1025	10	5.44
T24-2	400	6	19.3	1.1	140	1025	30	10.32
T24-3	400	6	19.3	1.1	140	1025	60	11.39
T24-4	400	6	19.3	1.1	140	1025	150	13.98
T24-5	400	6	19.3	1.1	140	1025	300	16.72
T11-1	225	5	30.3	25	158	1030	10	7.15
T11-2	225	5	30.3	25	158	1030	30	22.23
T11-3	225	5	30.3	25	158	1030	60	38.36
T11-4	225	5	30.3	25	158	1030	150	80.72
T11-5	225	5	30.3	25	158	1030	300	91.52

Appendix 3 (cont.)

Operating Conditions and Sorbent Conversions in Kinetic Tests

Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (°F)	GC (PPMV)	RT (SEC)	CNV (%)
M13-1	175	5	10.37	25	116	530	10	10.82
M13-2	175	5	10.37	25	116	530	60	20.02
M13-3	175	5	10.37	25	116	530	150	60.2
M13-4	175	5	10.37	25	116	530	300	82.53
M13-5	175	5	10.37	25	116	530	600	98.8
M17-1	200	6	10.37	15	116	530	10	5.05
M17-2	200	6	10.37	15	116	530	60	20.47
M17-3	200	6	10.37	15	116	530	150	23.83
M17-4	200	6	10.37	15	116	530	300	37.25
M17-5	200	6	10.37	15	116	530	300	46.61
M19-1	225	10	10.23	8	115	520	10	5.51
M19-2	225	10	10.23	8	115	520	60	21.3
M19-3	225	10	10.23	8	115	520	150	18.43

Appendix 3 (cont.)

Operating Conditions and Sorbent Conversions in Kinetic Tests

Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (°F)	GC (PPMV)	RT (SEC)	CNV (%)
M19-4	225	10	10.23	8	115	520	300	23.66
M19-5	225	10	10.23	8	115	520	600	25.68
M22-1	300	10	9.86	2.2	114	501	10	5.09
M22-2	300	10	9.86	2.2	114	501	60	9.12
M22-3	300	10	9.86	2.2	114	501	150	10.53
M22-4	300	10	9.86	2.2	114	501	300	14.39
M22-5	300	10	9.86	2.2	114	501	600	16.28
H13-1	175	6	9.97	25	115	4961	10	36.32
H13-2	175	6	9.97	25	115	4961	60	82.27
H13-3	175	6	9.97	25	115	4961	150	97.35
H13-4	175	6	9.97	25	115	4961	300	100.0
H17-1	200	6	10.05	15	115	5030	10	26.2
H17-2	200	6	10.05	15	115	5030	60	43.15

Appendix 3 (cont.)

Operating Conditions and Sorbent Conversions in Kinetic Tests											
Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (%)	GC (°F)	(PPMV)	RT (SEC)	CNV (%)		
H17-3	200	6	10.05	15	115	5030	150	46.68			
H17-4	200	6	10.05	15	115	5030	300	56.28			
H19-1	225	8	10.06	8	115	4960	10	17.07			
H19-2	225	8	10.06	8	115	4960	60	28.80			
H19-3	225	8	10.06	8	115	4960	150	34.94			
H19-4	225	8	10.06	8	115	4960	300	33.54			
H22_1-1	300	10	10.02	2.2	115	15230	30	13.2			
H22_1-2	300	10	10.02	2.2	115	15230	100	13.18			
H22_1-3	300	10	10.02	2.2	115	15230	300	15.5			
H22_1-4	300	10	10.02	2.2	115	15230	600	19.42			
H22_2-1	300	6	9.85	2.2	115	8035	30	14.17			
H22_2-2	300	6	9.85	2.2	115	8035	100	16.75			
H22_2-3	300	6	9.85	2.2	115	8035	300	17.47			
H22_2-4	300	6	9.85	2.2	115	8035	600	21.26			

Appendix 3 (cont.)

Operating Conditions and Sorbent Conversions in Kinetic Tests

Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (°F)	GC (PPMV)	RT (SEC)	CNV (%)
H22_3-1	300	6	10.05	2.2	115	5030	30	13.5
H22_3-2	300	6	10.05	2.2	115	5030	100	15.52
H22_3-3	300	6	10.05	2.2	115	5030	300	16.76
H22_3-4	300	6	10.05	2.2	115	5030	600	18.97
S12SP-1	175	10	19.84	45	143	1025	10	16.4
S12SP-2	175	10	19.84	45	143	1025	60	68.2
S12SP-3	175	10	19.84	45	143	1025	150	92.3
S12SP-4	175	10	19.84	45	143	1025	300	100.0
S19-1	225	10	10.02	8	143	1015	10	9.52
S19-2	225	10	10.02	8	143	1015	60	25.33
S19-3	225	10	10.02	8	143	1015	150	29.93
S19-4	225	10	10.02	8	143	1015	300	44.93
S26-1	400	5	10.01	0.6	140	1040	10	9.04

Appendix 3 (cont.)

Operating Conditions and Sorbent Conversions in Kinetic Tests

Test ID	RXT (°F)	RXP (INWG)	MC (%)	RH (%)	DP (°F)	GC (PPMV)	RT (SEC)	CNV (%)
S26-2	400	5	10.01	0.6	140	1040	10	17.3
S26-3	400	5	10.01	0.6	140	1040	10	21.34
S26-4	400	5	10.01	0.6	140	1040	10	23.13

Legend :

RXT - Reaction temperature
 RXP - Reactor Pressure
 MC - Moisture content of the test gas
 CNV - Sorbent conversion in the test
 RH - Relative humidity of the test
 GC - Gas concentration of the test
 RT - Reaction time of the test
 DP - Dew point temperature of test

APPENDIX - 4

Appendix 4

Parameters of Best Fit Equations for Kinetic Tests

Test ID	Temperature (°F)	Moisture content (% v/v)	Relative humidity (%)	Gas concn. (ppmv)	A	B	R
NM175	175	0	0	1000	4	131	0.971
NM200	200	0	0	1000	4.15	115	0.985
NM225	225	0	0	1000	5.4	60	0.997
NM300	300	0	0	1000	8.75	80	0.982
NM400	400	0	0	1000	13.5	53	0.991
T15	175	3.2	8	1000	28	75	0.953
T14	175	7	15	1000	33	61	0.969
T18	200	7	8	1000	38	88	0.961
T20	225	7	6	1000	26.2	46	0.982
T23	300	7	1.5	1000	12	53	0.851
T27	400	7	0.40	1000	11/5	35	0.948
T13	175	10	25	1000	100	93	0.999
T17	200	10	15	1000	45	70	0.983
T19	225	10	8	1000	31	53	0.975

Appendix 4 (Cont.)

Parameters of Best Fit Equations for Kinetic Tests

Test ID	Temperature (°F)	Moisture content (% v/v)	Relative humidity (%)	Gas concn. (ppmv)	A	B	R
T22	300	10	2.2	1000	16.5	57	0.881
T26	400	10	0.6	1000	11.2	90	0.973
T12SP	175	20	45	1000	98	53	0.998
T12	200	20	25	1000	90	83	0.987
T16	225	20	15	1000	42	58	0.989
T21	300	20	4.5	1000	32	70	0.944
T24	400	20	1.1	1000	16	40	0.969
T11	225	30	25	1000	100	97	0.992
M13	175	10	25	500	97	165	0.992
M17	200	10	15	500	45	140	0.969
M19	225	10	8	500	24.5	60	0.932
M22	300	10	2.2	500	15.2	50	0.946

Appendix 4 (Cont.)

Parameters of Best Fit Equations for Kinetic Tests

Test ID	Temperature (°F)	Moisture content (% v/v)	Relative humidity (%)	Gas concn. (ppmv)	A	B	R
H13	175	10	25	5000	98	25	0.987
H17	200	10	15	5000	52	28	0.996
H19	225	10	8	5000	35.5	25	0.974
H22_1	300	10	2.2	15000	16	21	0.999
H22_2	300	10	2.2	8000	19.7	26	0.969
H22_2	300	10	2.2	5000	17	45	0.981
S12SP*	175	20	45	1000	96	38	0.958
S19*	225	10	8	1000	39	50	0.989
S26*	400	10	0.6	1000	22.7	40	0.992

APPENDIX - 5

Appendix 5

Operating Conditions and Results in Product Analyses Tests

Test ID	RXT (°F)	MC (%)	RH (%)	GC (PPMV)	RT (MIN)	CNV (%)	AP (%)	APA (%)	WC (mg/g)
TLNM200	200	0	0	1000	10	3.33	88.8	92.85	4.64
TLNM200	200	0	0	1000	20	3.75	94.55	92.16	4.46
TLNM200	200	0	0	1000	60	6.11	92.1	-	3.74
TL200	200	10	15	1000	10	22.74	65.23	54.88	45.6
TL200	200	10	15	1000	20	38.60	43.41	39.44	81.8
TL200	200	10	15	1000	60	47.26	40.58	23.62	98.68
TL175	175	10	25	1000	5	27.0	69.52	51.73	78.23
TL175	175	10	25	1000	15	60.0	41.64	31.31	113.24
TL175	175	10	25	1000	45	92.26	13.02	7.23	250.0
TL400	400	10	0.6	1000	5	5.51	96.7	96.88	7.26
TL400	400	10	0.6	1000	15	9.49	79.11	-	10.80
TL400	400	10	0.6	1000	45	15.81	85.55	91.15	26.49

Appendix 5 (cont)

Operating Conditions and Results in Product Analyses Tests

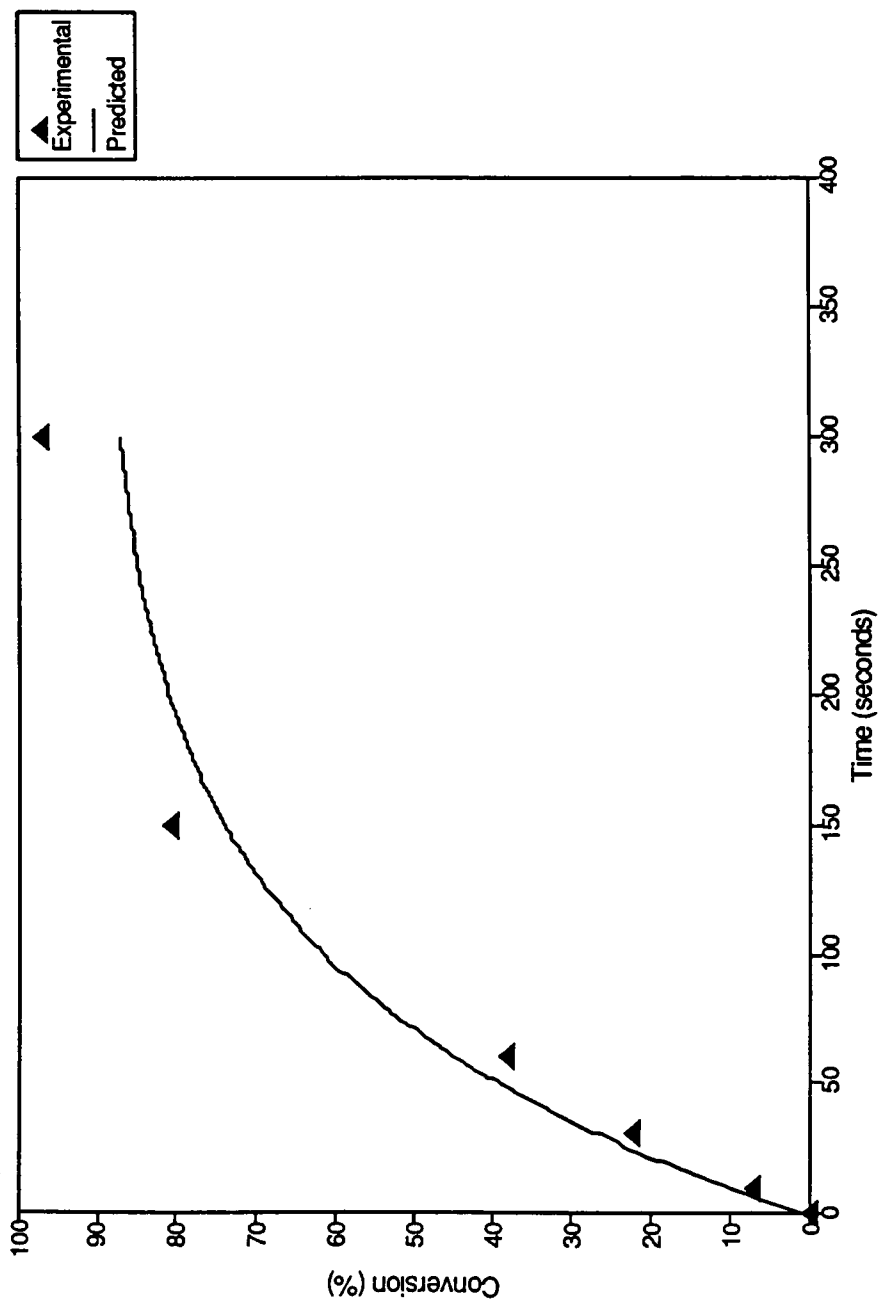
Test ID	RXT (°F)	MC (%)	RH (%)	GC (PPMV)	RT (SEC)	CNV (%)	AP (%)	APA (%)	WC (mg/g)
SC200	200	10	15	1000	10	31.62	*	*	*
SC200	200	10	15	1000	20	46.78	*	*	*
SC200	200	10	15	1000	60	58.05	*	*	*
TLPC200	200	10	15	1000	10	24.65	*	*	*
TLPC200	200	10	15	1000	60	47.02	*	*	*
LICL200	200	10	15	1000	10	28.0	*	*	*
LICL200	200	10	15	1000	60	61.9	*	*	*

Legend :

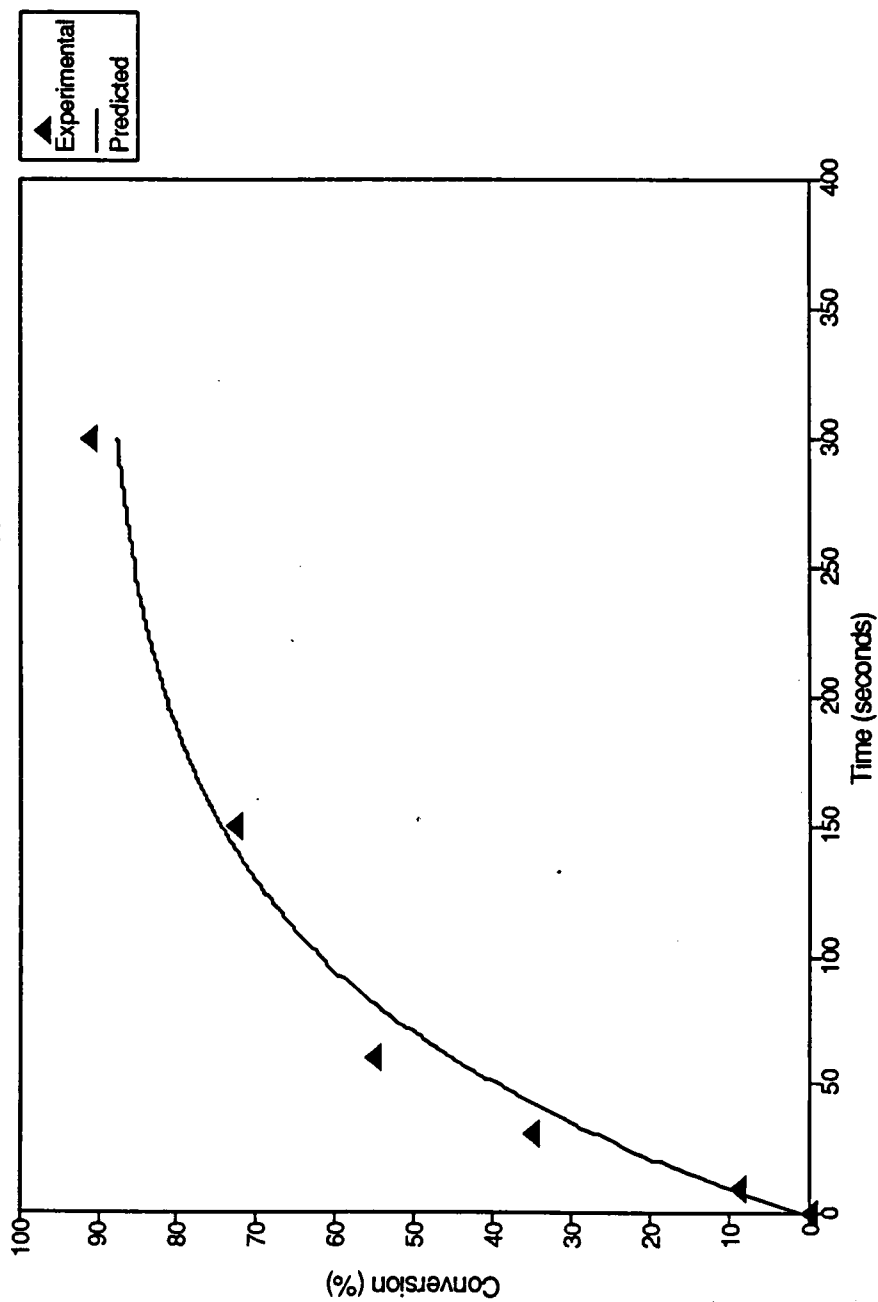
RXT - Reaction Temperature	RH - Relative Humidity of Test
MC - Moisture Content of Gas	GC - Gas Concentration of Test
RT - Reaction Time	CNV - Sorbent Conversion
RP - Available Porosity	APA - Available Pore Area
WC - Water Content of Reaction Product	* - Not Determined

APPENDIX - 6

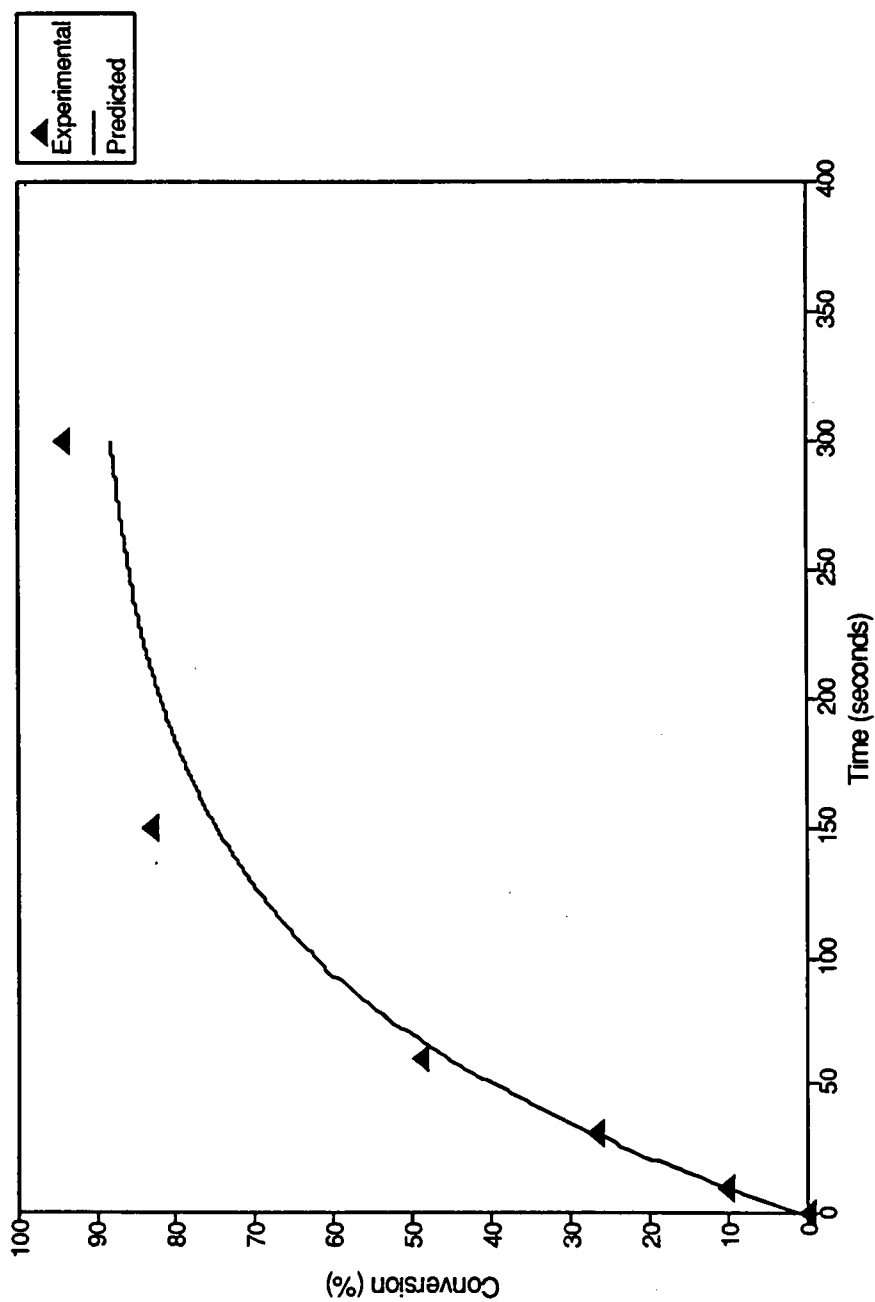
Test T11 225 F 25% RH 1000 ppmv HCl



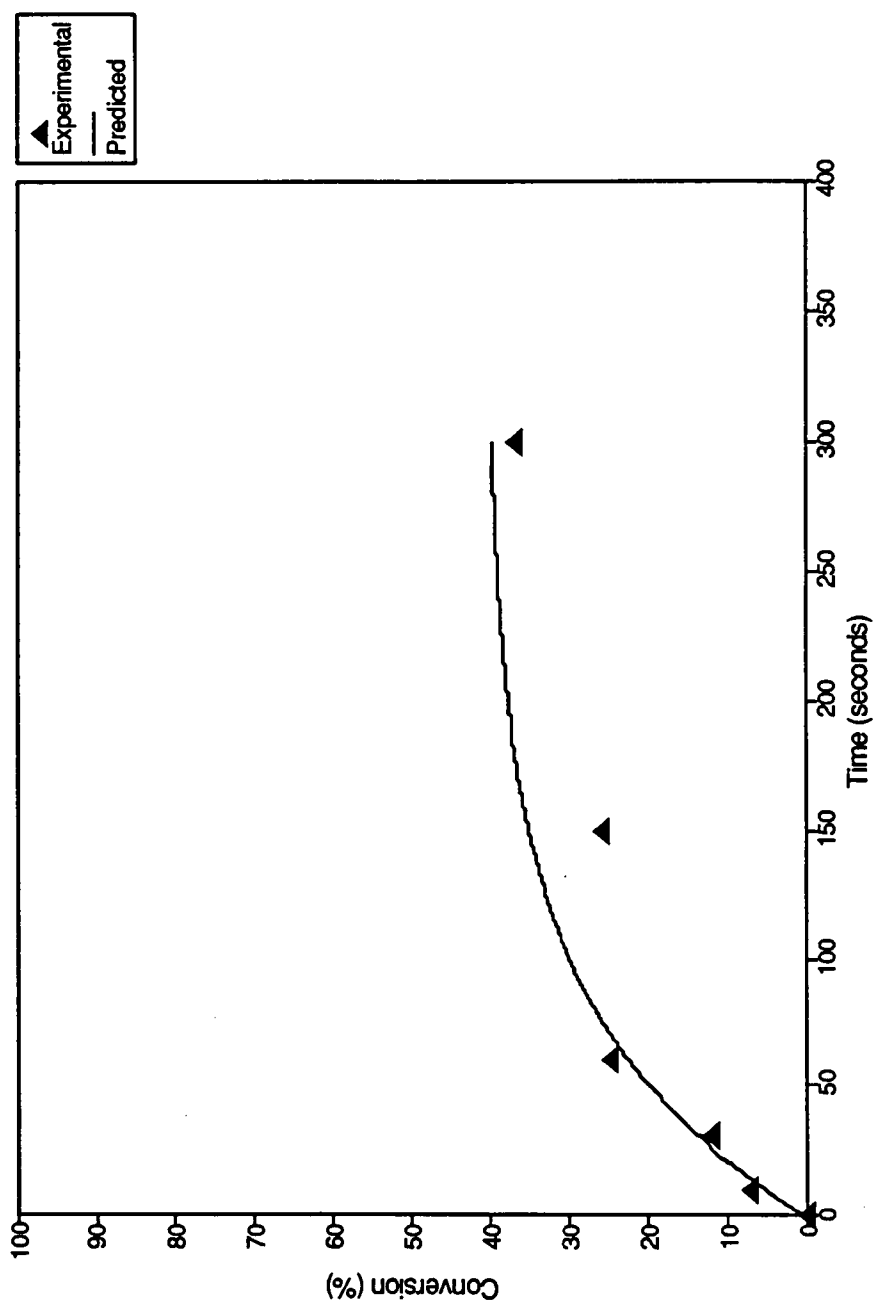
Test T12 200 F 25% RH 1000 ppmv HCl



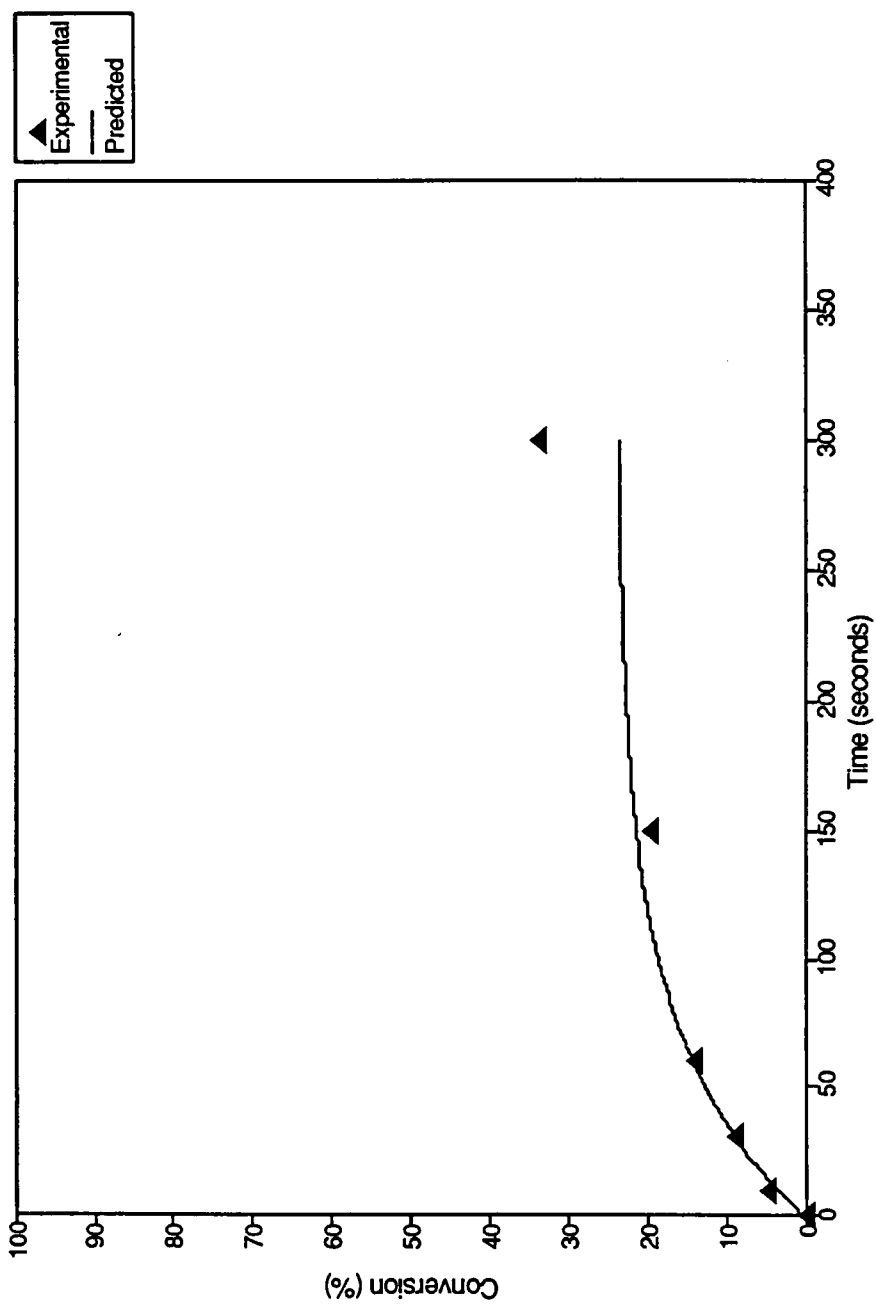
Test T13 175 F 25% RH 1000 ppmv HCl



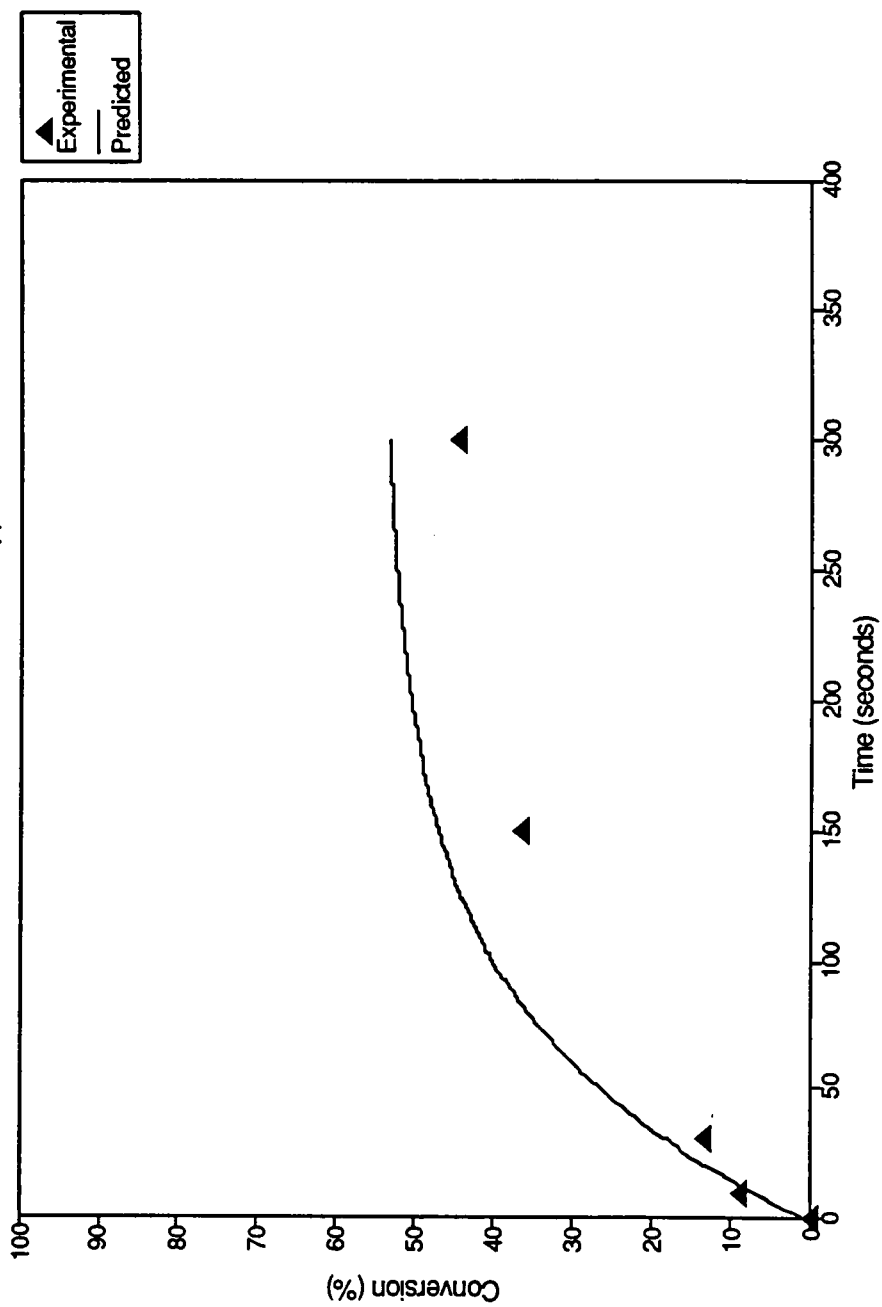
Test T14 175 F 15% RH 1000 ppmv HCl



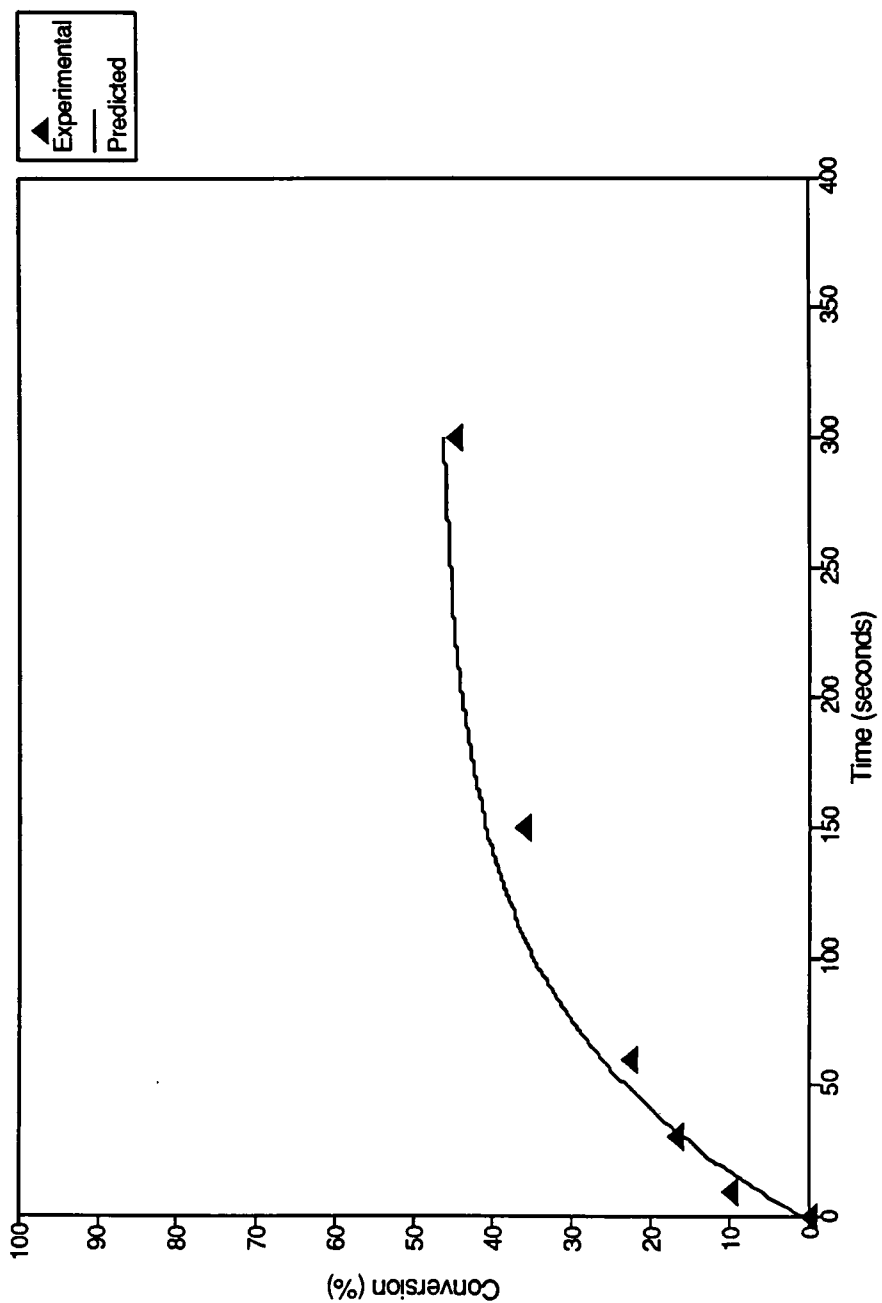
Test T15 175 F 8% RH 1000 ppmv HCl



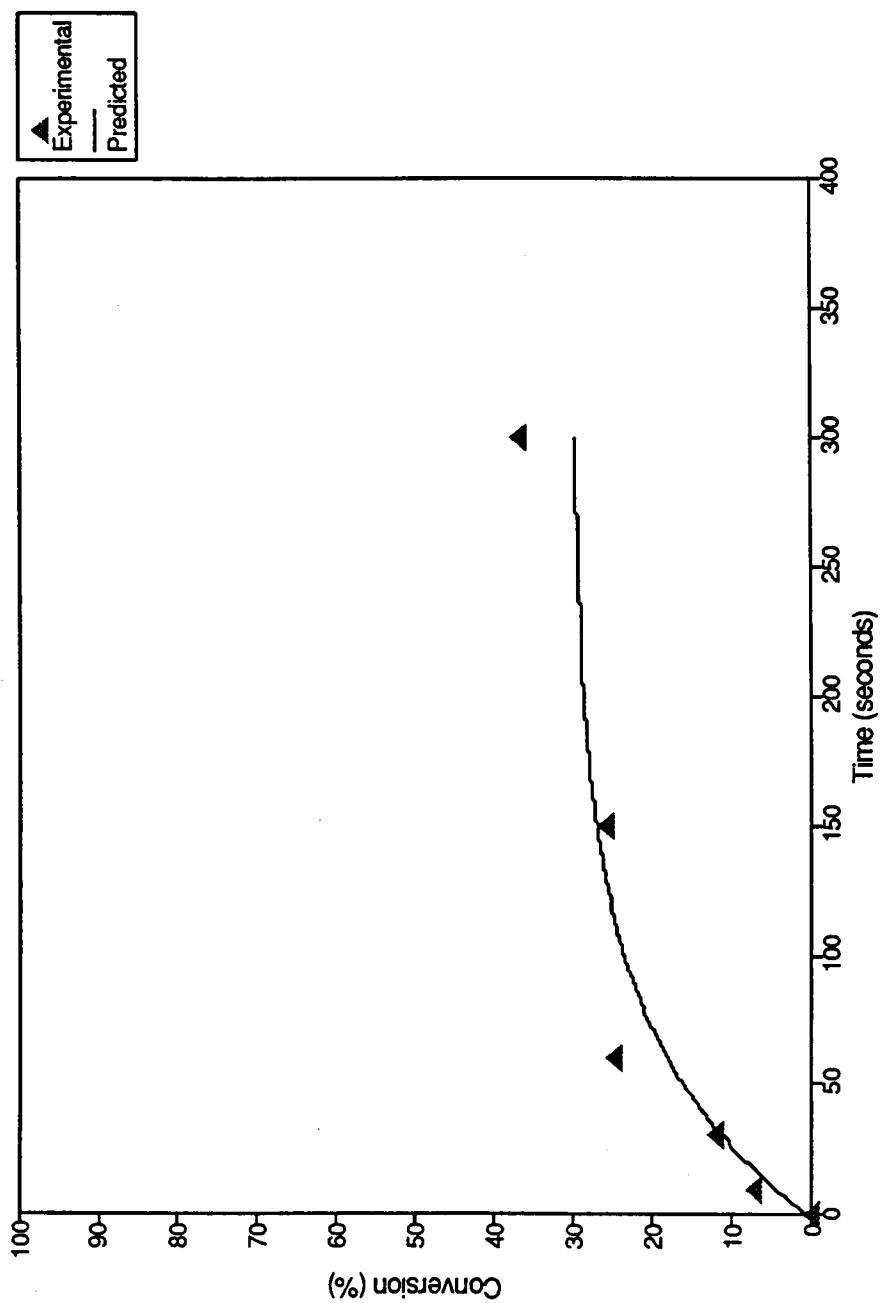
Test T16 225 F 15% RH 1000 ppmv HCl



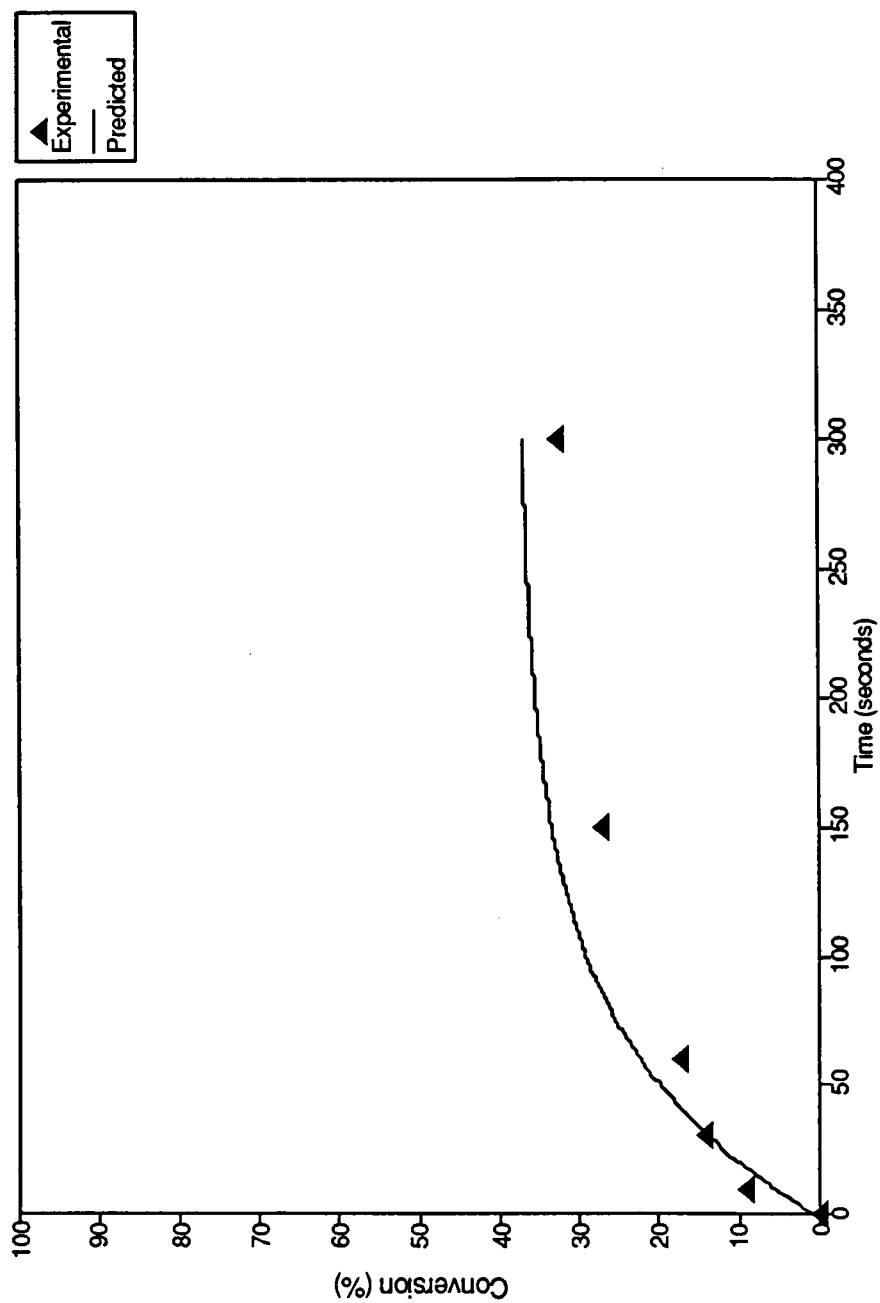
Test T17 200 F 15% RH 1000 ppmv HCl



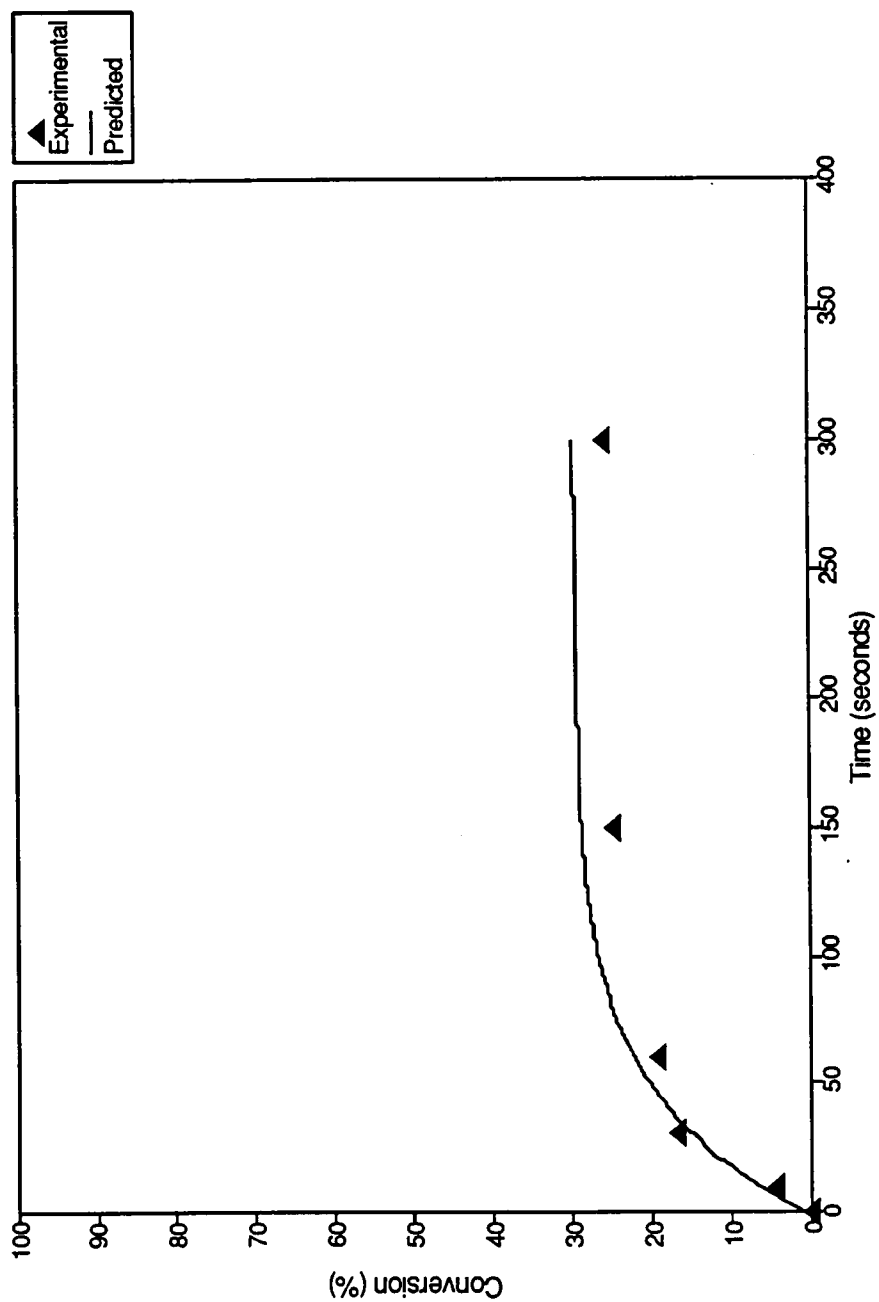
Test T18 200 F 8% RH 1000 ppmv HCl



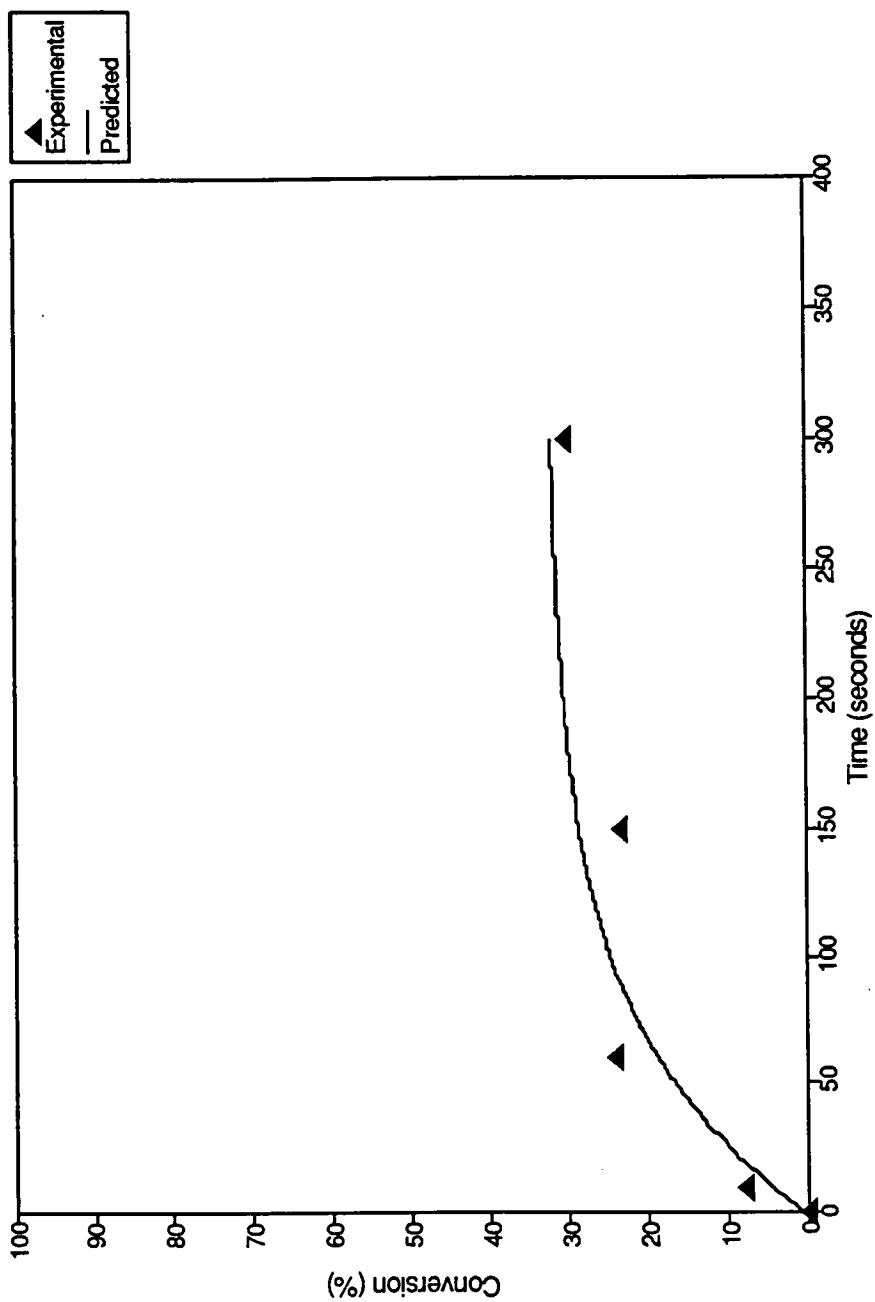
Test T19 225 F 8% RH 1000 ppmv HCl



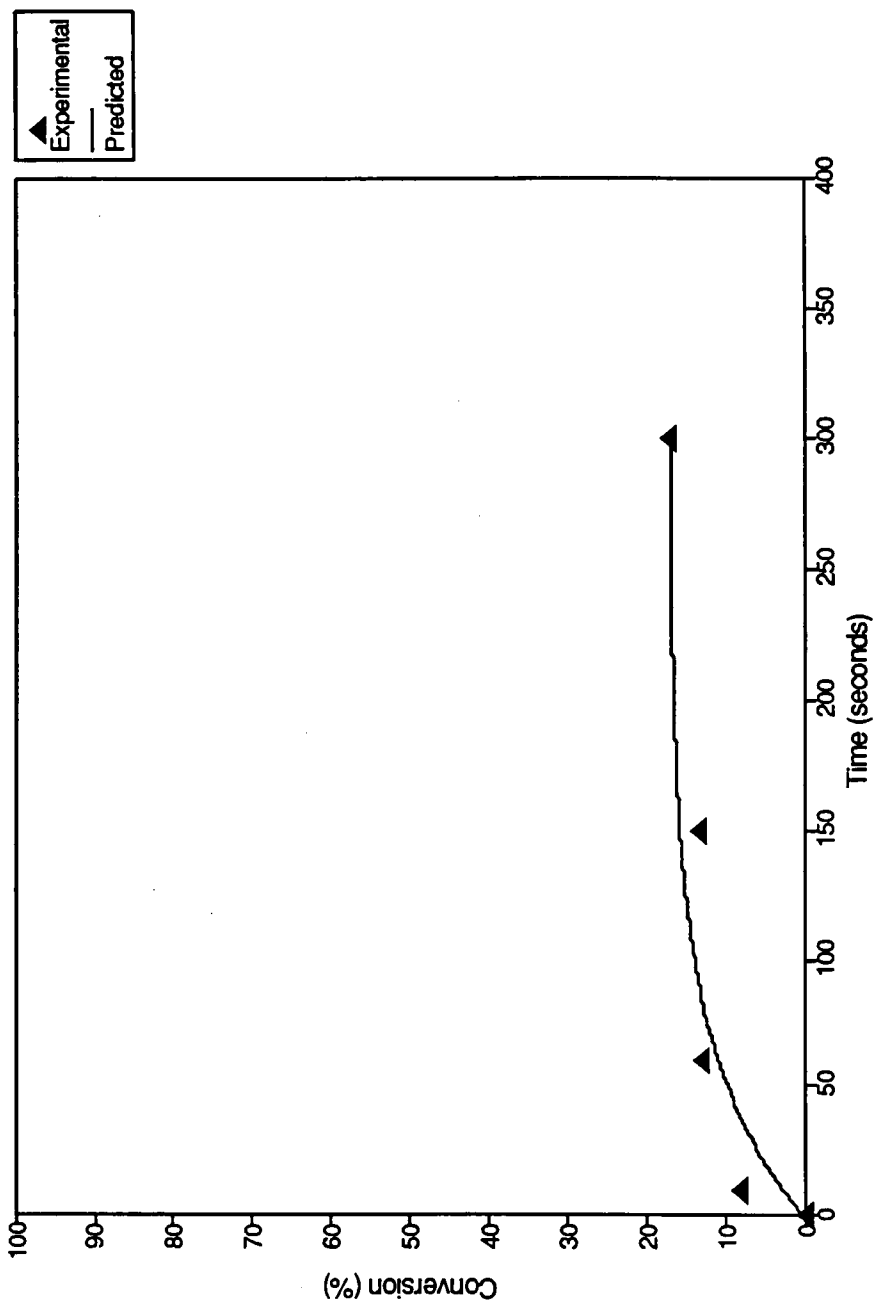
Test T20 225 F 6% RH 1000 ppmv HCl



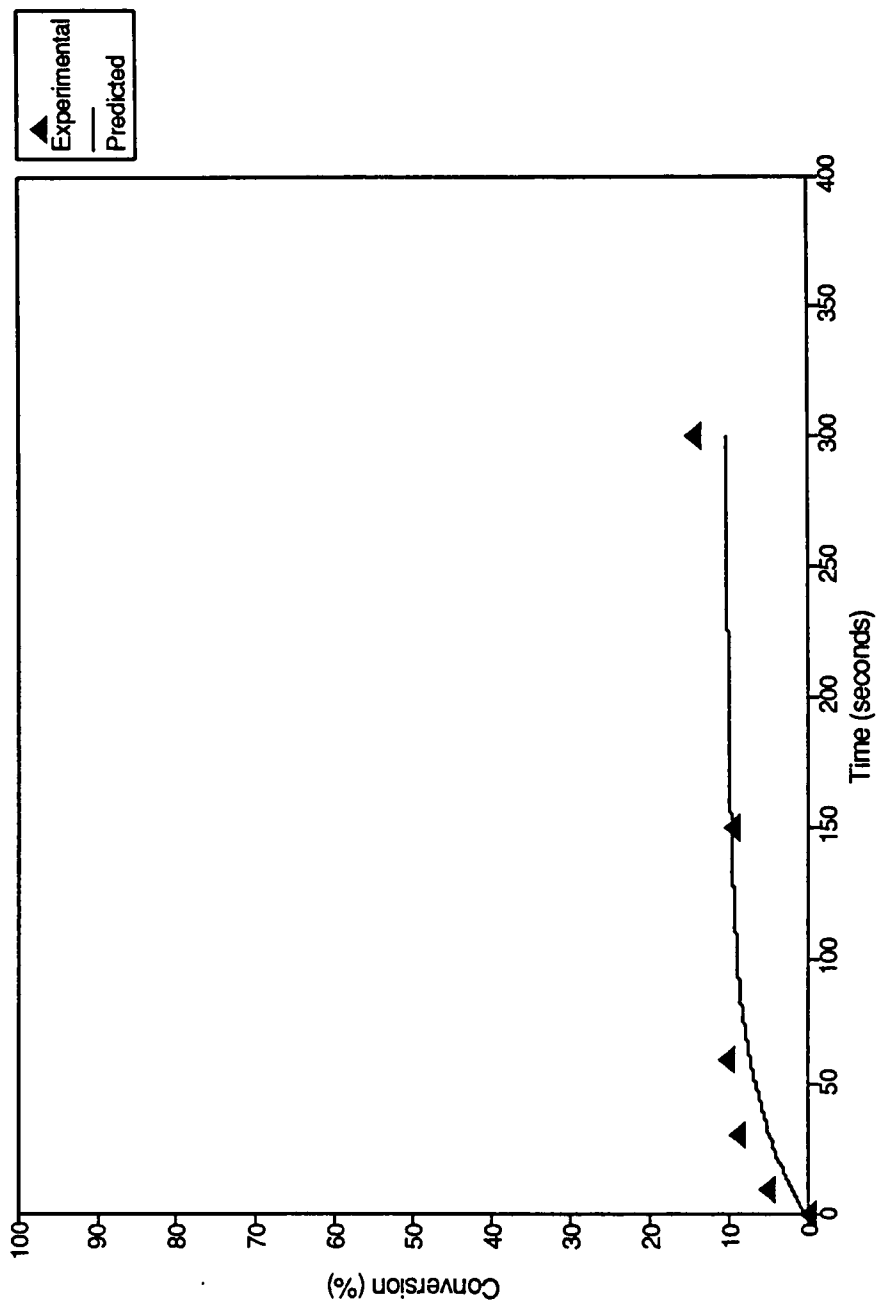
Test T21 300 F 4.5% RH 1000 ppmv HCl



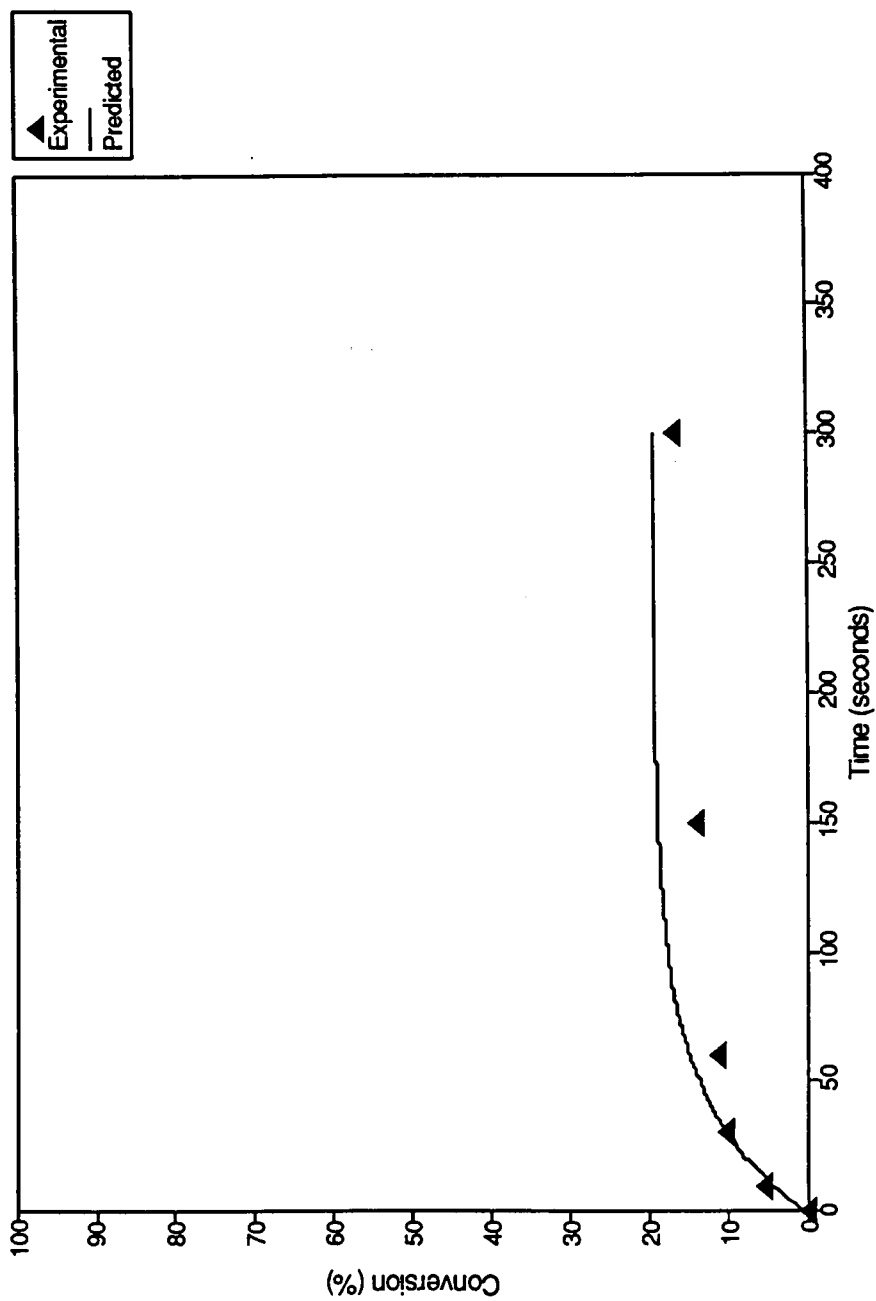
Test T22 300 F 2.2% RH 1000 ppmv HCl



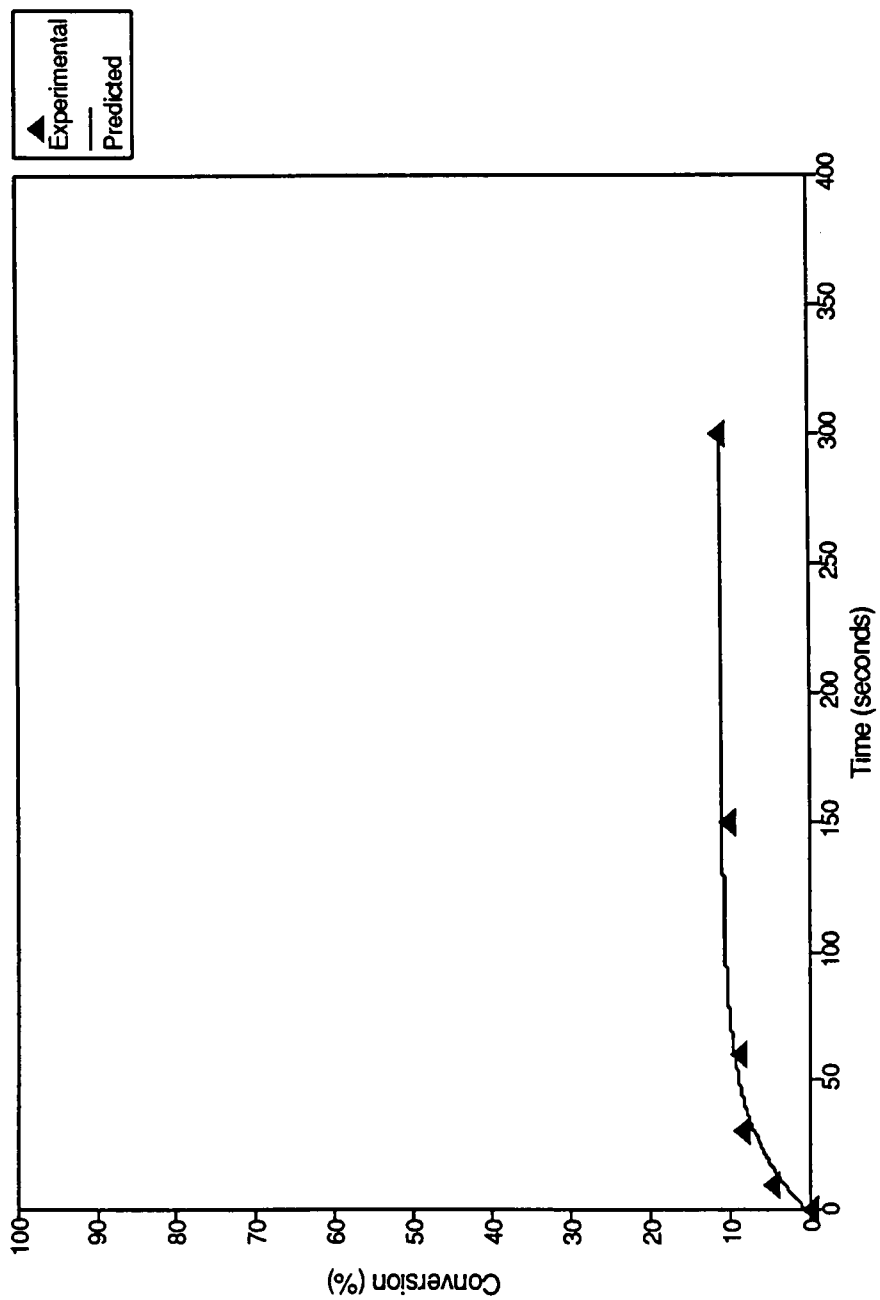
Test T23 300 F 1.1% RH 1000 ppmv HCl



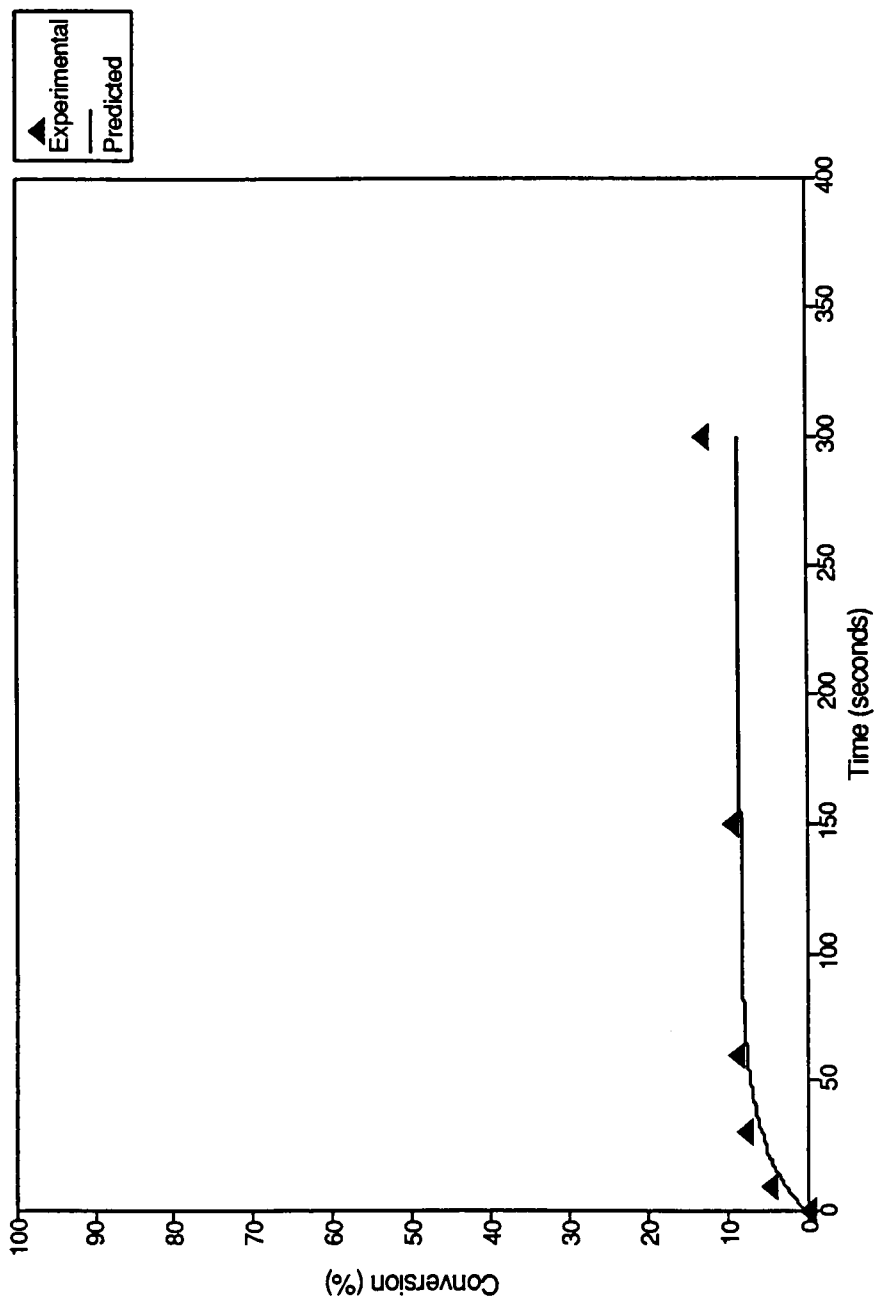
Test T24 400 F 1.1% RH 1000 ppmv HCl



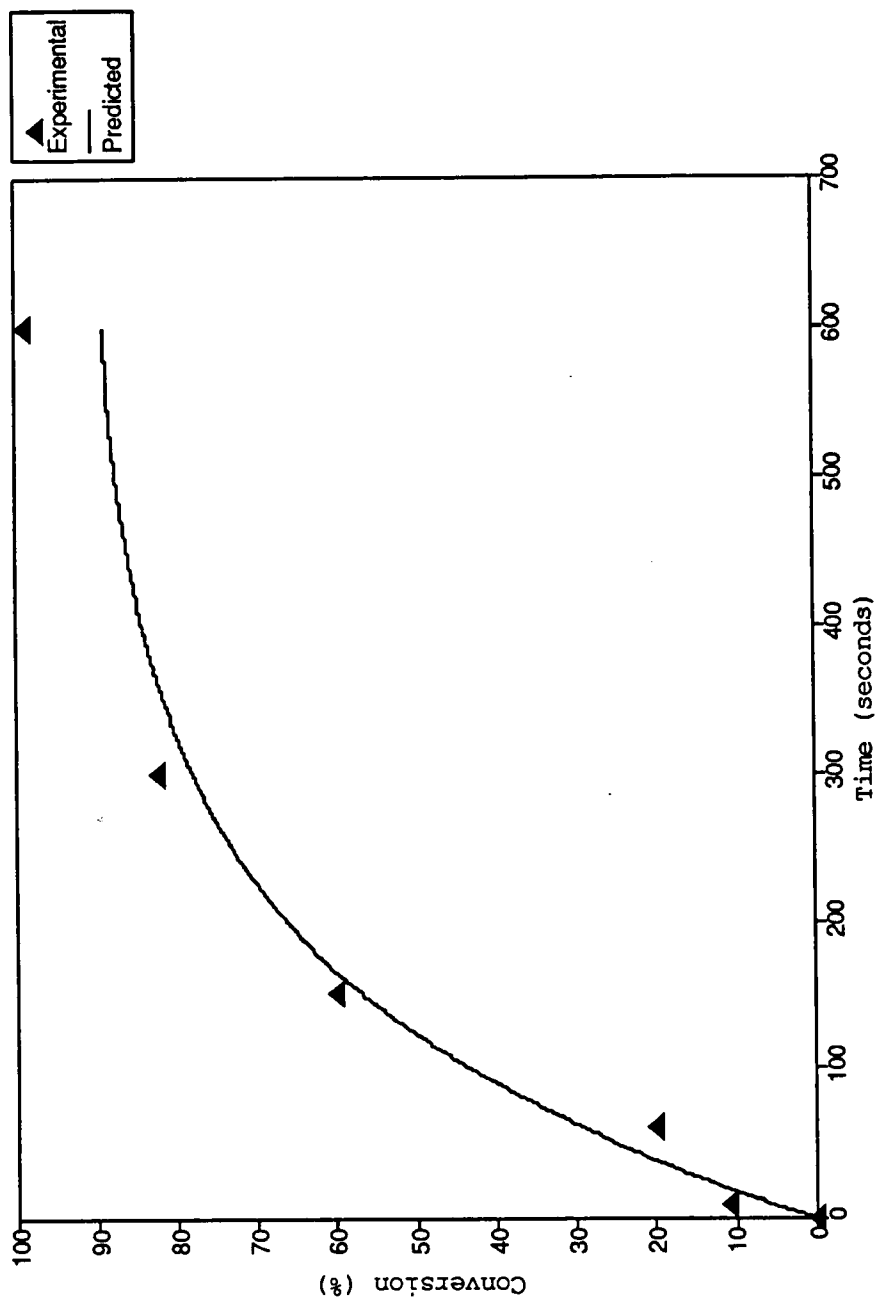
Test T26 400 F 0.6% RH 1000 ppmv HCl



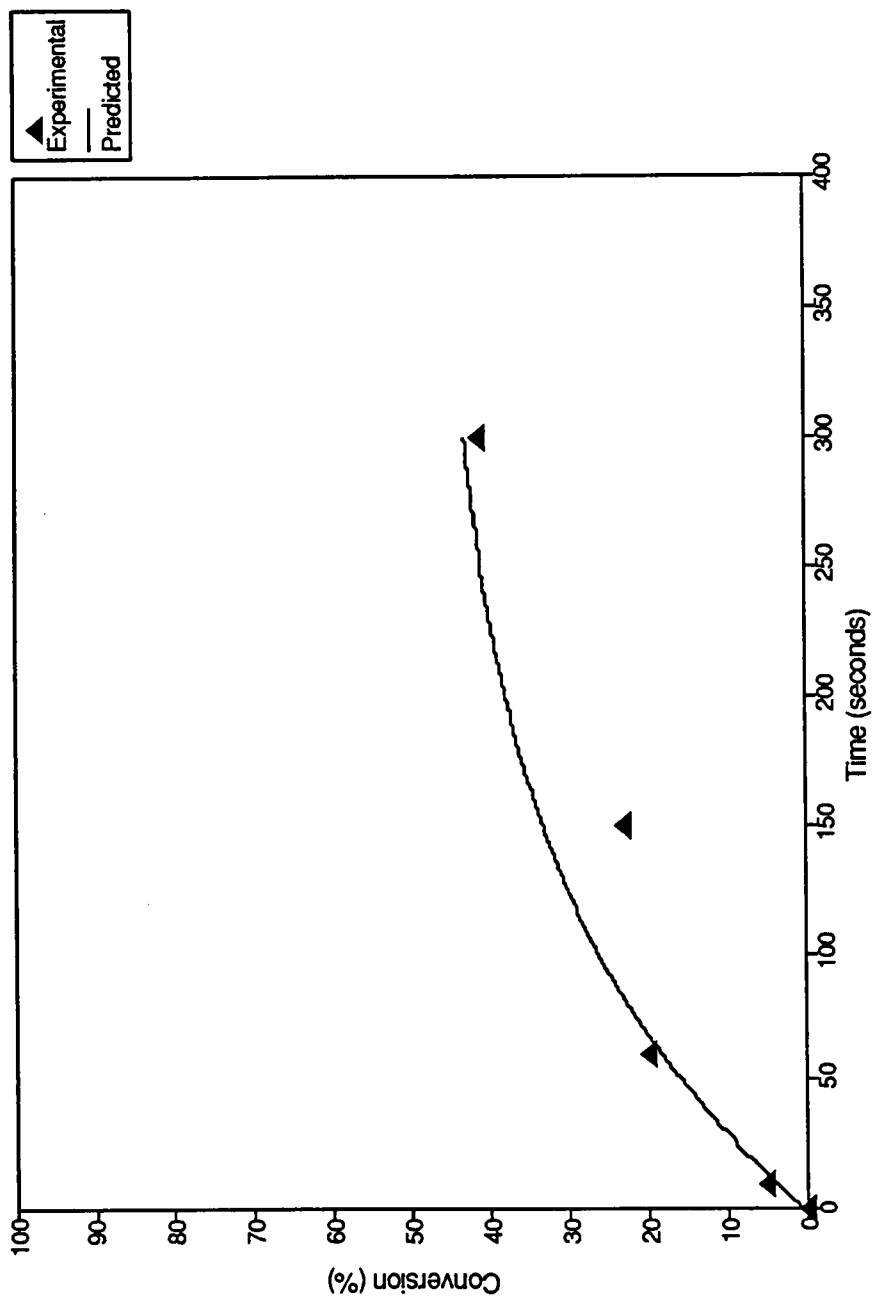
Test T27 400 F 0.4% RH 1000 ppmv HCl



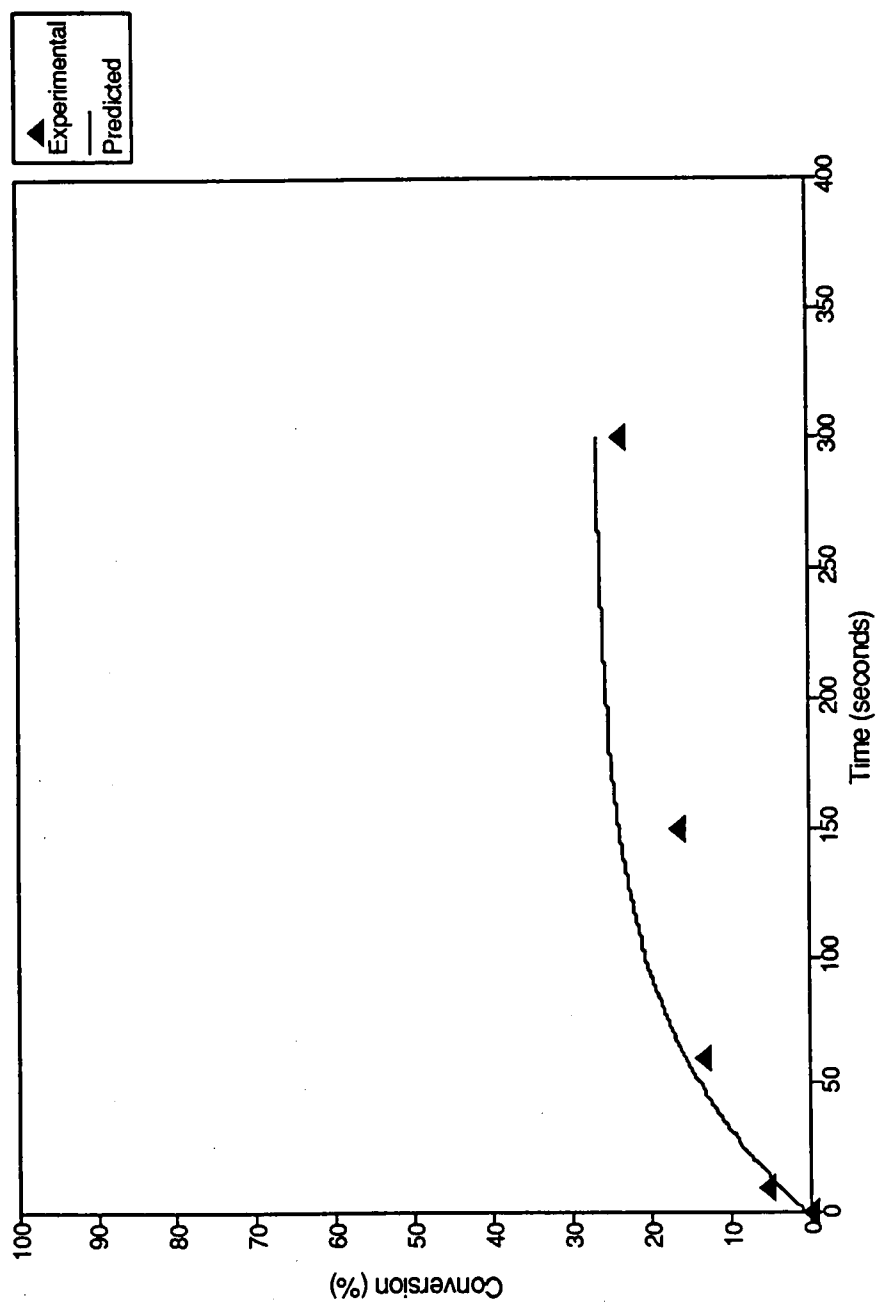
Test M13 175 F 25% RH 500 ppmv HCl



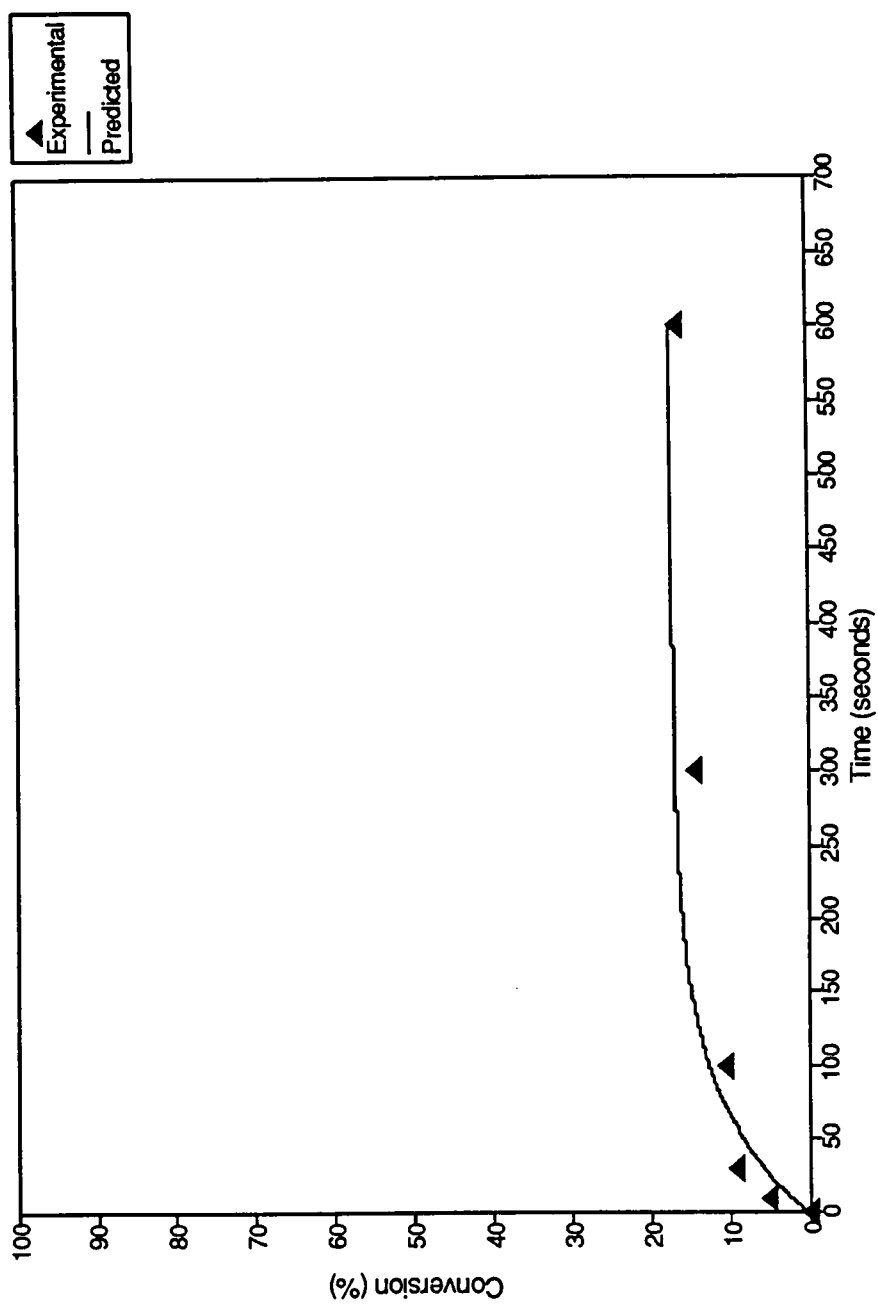
Test M17 200 F 15% RH 500 ppmv HCl

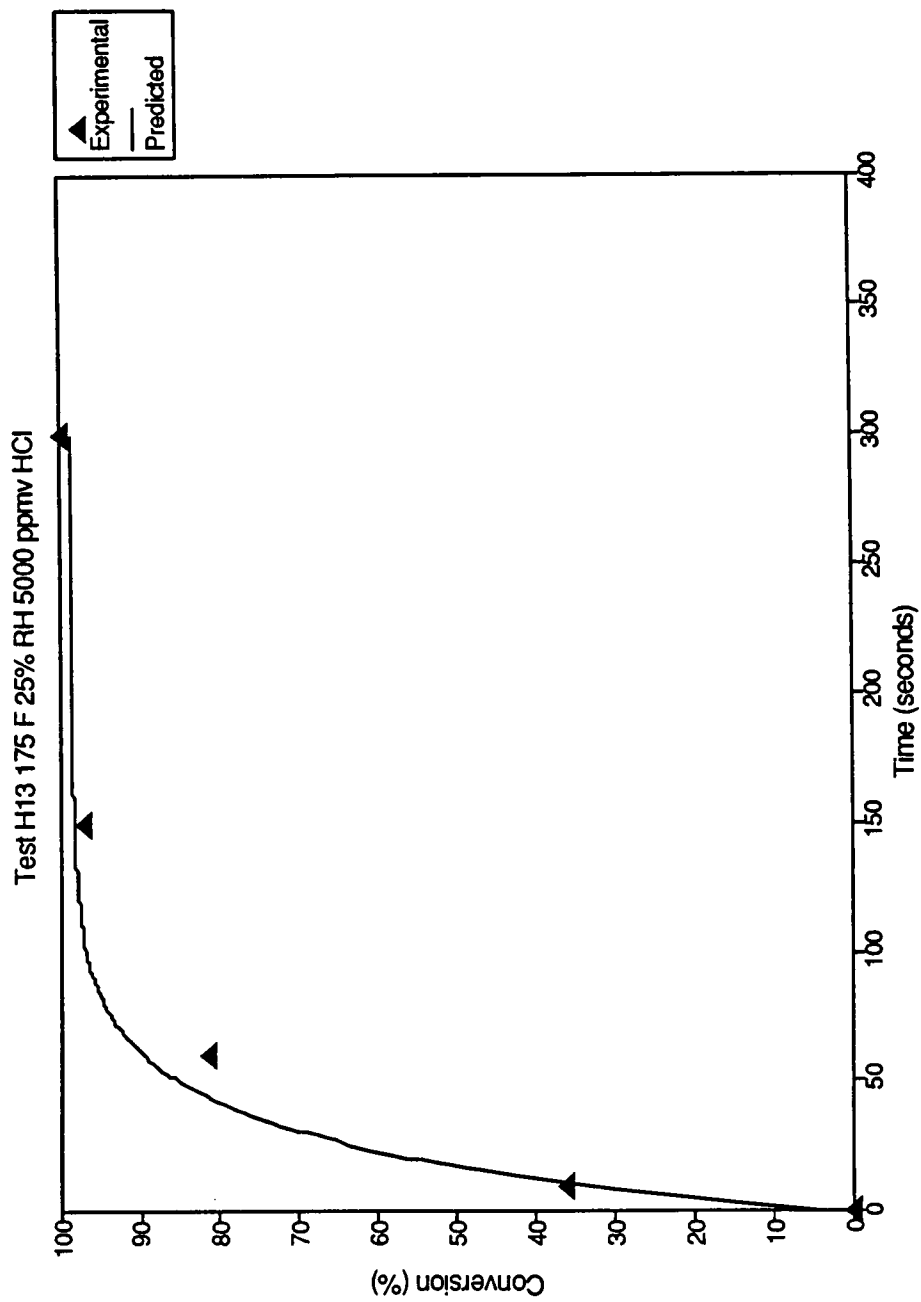


Test M19 225 F 8% RH 500 ppmv HCl

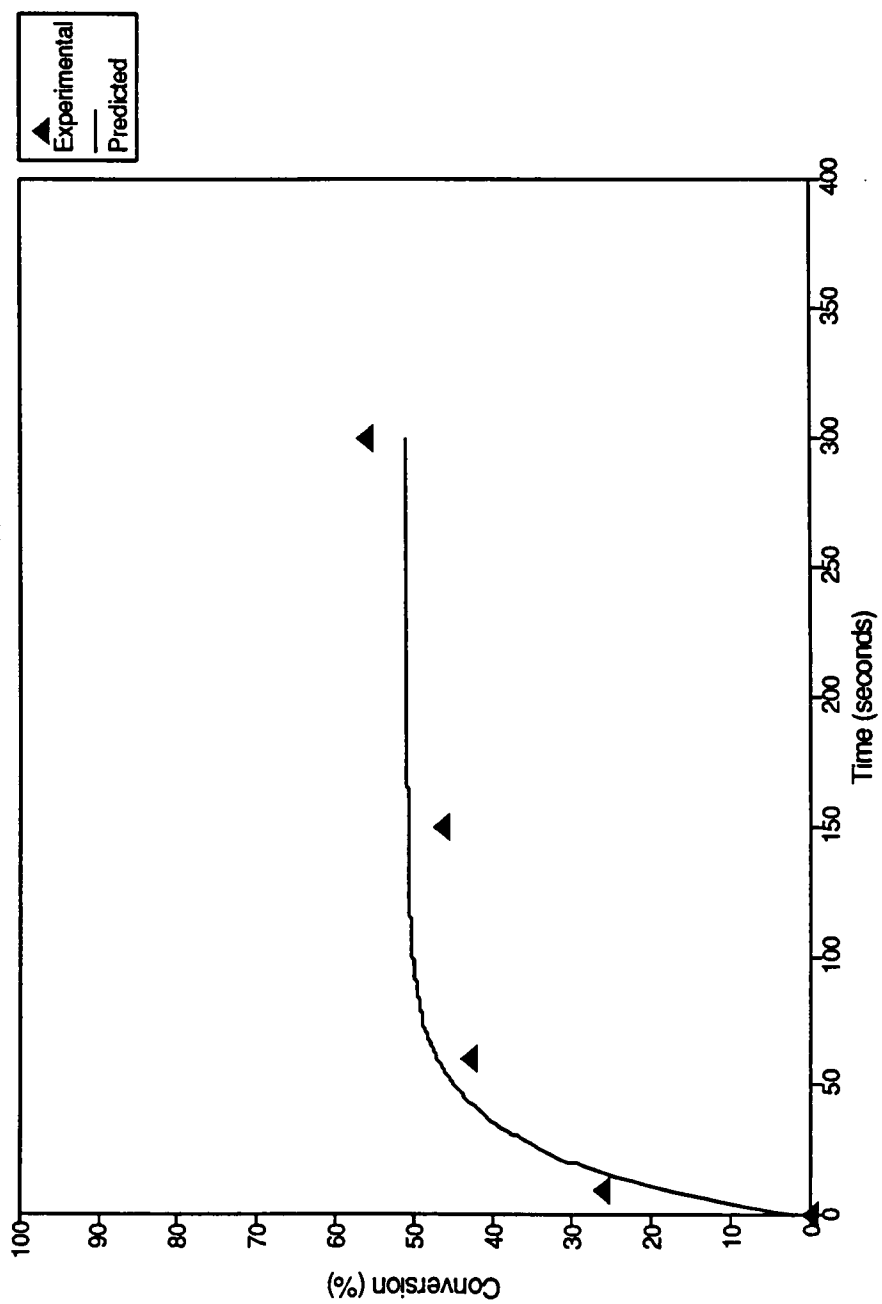


Test M22 300 F 2.2% RH 500 ppmv HCl

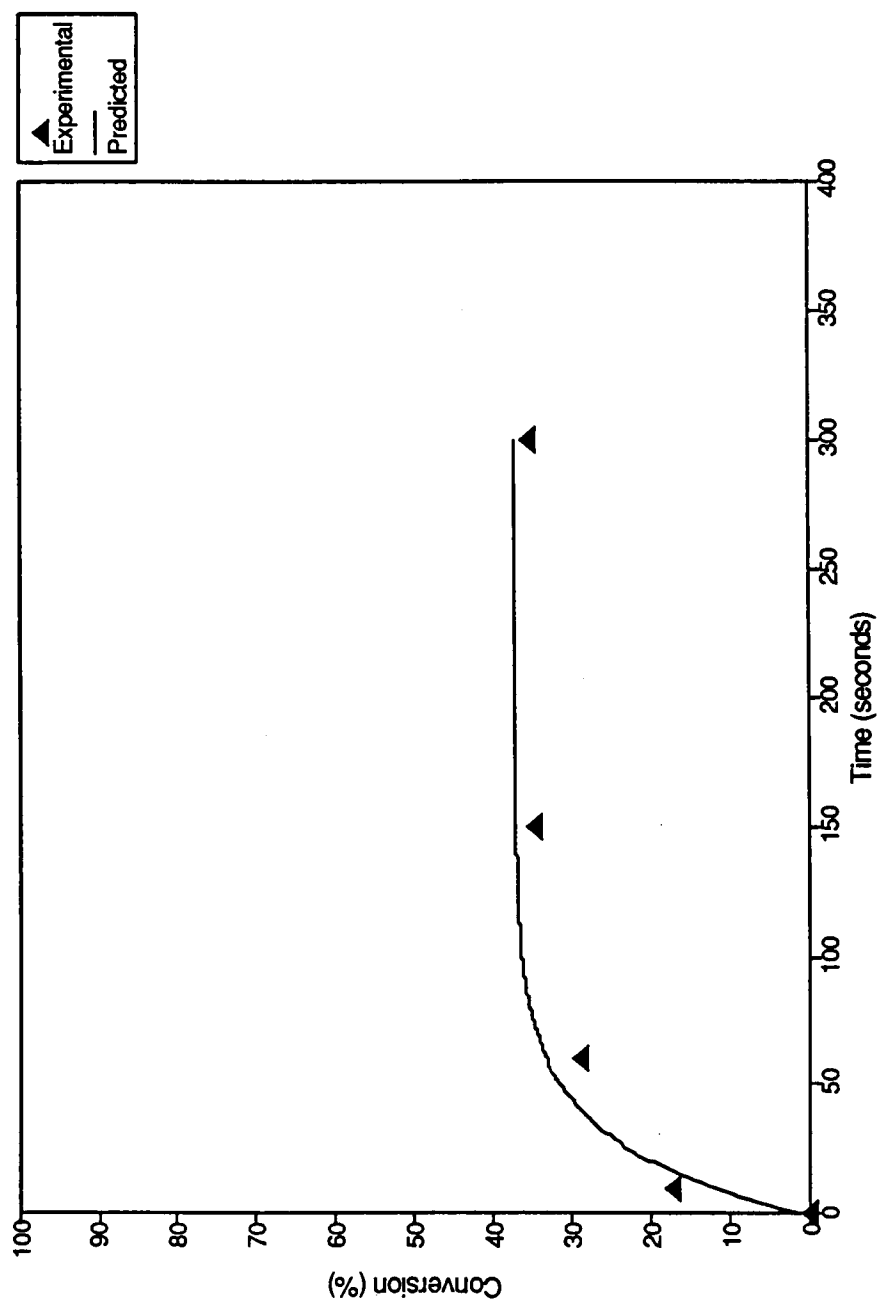




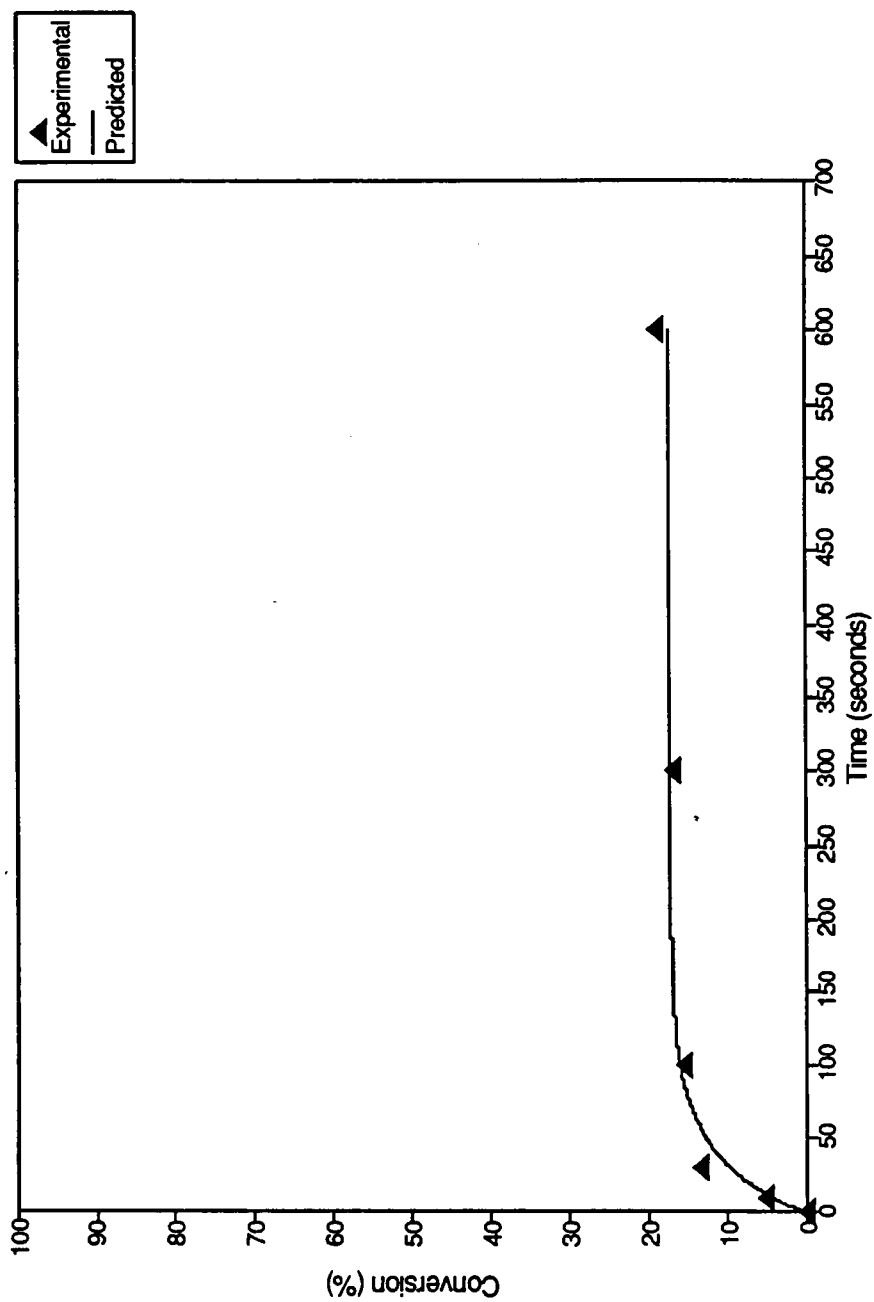
Test H17 200 F 15% RH 5000 ppmv HCl



Test H19 225 F 8% RH 5000 ppmv HCl



Test H22_3 300 F 2.2% RH 5000 ppmv HCl



VITA

Arijit Pakrasi was born in Calcutta, India and graduated from Jadavpur University with a B.S. in Chemical Engineering in 1975. After graduation, he worked for Flakt Ltd, a leading international company specializing in air pollution control, as an assistant engineer and later as a senior engineer. He joined graduate study at The University of Tennessee, Knoxville in 1986, and received his M.S. in Environmental Engineering in 1986. He received his doctoral degree in Civil (Environmental) Engineering in 1992 from the same university.

Arijit Pakrasi is a member of Tau Beta Pi, Phi Kappa Phi, and Chi Epsilon academic honor societies. He is also a member of Air and Waste Management Association, American Institute of Chemical Engineers and Indian Institute of Chemical Engineers. He was awarded the first prize in graduate fellowship competition by Air and Waste Management Association in 1989. He was also awarded Hilton A. Smith graduate fellowship by The University of Tennessee in both 1989 and 1990.