ABSTRACT
THE REMOVAL OF HCl FROM HOT GASES WITH CALCIUM COMPOUNDS

by
Qian Lao

The use of $CaCO_3$, $Ca(OH)_2$, and CaO as adsorbents for removal of HCl from hot gas streams is investigated through a series of experiments. The experiments are conducted to evaluate the influence of key parameters such as temperature, (500 K to 1000 K), particle size, (0.037 mm to 3.36 mm), pressure drop of the packed bed, (0.1 cm H_2O to 25.5 cm H_2O), and concentration of HCl in the feed gas, (1,550 ppm to 20,000 ppm), on HCl adsorption. The results of these experiments show that all three of the calcium compound powders are excellent adsorbents when used in their individual active temperature ranges. The active temperatures are: $Ca(OH)_2$, 600 K to 700 K; CaO, 700 K to 800 K; and $CaCO_3$, 700 K to 850 K. The highest reactant conversion rate for each compound is: $Ca(OH)_2$, 75.5%; CaO, 65%; and $CaCO_3$, 80.5%.

When calcium compound particles are pretreated at temperatures over 1000 K, but below 1100 K, adsorbents with large surface area were produced, which allowed much higher conversion rates with relatively low pressure drop. The conversion rate of these adsorbents, measured as amount of calcium used, are all improved by a factor of three.

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by
Qian Lao

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This thesis is dedicated to

my father Shui-Nian Lao, mother Shou-Xian Liang
grandmother Ru-Qi Shen, and brothers
Larry and Edward.

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1 INTRODUCTION

The preservation of the environment is vital to the entire population of the world. During the past decade, there has been an increased awareness by the general public of the necessity for environmental protection. This has resulted in urgent attention being given to some requirements for the disposal of chemical wastes. This growing awareness of the hazards to environmental health has led to consideration of adequate disposal methods for these wastes.

The decision on whether one method is more suitable than another will depend on the available information relating to the waste and the properties of the waste.

In general, a chemical waste is considered as hazardous when it has the potential for acute or chronic adverse health or ecological effects when its disposal is uncontrolled. Those wastes can be in their solid, liquid or gaseous forms and may be toxic.

Chlorinated compounds present environmental hazards in a number of different ways. Chlorinated hydrocarbons are widely used in dry cleaning and degrading operations, organic chemicals manufacturing, automotive painting operations, etc. Chlorinated compounds can be found as air pollutants which affect stratosphere ozone and water pollutants which affect human health because of their carcinogenicity. Some chlorocarbons found in potable water are known to be toxic to humans through the damage they cause to the liver. Chlorocarbons are very stable and are often recycled when economically feasible.

The best disposal method for chlorocarbons, when they are too dilute to be recycled is by incineration. Many waste materials can be safely landfilled but incineration accomplishes the destruction of these materials in seconds or minutes whereas biological degradation in a landfill may take months or even years. Although it can be expensive, incineration may be the most environmentally sound option for implementing hazardous waste disposal, providing the problems associated with incineration are assessed and dealt with appropriately. Among these is the removal of air pollutants such as hydrogen chloride (HCl), sulphur oxides (SO_x), nitrogen oxides (NO_x) as well as others. Hydrogen chloride gas, emitted from incinerators,is produced from the destruction of toxic halogenated organic wastes, such as pesticides, chlorinated hydrocarbon solvents, polyvinyl chloride (PVC) contained in solid refuse, and waste polychlorinated biphenyls (PCBs).

The processes that can be considered for the reduction of HCl emissions when chlorinated hydrocarbons are incinerated can be classified into "wet" and "dry" processes. Removal of the gas could take place during or after the incineration process. The wet methods employ a slurry or solution of some suitable absorbent whereas the dry systems use dry particles of absorbent in such gas-solid contacting devices as fluidized beds, packed beds or entrainment reactors.

The wet processes incorporated two stage gas-liquid contacting devices. In the first stage, usually referred to as the pre-scrubber, the hot gas is cooled to about 333 K and is saturated with water. This method would produce an excessive quantity of HCl solution which would present a very difficult disposal problem.

Unlike wet processes, dry processes have the advantages of avoiding scaling and plugging of slurry pipelines, and corrosion and effluent disposal problems which could result in high maintenance costs and low plant availabilities. Furthermore, dry processes do not require cooling of the hot gases for scrubbing to take place.

The purpose of our work is to devise a simpler, safer and hopefully less expensive procedure by which HCl hot gas could be adsorbed without cooling down the hot gas. We considered the effects of different adsorbing materials such as calcium carbonate ($CaCO_3$), calcium oxide (CaO), and calcium hydroxide ($Ca(OH)_2$), as well as different operating conditions such as temperature, different particle size and feed gas concentration.

2 BACKGROUND

2.1 Non-Catalytic Gas-Solid Reactions

Non-catalytic heterogeneous reactions include solid-fluid, non miscible liquid-liquid, and liquid-gas systems. In this treatment, the heterogeneous non-catalytic reaction systems involving gas-solid reaction are considered in detail.

In our research, the following reaction are involved:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

$$CaCO_3(s) + 2HCl(g) \rightarrow CaCl_2(s) + CO_2(g) + H_2O(g)$$

$$Ca(OH)_2(s) + 2HCl(g) \rightarrow CaCl_2(s) + 2H_2O(g)$$

$$CaO(s) + 2HCl(g) \rightarrow CaCl_2(s) + H_2O(g)$$

Such reaction systems are usually the result of the interaction between physical and chemical processes. It is important to study the influence effects in order to design a reactor successfully.

2.2 Review of Gas-Solid Reaction Models

A conceptual model or picture is necessary to give a reasonable illustration of the phenomenological results and to analyze quantitatively a single particle reaction system. This model is discribed in this section following the treatment that Daoudi (1987) presented in his doctoral dissertation. A group of equations may then be set up to describe the system and allow a quantitative relationship to be established among system parameters. The criterion for a good model is that it is the closest representation of the actual phenomenon which can be treated without undue mathematical complexities.

The steps that are to be considered in the conceptual model and which will determine the global, or overall, rate of reaction for a solid-gas system consist of the following [Wen. C.Y., 1968, Smith. J.M., 1981] :

1. Transport of the gas reactants from the bulk gas to the gas-solid interface.
2. Intraparticle transport of gas reactants through the porous solid or product layer.
3. Adsorption of the gas reactions at the solid reactant surface.
4. Chemical reaction between gas and solid reactants.
5. Desorption of the gas products from the solid reaction surface.
6. Transport of gas product from the reaction surface through the porous solid medium.

7. Transport of gas products from the gas-solid interface into the bulk gas stream.

Finally, another event which is seldom considered in gas solid reaction modeling, but nevertheless is important, is the following:

8. Structural changes such as size, shape, sintering etc. due to chemical reaction. Changes in size, due to different densities of solid reactant and product are always included in modelling efforts.

For heterogeneous reactions the first seven steps occur consecutively and may be regarded as resistances in series. In developing the mathematical model, one would consider the various steps as they occur over a wide range of conditions. This is due to the fact that in practical systems, one single rate determining step is a limiting case, and therefore, a combination of these steps is usually rate controlling. However, a rigorous mathematical treatment of a model accounting for all events is very difficult. Therefore certain assumptions have to be made in order to develop a more detailed understanding of the rate controlling step(s).

a. Usually steps 3, 4 and 5 are combined and the overall surface effects are treated as an n order rate equation in the model [Wen, C.Y., 1968]. Alternatively, steps 3 and 5 may not even be visualized as part of the sequences which determine the global rate [Levenspiel, O., 1962].

b. The resistance offered by steps 6 and 7 may be neglected in the case of irreversible reactions or where no gaseous products are formed.

With the above assumptions, the only remaining resistances are gas-phase mass transfer resistance, the internal diffusion resistance in the solid, and the intrinsic reaction resistance.

Among the several reaction models that have been proposed in the literature for reactions similar to the ones described above, three of these models, the unreacted core model, the volume reaction model and the grain model are discussed in some detail and mathematically analyzed by Daoudi (1987). The major developments of these models are extensively studied in the literatures [Wen, C.Y., 1968; Sampaph, B.S., and Hughes, R., 1973; Szekely, J., Evans, J.W., and Sohn, H.Y., 1976; Sohn, H.Y., and Wadsworth, M.E., 1979]. A review of these models has been presented [Ramachandran, P.A., and Doraiswamy, L.K., 1982] where structural changes during the course of the reaction have been considered.

In this review, the basic porous nature of the solid and pore size distributions have been allowed for in the mathematical developments. This led to the developments of modified models such as the modified volume reaction model, and the modified grain model. Other models describing pore evolution such as the single pore model, the parallel pore model, and the distributed pore model or random pore model have also been used [Ramachandran, P.A., and Smith, J.M., 1977; Lee, H., 1980; Christman, P.G., and Edgar, T.F., 1980]. Since there is a difference in the validity of an assumption used to simplify the mathematical equations for gas-solid and liquid-solid system, the literature review is restricted to gas-solid reactions instead of the more general fluid-solid systems.

2.3 Thermodynamic Feasibility of The Reaction

2.3.1 Evaluation of Thermodynamic Feasibility

Limestone and its derivatives can react with HCl according to the reaction mechanisms given below:

Limestone

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2 \qquad (1)$$

$$\Delta H^o = -7,843 \text{ cal.}$$

Lime

$$CaO + 2HCl \rightarrow CaCl_2 + 2H_2O \qquad (2)$$

$$\Delta H^o = -108,140 \text{ cal.}$$

Hydrated Lime

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O \qquad (3)$$

$$\Delta H^o = -24,240 \text{ cal.}$$

The principle of free energy minimization was used to predict the equilibrium conditions of the above reactions. The change in free energy of a system, (ΔG^o), is a measure of the thermodynamic potential of a reaction and was used to calculate the likelihood that a reaction will occur. The full details of the derivations involved are well described by Smith and Van Ness (1937) lead to the following equations

$$\Delta H^\circ_T = \Delta H_O + \int \Delta C_{p_m} . dT \qquad (4)$$

where

ΔH°_T - Heat of reaction at temperature T, cal/mol

ΔC_{p_m} - Change in specific heat of mixture, cal/mol*K

ΔH_o - Constant with a finite value at T_O = 298 K, cal/mol

and

$$\Delta C_{p_m} = \Sigma m_i (\alpha_i + \beta_i T + \gamma_i / T^2) \qquad (5)$$

$$\Delta H_o = \Delta H^\circ_{298} - \Sigma m_i (\alpha_i T_o + (\beta_i / 2) T_o^2 - \gamma_i / T_o) \qquad (6)$$

where

m_i - Stoichoimetric coefficients (negative for reactants)

α_i, β_i, γ_i - Specific heat constants for reactants and products given in Table 2.1

ΔH°_{298} - Heat of reaction at 298 K (computed from heat of formation of products and reactants (Table 2.2), cal/mol

$$\Delta H^\circ_{298} = \Sigma m_i \, \Delta H^\circ_{f\,298_i}$$

Also,

$$\text{Ln } K = 1/R \int (\Delta H^\circ / T^2) . dT + I \qquad (7)$$

with

$$I = \frac{\Delta H_O}{RT} - \frac{\Delta G^\circ_T}{RT} - \frac{\Delta \alpha}{R} \text{Ln } T - \frac{\Delta \beta}{2R} T - \frac{\Delta \gamma}{2RT^2} \qquad (8)$$

and,

$$\Delta G^O = - RT \text{ Ln } K \qquad (9)$$

Table 2.1 SPECIFIC HEAT CAPACITY DATA

$C_p = \alpha + \beta T + \gamma T^{-2}$ (cal/(mol K)

	α	$10^3 \beta$	$10^{-5} \gamma$	T range/K
$CaCO_3$	24.98	5.24	-6.20	298-1200
CaO	11.67	1.08	-1.56	298-2000
$Ca(OH)_2$	19.07	10.80	-	298-700
$CaCl_2$	17.18	3.04	-0.60	298-1055
HCl	6.27	1.24	+0.30	298-2000
CO_2	10.57	2.10	-2.06	298-2500
H_2O	7.30	2.46	-	298-2750

Table 2.2 DATA FOR HEAT AND FREE ENERGY OF FORMATION

	$\Delta H^\circ_{f\ 298}$/(cal/mol)	$\Delta G^\circ_{f\ 298}$/(cal/mol)
$CaCO_3$(s)	-288450	-269780
CaO (s)	-151900	-144400
$Ca(OH)_2$ (s)	-235800	-214330
$CaCl_2$ (s)	-190000	-179300
HCl (g)	-22778	-22064
CO_2 (g)	-94051	-94258
H_2O (g)	-57798	-54635

Where

K - Equilibrium constant

ΔG^{o} - Free energy change, cal/mol

I - Constant determined for ΔG^{o}_{298} computed from free energy of formation (Table 2.2)

$$\Delta G^{\circ}_{298} = \Sigma m_i \, \Delta G^{\circ}_{f\,298\,i}$$

T - Temperature, K

$$\Delta\alpha = \Sigma m_i \alpha_i, \quad \Delta\beta = \Sigma m_i \beta_i, \quad \Delta\gamma = \Sigma m_i \gamma_i$$

The use of the above equations permit the evaluation of the equilibrium constant as a function of temperature.

The equilibrium constant K is then related to concentration of the compounds involved as follows:

$$K = \Pi S_i^{m_i} \qquad (10)$$

Where,

S_i - activity of solid and gas (reactants and products)

m_i - Stochiometric coefficients

With unit activities for solid compounds, equation (10) becomes

$$\Pi (Y_i \phi_i)^{m_i} = P^{-m} K \qquad (11)$$

Where,

m - m_i

P - operating pressure

Y_i - concentration of gas i

ϕ_i - fugacity coefficient of ideal gas related to critical parameters

As an illustrative example of the reaction of lime with HCl, K would be expressed as:

$$K = (Y(H_2O)/Y^2(HCl)) * (\phi(H_2O)/\phi^2(HCl))$$

with P = 1 atm.

where ϕ is given by:

$$\ln \phi = \frac{P_r}{T_r}(B^\circ + B'\omega)$$

with $B^\circ = 0.083 - \frac{0.422}{T_r^{1.6}}$ (4.11), and $B' = 0.139 - \frac{0.172}{T_r^{4.2}}$

P_r - Reduced pressure

T_r - Reduced temperature

From thermodynamic data given in Tables 2.1 and 2.2 and using the above development of thermochemistry, a computer program was used by Daoudi (1987) to compute the heat of reaction, the free energy and the equilibrium constant at various temperatures for reactions (1), (2), and (3).

Finally, the concentration of HCl in ppm in equilibrium with the solid was calculated for a given feed gas composition using Equation (10).

2.3.2 Calcination of limestone

Thermodynamic prediction of the calcination of limestone was investigated by Reid [1970] using tabulated free energy data. For this reaction, CO_2 normally in the products tends to slow down the release of CO_2 from heated limestone. Figure 2.1 shows how the calcination temperature must increase as the CO_2 concentration increases. The results show that for an atmosphere of 14.5% CO_2 the temperature would have to be higher than 1415 ^oF (1042 K) for calcination to take place. At 3.5% CO_2 the temperature would be 1200 ^oF (922 K), and therefore the calcining temperature is significantly higher in flue gas than in air. It is important to note that if the temperature drops below that corresponding to the predicted CO_2 concentration, equilibrium will theoretically favour formation of $CaCO_3$ over CaO as shown on Figure 2.1.

2.3.3 Reaction of HCl with Limestone ($CaCO_3$)

Limestone can react with HCl according to reaction (1). The equilibrium results reported in Table 2.3 show that HCl concentrations of 16 and 36 ppm can be obtained with $CaCO_3$ at 873 K and 3% H_2O for 3.5 and 14.5% CO_2, respectively. These calculations also show that even for high CO_2 content in the flue gas (i.e. 70%) and where $CaCO_3$ is present throughout the whole range of temperatures, low levels of HCl could still be achieved (122 ppm at 1050 K).

Therefore, based on thermochemistry, calcination is not necessary for the reaction of HCl with limestone. However, these predicted concentrations depend very much on the time needed to achieve equilibrium, and hence, reaction rates could be very slow.

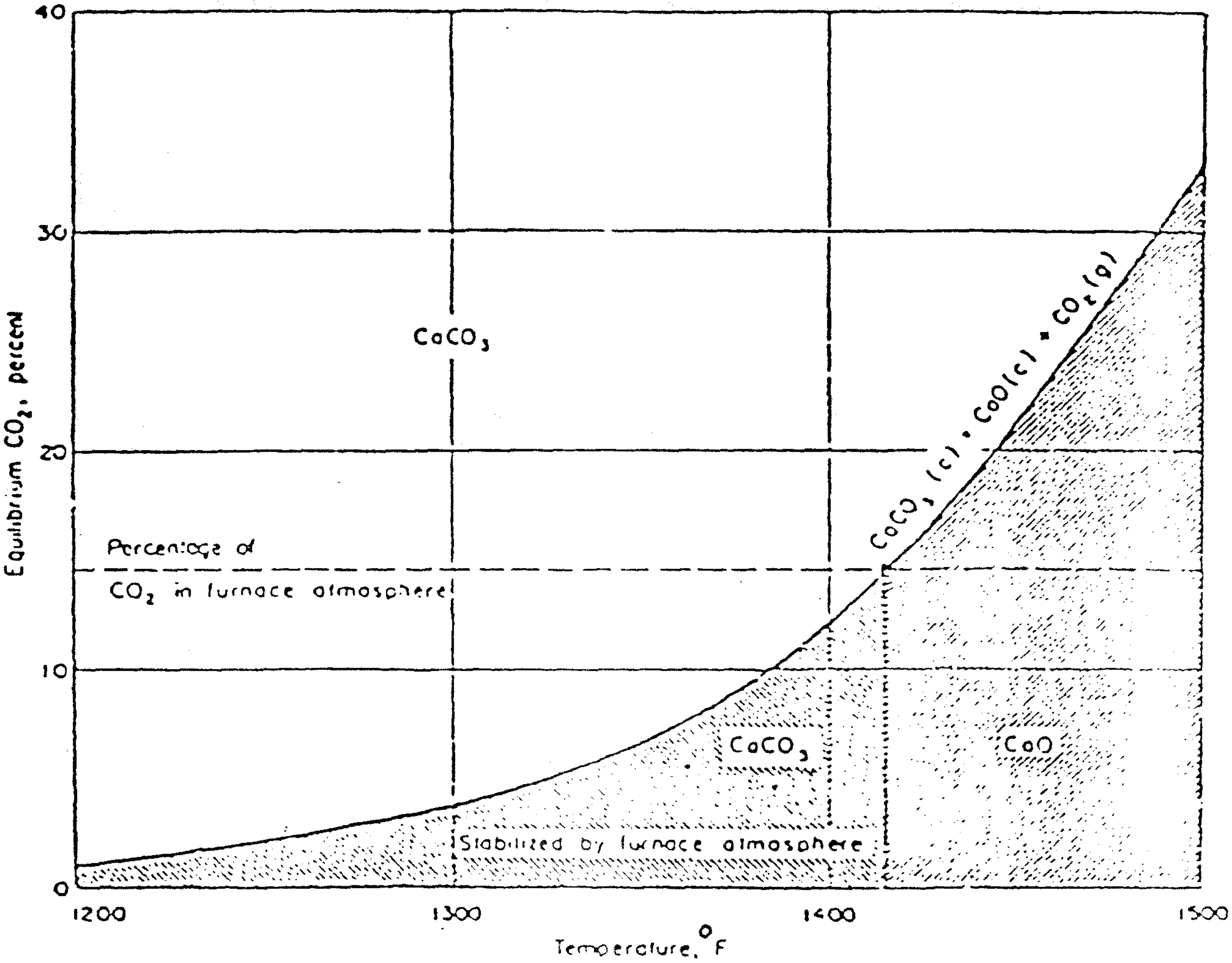


Figure 2.1 Effect of Furnace Atmosphere on Dissociation of $CaCO_3$

Table 2.3 EQUILIBRIUM LEVELS OF HCl IN CONTACT WITH $CaCO_3$

Temperature K	HCl concentration (ppm) 3% vol H_2O		
	3% vol CO_2	14.5% vol CO_2	70% vol CO_2
673	7.7	17.0	37.0
773	12.0	26.0	57.0
873	16.0	36.0	79.0
973	21.0	47.0	100.0
1050	25.0	56.0	122.0

Table 2.4 EQUILIBRIUM LEVELS OF HCl IN CONTACT WITH CaO

Temperature K	HCl concentration (ppm)	
	3% vol H_2O	10% vol H_2O
673	0.1	0.2
773	1.2	2.1
873	7.8	14.3
973	36.0	66.0
1050	96.0	176.0

2.3.4 Reaction of HCl with Lime (CaO)

Using the same type of thermodynamic calculations as above, HCl concentrations in flue gas in equilibrium with CaO can be predicted. Table 2.4 lists the results of calculations obtained for a wide range of temperature, with an upper limit set by the melting point of $CaCl_2$ (1045 K). It is evident that HCl concentrations increase with increasing temperature. Concentrations of 96 and 176 ppm are reached for 3% and 10% water vapor in the flue gas. At temperatures representative of catalytic combustion of chlorinated solvents, e.g., 773 K, the equilibrium HCl concentrations would be less than 3 ppm.

Based on these calculations, a desirable temperature range for HCl removal can be taken as being in the range of 773 to 1023 K. The lower temperature is not a limit since CaO will react with HCl down to room temperature in a CO_2 free atmosphere and with $CaCO_3$ where CO_2 is present. But because predicted equilibrium concentrations are limited by the rate of the reaction which is higher at high temperatures, and because 1 ppm represents essentially complete removal of HCl, the practical range of temperatures given above was considered in this study. Figure 2.2 shows the relationship between HCl in equilibrium with CaO over a wide range of temperatures. It is seen from this graph that if 100 ppm is the highest acceptable value that could be emitted to the atmosphere, a further increase of the

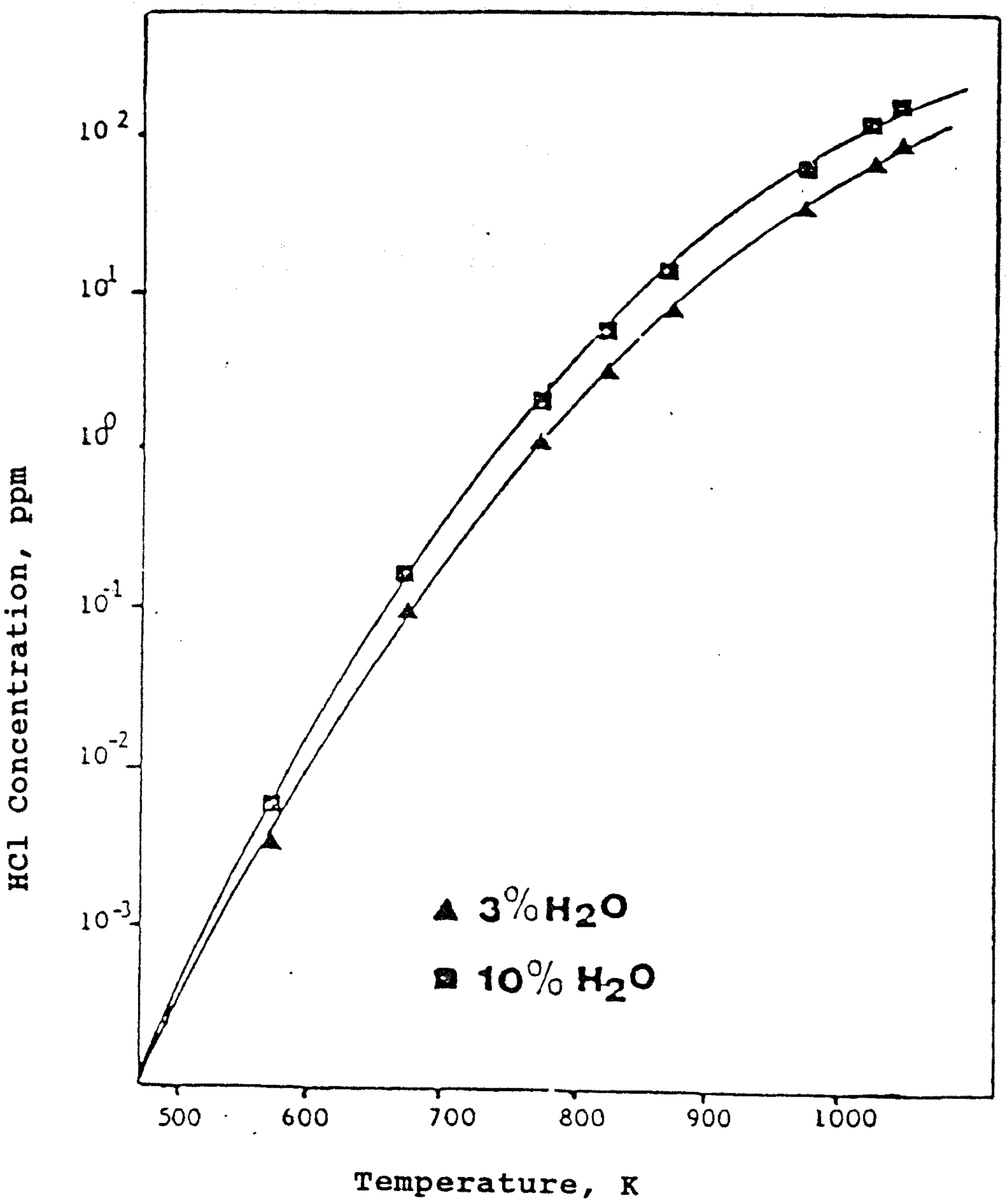


Figure 2.2: Calculated Equilibrium HCl in Contact with CaO

temperature will not increase HCl concentration as sharply as at lower temperature.

2.3.5 Effect of Hydrated Lime ($Ca(OH)_2$)

Hydrated lime reacts with HCl according to reaction 3. Hydrated lime presents another alternative for high temperature removal of HCl from flue gases. Table 2.5 shows the calculated levels of HCl in equilibrium with $Ca(OH)_2$. The operating temperatures, in this case, are set by the stability of hydrated lime, which is thermodynamically unstable above 728 K in steam at 1 atmosphere. Hence at temperatures higher than that of the decomposition temperature, hydrated lime would be converted to lime (CaO) and the system would behave thermochemically as though it were based on CaO. Therefore, at lower temperatures, both solids are theoretically capable of removing essentially all HCl from the flue gas. But, reaction rates may be slow and the time to reach equilibrium could be high.

2.4 Conclusion

It is seen from the preceeding thermodynamic considerations by Daoudi (1987) that limestone and its derivatives are all capable of removing hydrogen chloride gas at concentrations between 1 ppm and 200 ppm in the temperature range of 573 to 1023 K, and where furnace conditions are likely to be favorable. However, the time to approach equilibrium is based on kinetics and not thermodynamics. Predictions of

Table 2.5 EQUILIBRIUM LEVELS OF HCl IN CONTACT WITH $Ca(OH)_2$

Temperature K	HCl concentration (ppm) 3% vol H_2O
473	7.9E-6
573	7.04-5
623	1.6E-4
723•	1.5E-4•
873•	2.5E-3•

• $CA(OH)_2$ dissociates in flue gas.

these rates is very difficult since the overall reaction rate of a gas on a solid surface could be limited by gas phase mass transfer, chemical reaction at the surface, and pore diffusion, singly or as a combination. Reaction rates could be improved by working with a fine powder of the solid reactant which would therefore have a larger surface area per unit mass.

3 EXPERIMENTAL

3.1 Equipment

The equipments used in the experimental evaluation of the ability of calcium compounds to react with HCl gas is described in this section.

3.1.1 The Reactor and Furnace

Experiments were conducted in a laboratory-scale tubular reactor system as shown in Figure 3.1. This reactor system consists of a 2.5 cm inside diameter quartz tube reactor in a vertical three-zone controlled furnace capable of controlling temperatures between 373 and 1373 K to ± 1 K. The middle zone was designed to maintain a flat temperature profile over the length of the reaction bed which contained a certain height of solid on a quartz fritted disc. The quartz fritted disc provided support for the adsorbent and did not react with HCl in the range of reaction temperatures. Reaction bed heights of 1.8 cm, 2.0 cm, 3.0 cm, 3.5 cm, 4.0 cm, and 10.0 cm were used in the experiments, depending on the calcium compounds used and the particle sizes.

3.1.2 Hydrogen Chloride Feed System

Dry dilute hydrogen chloride gas in nitrogen was fed from a cylinder through a regulator to the reactor. During an experiment low pressure air was used to maintain a purge flow through the bed to avoid overheating. The gas flow rates were monitored through calibrated rotameters equipped with needle valves for flow rate control. The gases were used as received without further purification.

Because the supplied and measured HCl concentration in cylinder was not constant with time, we checked HCl feed concentration before and after each experiment. We used the average concentration to calculate adsorption. Low pressure dry air was used to purge the reaction system before and after each experiment.

Figure 3.1 shows the gas feed system.

3.1.3 Temperature Measurements

The temperature shown on the furnace indicator does not correspond to the reaction temperature. Therefore, the adsorption temperature was monitored with two 0.16 cm chromel-alumel (K-type) thermocouples which were inserted in both sides of the quartz tube reactor and placed on the center line immediately in front of and behind the adsorption bed.

The thermocouple in front of the reaction bed touched the solid reactants and measured the solid adsorbent temperature which usually was higher than the indicated furnace temperature by about 30 K. The thermocouple behind the reaction bed did not touch the fritted disc support and measured the temperature of the flow out gases which was usually higher than the indicated furnace temperature by several K. The thermocouple output was fed to a Omega Model

650 indicator which continuously presented the sample temperatures during the reaction. The furnace wall temperature was measured with another chromel-alumel (K-type) thermocouple and used with a controller and temperature programmer to control the furnace. Figure 3.1 gives a schematic representation of the whole experimental apparatus. Figure 3.2 gives the general view of the apparatus.

3.1.4 Pressure Drop Measurement

Pressure drop across the adsorbent bed was measured with a water U-tube manometer as a function of flowrate, height of adsorption bed, and particle size of the solid adsorbents. The manometer consisted of a 1,000 mm high U-tube, 2 mm inside diameter. For each experiment, pressure drop was measured before and after each run. These data are needed for process design.

3.1.5 Analytical Equipment

After the feed gas passed through the adsorption bed, the unreacted HCl gas concentration which we called "HCl effluent concentration" was measured at a pre-set flowrate by suction through a series of scrubbers, each containing 25.00 ml $AgNO_3$ standard solution with a Specific Ion Electrode Meter to indicate the end point of each scrubbing vessel. The end point was defined as the point where the biggest change of the absolute potential in millivolts of

Figure 3.1 Flow Schematic of Adsorption Equipment

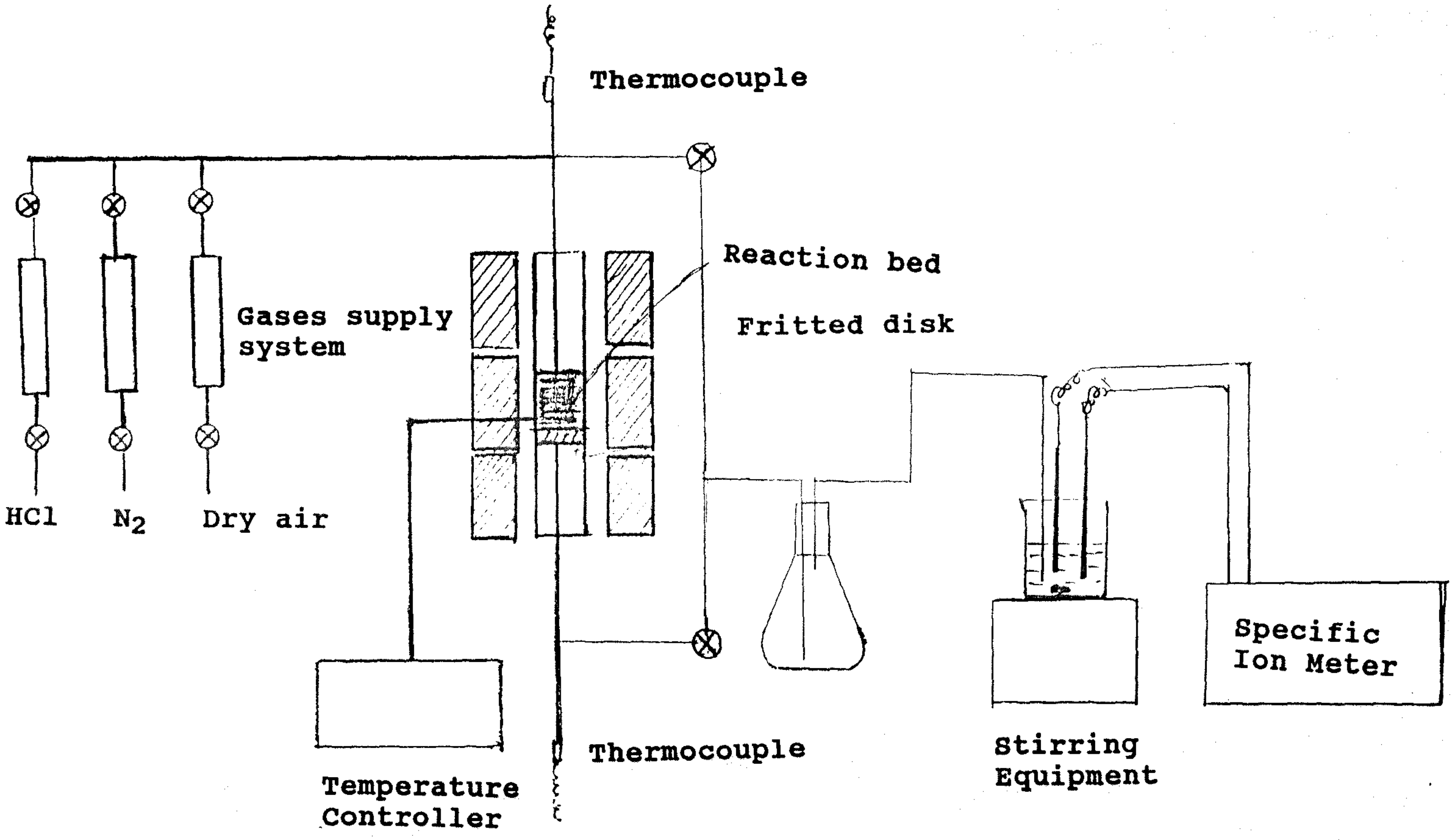
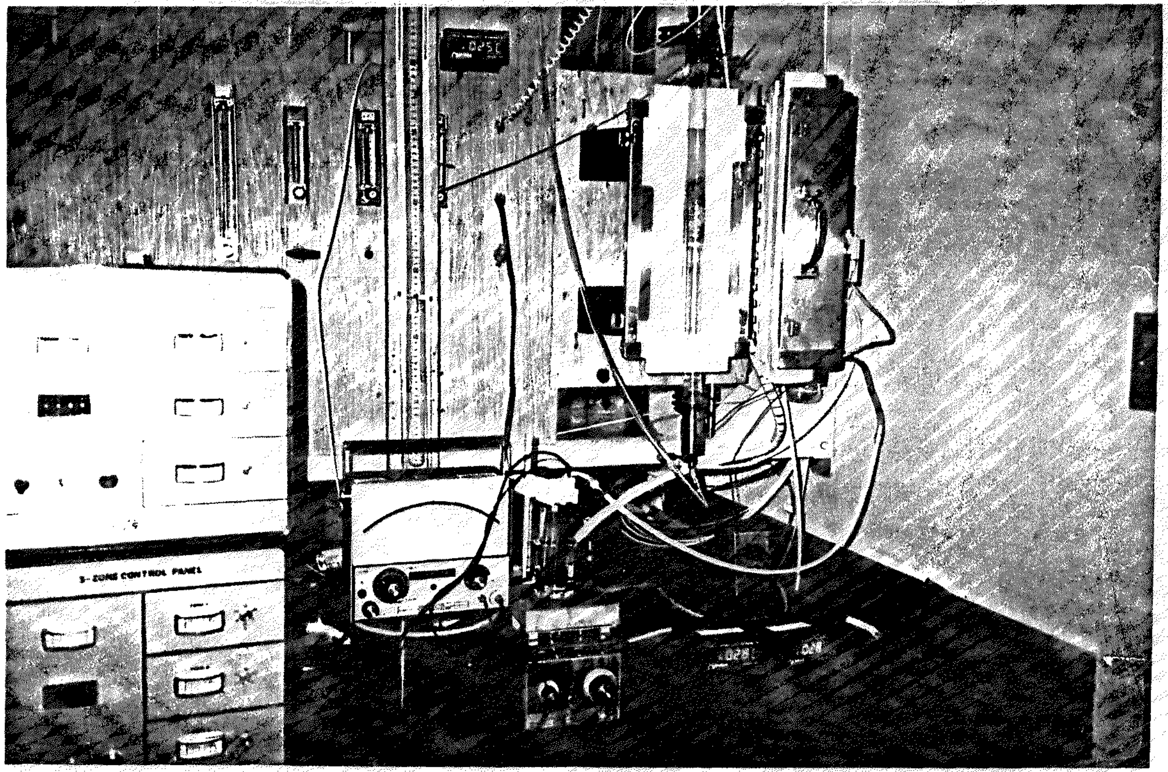


Figure 3.2 The General View of the Apparatus



the scrubbing solution occurs, i.e., when Ag^+ ions in each scrubber is consumed. Because the absolute potential in millivolts of the scrubbing solution changed significantly before and after the AgCl precipitation reaction, especially near the end point, we can measure the millivolts of the solution to indicate the end point with an Orion Model 407A Specific Ion Meter with a chloride electrode and a reference electrode in the scrubbing solution. This analytical equipment was obtained from the NJIT Chemistry Division storeroom. Further details on the Specific Ion Meter may be found in the Orion Research Instruction Manual. A stop watch was used to record reaction time, and each scrubber reaction time. The Specific Ion Meter can also be used in measuring $CaCl_2$ product.

3.2 Materials

3.2.1 Solid reactants

The powdered reactants used in this research were obtained from the NJIT Chemistry Department storeroom. They are calcium carbonate ($CaCO_3$), calcium oxide (CaO), and calcium hydroxide ($Ca(OH)_2$). Their characteristics are listed in Tables 3.1, 3.2, and 3.3. The different particle size calcium carbonate was provided by Mr. Lamond of the L.M. Huber Corporation, Quincy, Illinois. The sizes are 6-20 mesh (0.841 - 3.36 mm) $CaCO_3$, 100 mesh (0.149 mm) $CaCO_3$, 40-200 mesh (0.074 - 0.420 mm) $CaCO_3$, and 20-60 mesh (0.250 - 0.841

Table 3.1: Composition of Calcium Carbonate powder

(FISHER SCIENTIFIC COMPANY)

Certificate of Actual Lot Analysis

$CaCO3$	**F.W.100.09**
Sodium (Na)	0.04 %
Strontium (Sr)	0.05 %
Insoluble in dilute Hydrochloric Acid	0.006 %
Alkalinity	P.T.
Chloride (Cl)	0.001 %
Oxidizing Substances (asNO_3)	0.002 %
Sulfate (SO_4)	0.006 %
Ammonnium (NH_4)	0.003 %
Barium (Ba)	0.003 %
Heavy Metals (as Pb)	0.0005 %
Iron (Fe)	0.0005 %
Magnesium (Mg)	0.02 %
Ammonium Hydroxide ppt	0.008 %
Potassium (K)	0.001 %
Fluoride (F)	0.0003 %

Table 3.2: Composition of Calcium Oxide powder

(MERCK & CO. Inc.)

CaO **Mol. wt. 56.08**

Maximum Impurities

Ammonium Hydroxide precipitate	1.5 %
Loss on ignition	5.0 %
Chloride (Cl)	0.005 %
Nitrate (NO_3)	0.05 %
Sulfate (SO_4)	0.3 %
Magnesium (Mg)	0.8 %
Heavy metals (as Pb)	0.01 %
Iron (Fe)	0.10 %
Zinc (Zn)	0.015 %

Table 3.3: Composition of Calcium Hydroxide powder

(J.T. BAKER CHEMICAL CO.)

$Ca(OH)_2$ Suitable for Thin-Layer Chromatography FW 74.1

ACTUAL ANALYSIS, LOT 632421 MEETS A.C.S. SPECIFICATIONS

Assay ($Ca(OH)_2$)	97.2 %
Insoluble in HCl	0.02 %
Chloride (Cl)	0.005 %
Sulfur Compounds (as SO_4)	<0.5 %
Heavy Metals (as Pb)	<0.001 %
Iron (Fe)	<0.05 %
Magnesium and Alkalies (as SO_4)	1.0 %
Suitability for TLC	PASSES TEST

mm) $CaCO_3$. The powder reactant particle sizes are less than 400 mesh or less than 0.037 mm.

3.2.2 Gas Reactants

A series of gas cylinders containing different HCl concentration were purchased from the Matheson Gas Company. The concentration of HCl gas in these cylinders varied from 1,500 ppm to 20,000 ppm. The balance gas in these cylinders was nitrogen. These HCl reactant gases were used directly from cylinders, in the experiments.

High purity nitrogen gas cylinders were also supplied by the Matheson Gas Company and used without further treatment.

3.3 Operating Procedure

Checking the HCl concentration in the cylinder was carried out before each run to determine the feed concentration. Each adsorption compound sample was placed on weighing paper and weighed on an ordinary laboratory balance and then transferred to the fritted disc in the reactor to form the adsorption bed. The height and pressure drop of the reaction bed were measured before each run.

For large particle size calcium carbonate, the sample was calcined at around 1,000 K in a continuous flow of nitrogen. The concentrations of CO_2 were measured using a Hewlett Packard 5890 gas chromatograph with a flame ionization detector. The CO_2 was first hydrogenated to CH_4

before detection by the FID. When CO_2 dropped to a very low concentration, then complete calcination was assumed. Analysis showed that the remaining $CaCO_3$ content was less than 0.5%. The resulting product (CaO) left on each particle a large number of pore holes which were the pathways of the CO_2 gas from calcination. This resulted in an adsorption bed which had relatively high surface area and low pressure drop than equivalent calcium carbonate. Excessive heating during calcination produced a powder product instead of the desired large particle size product.

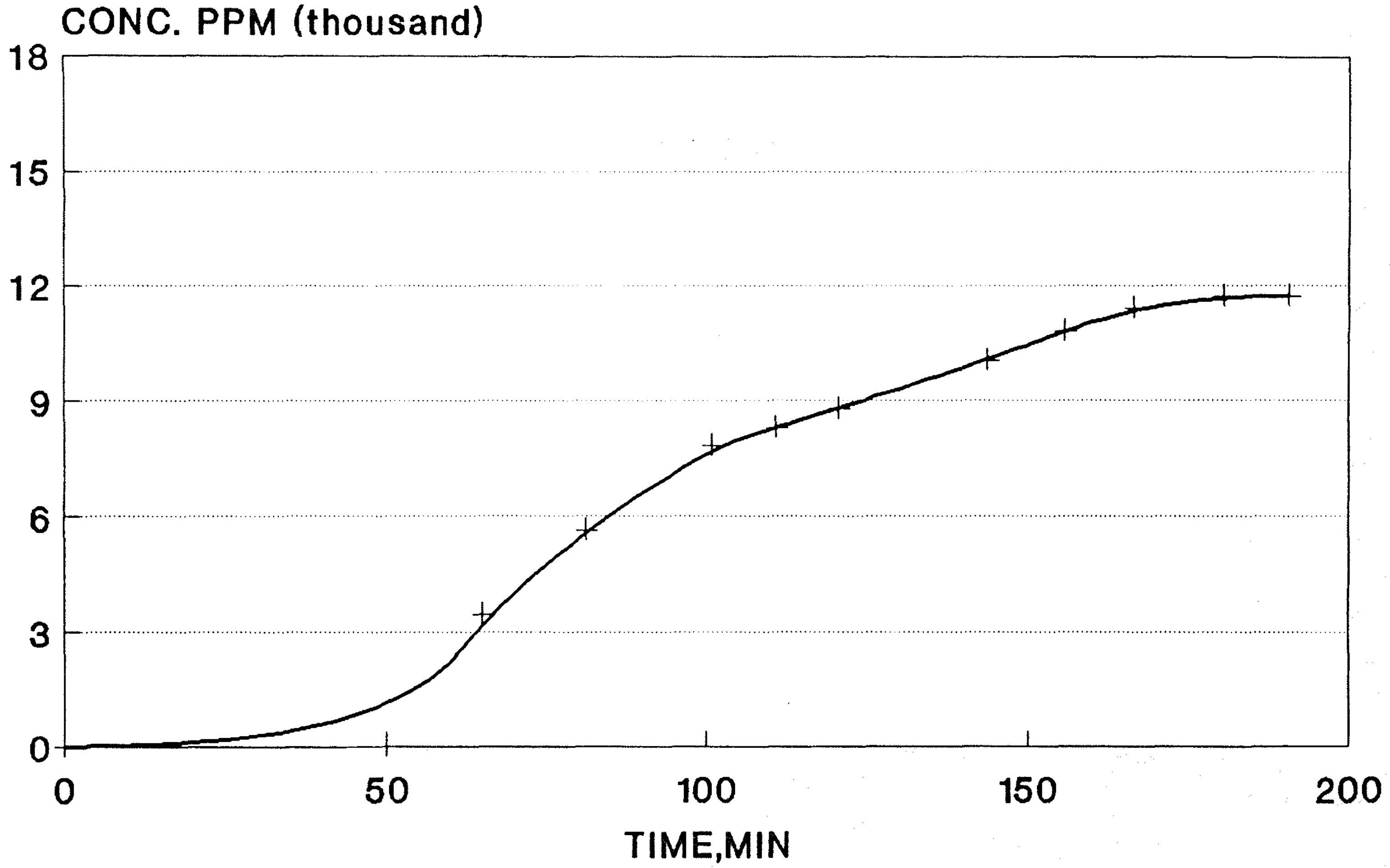
The adsorption solid samples were brought to the desired temperature with either a low flow rate of nitrogen or air. After thermal equilibrium was achieved, the desired concentration of HCl gas was switched to the reactor and the initial reaction time was recorded, and the stop watch turned on.

The off-gas from the reactor was bubbled through a number of beakers which contained 25.00 ml $AgNO_3$ standard solution to absorb the unreacted gases before emitting the gases to the hood. The unreacted gases were absorbed and their concentrations measured.

As the reaction proceeded, the unreacted gas concentration increased to reach a constant value (it was not necessary to reach the original concentration) as shown in Figure 3.3. At the end of a run, the system was purged with high purity nitrogen before it was cooled down and the product removed for analysis. Among the methods used to

Figure 3.3

HCl Effluent Concentration Curve
Ca(OH)2 Powder Adsorbed HCl at 700 K



HCl = 18000 ppm
Ca(OH)2 = 0.05 Mole

analyze the end product ($CaCl_2$) were measuring the weight increase by an ordinary laboratory balance for a final conversion measurement and titrating with $AgNO_3$ for the quantitative measurement. After reaction, the pressure drop of the reaction bed was also measured.

Adsorption studies were conducted over the temperature range of 600 - 1,000 K with hydrogen chloride concentrations in the range of 1,550 ppm to 20,000 ppm. The specific surface area of the solid reactant was measured by the standard BET method. The particle sizes of the solid reactants were from 400 mesh (0.037 mm) powder to 6-20 mesh (0.841 - 3.36 mm) particles.

4. RESULTS AND DISCUSSION

A number of different particle size limestone samples and calcination derivatives were tested as HCl adsorbents. The effects of temperature, particle size, bed height, and HCl concentration in the feed gases were evaluated.

The objectives of this research were:

- To evaluate the potential of adsorbing HCl gas at high temperatures,
- To determine the optimum conditions for HCl adsorption,
- To evaluate methods to minimize pressure drop, and
- To evaluate the methods of improving the surface area of the large particle size materials in order to improve calcium utilization.

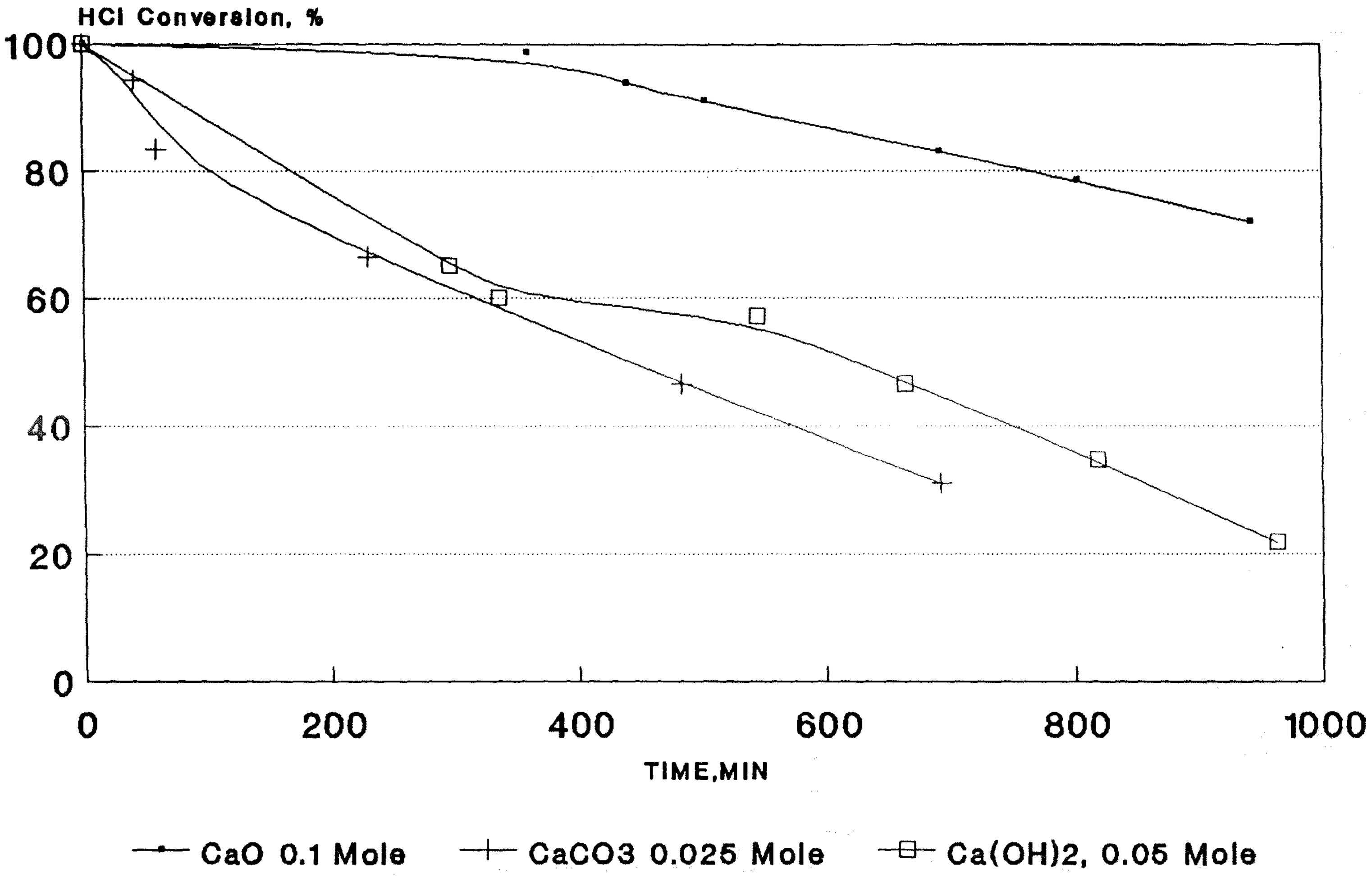
4.1 Effects of Operating Parameters on HCl Removal

4.1.1 HCl Conversion as a Function of Reaction Time

The relationship between HCl adsorption and time was determined using limestone and its calcium derivatives.

Figure 4.1 shows the experimental results for powder charges of 0.025 mole $CaCO_3$, 0.1 mole CaO, and 0.05 mole $Ca(OH)_2$. At the beginning of these experiments, no effluent HCl was observed, the adsorption of HCl was 100 %. Then, the adsorption of HCl dropped slowly with reaction time. The greater the number of moles of solid reactants, the longer it took for HCl to appear in the effluent gas stream. The higher the HCl concentration in the feed gas, the shorter

Figure 4.1 HCl Conversion Curve
CaCO3, CaO, Ca(OH)2, Powder at 800 K



HCl Conc. = 3000 ppm

reaction time before HCl appeared in the effluent stream. By comparing the breakthrough time and HCl conversion of each experiment, insight was obtained on the effect of physical parameters on adsorption.

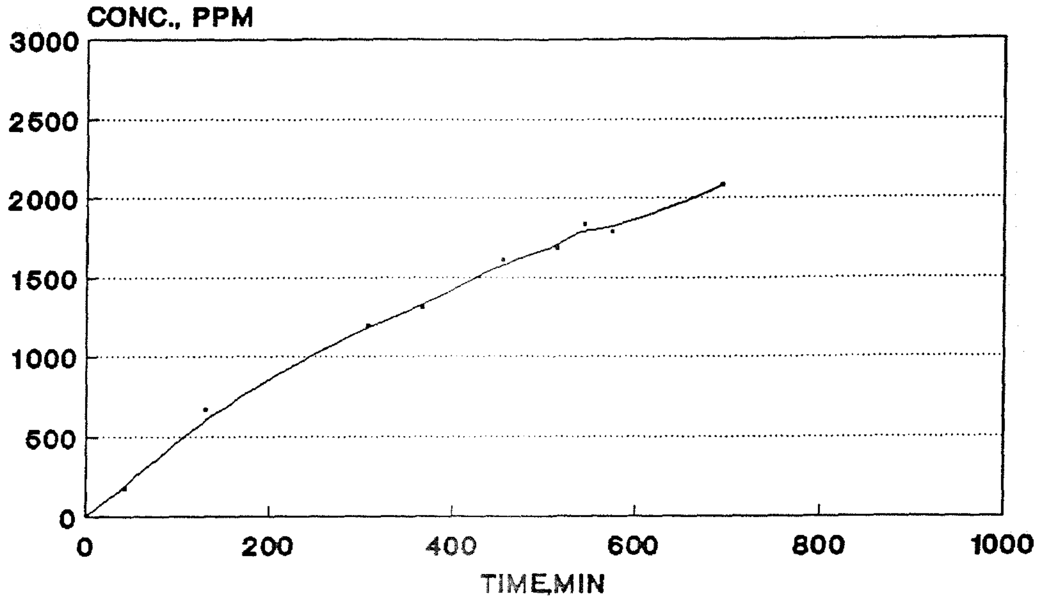
4.1.2 Calcium Utilization as a function of Reaction time

Similar to HCl conversion as a function of reaction time, the relationship between calcium utilization and time as a function of HCl feed gases was determined. Figures 4.2, 4.3, and 4.4 show the experimental results for powder charges of 0.025 mole $CaCO_3$, 0.1 mole CaO, and 0.05 mole $Ca(OH)_2$. In the experiments, the effluent HCl concentration was measured following the reaction time. Based on these kinds of HCl effluent curves, we calculated how many moles of HCl gas were adsorbed and how many moles of solid reactants were consumed at each point of reaction time. Therefore, we got HCl conversion curves and solid reactants conversion curves. With the solid reactants conversion curves, we obtained information about the effects of operating parameters which will be discussed in detail.

4.1.3 Effects of Temperature on HCl Adsorption

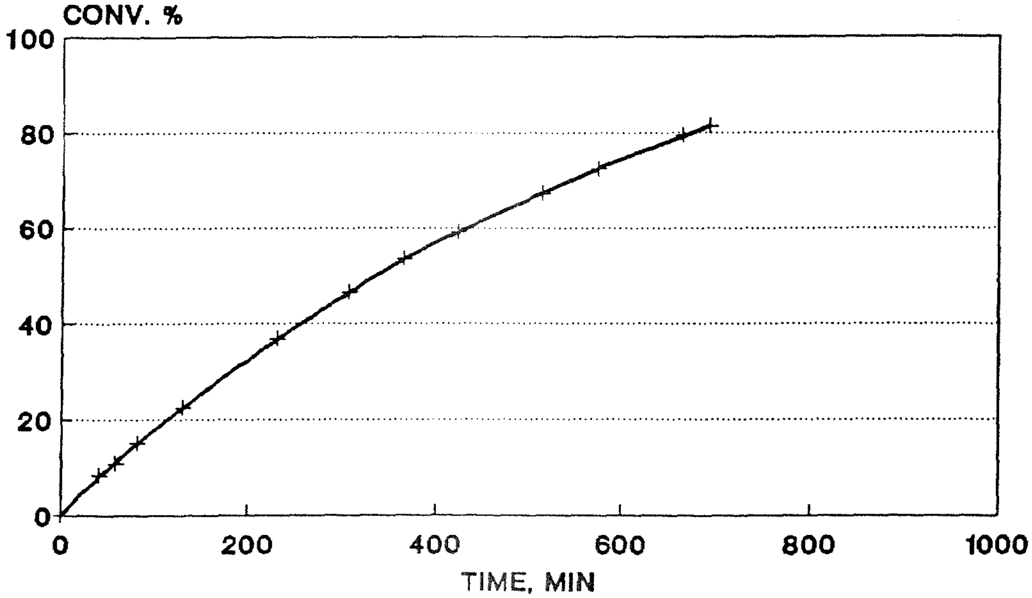
A number of experiments were carried out to test the adsorption of HCl by 0.05 mole CaO, $CaCO_3$, and $Ca(OH)_2$ powder as a function of temperature. These experiments were conducted with feed gases containing 10,300 ppm to 20,000

Figure 4.2
(a) HCl Effluent concentration
CaCO3 Powder Adsorbed HCl at 800 K



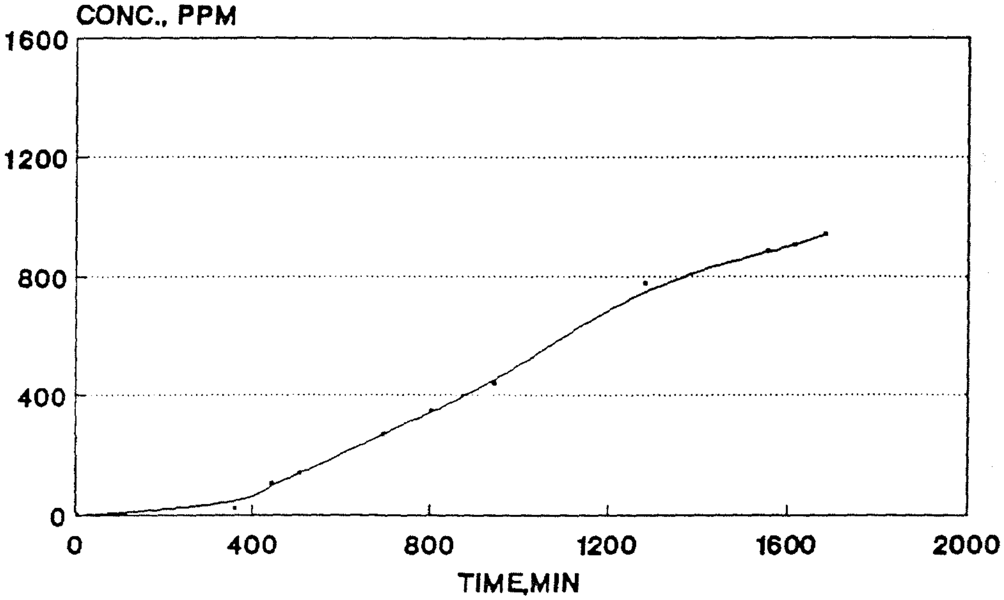
CaCO3 = 0.025 Mole
HCl Conc. = 3000 ppm

Figure 4.2
(b) CaCO3 Conversion Curve
CaCO3 Powder Adsorbed HCl at 800 K



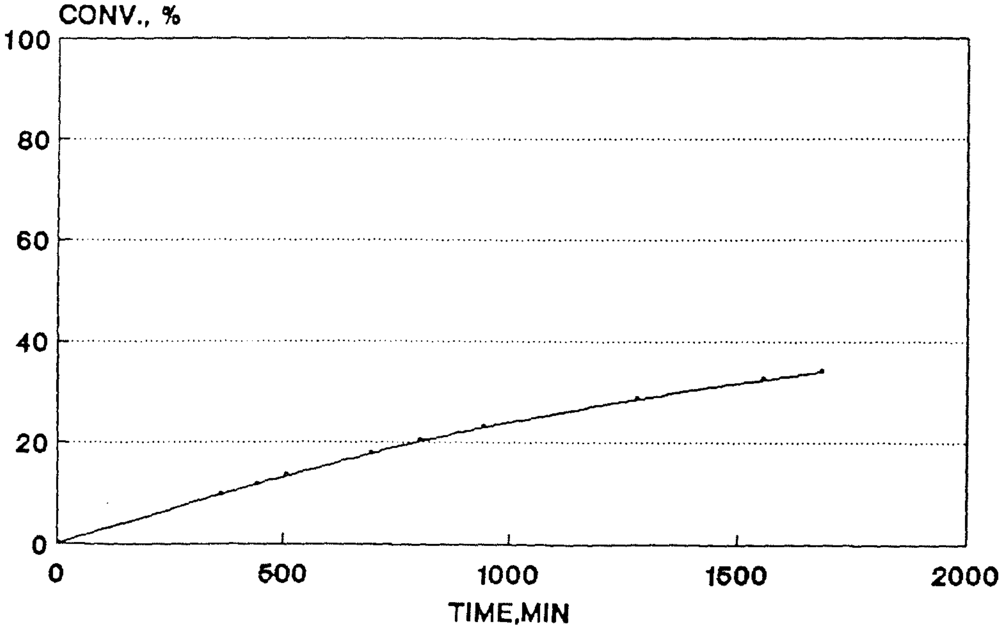
CaCO3 = 0.025 Mole
HCl = 3000 ppm

Figure 4.3
(a) HCl Effluent Concentration
CaO Powder Adsorbed HCl at 700 K



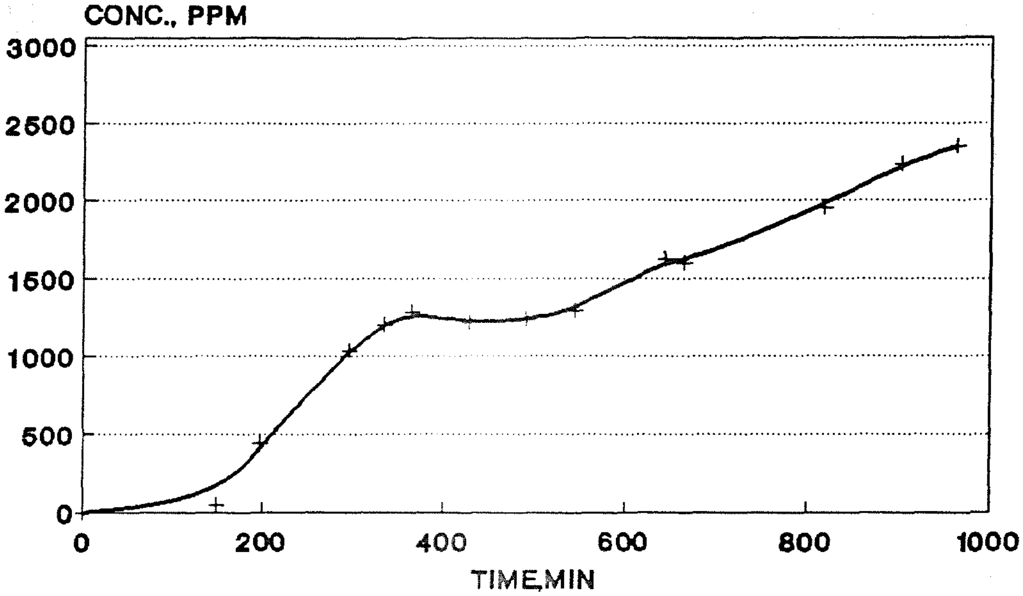
CaO Powder = 0.1 Mole
HCl Conc. = 1600 ppm

Figure 4.3
(b) CaO Conversion Curve



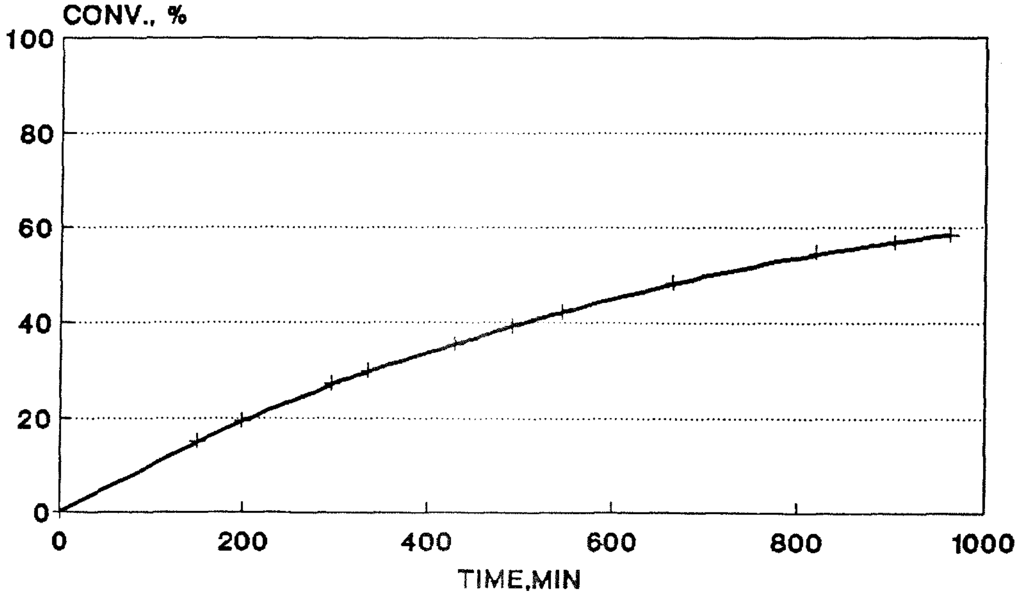
CaO = 0.1 Mole
HCl Conc. = 1600 ppm

Figure 4.4
(a) HCl Effluent Conversion
Ca(OH)2 Powder Adsorbed HCl at 800 K



Ca(OH)2 = 0.05 Mole
HCl Conc. = 3050 ppm

Figure 4.4
(b) Ca(OH)2 Conversion Curve
Ca(OH)2 Adsorbed HCl at 800 K



Ca(OH)2 = 0.05 Mole
HCl Conc. = 3050 ppm

ppm HCl in nitrogen flowing at 800 cc/min into the adsorption bed.

Results shown in Figures 4.5, 4.6, and 4.7 indicated that HCl was adsorbed by all three calcium compounds, but they showed different trends with increasing temperature.

In the case of calcium oxide (CaO), Figure 4.5 shows that adsorption of CaO improved with the increase of temperature from 700 K to 800 K. Continually increasing temperature, from 800 K to 1,000 K, reduced the adsorption ability of CaO. The sequence of CaO activity following the change of temperatures was

$$1{,}000 \text{ K} < 700 \text{ K} < 800 \text{ K}$$

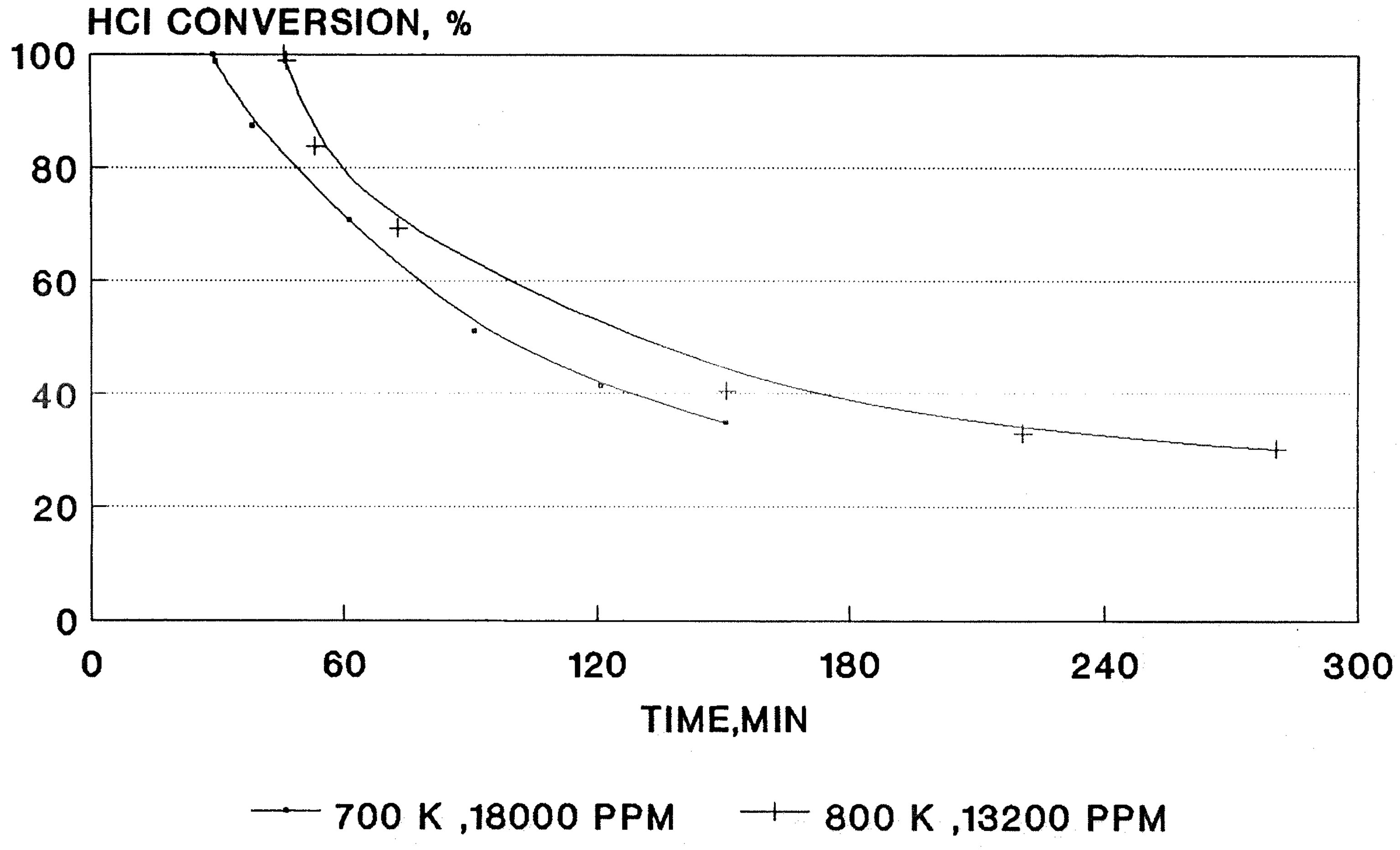
This result was similar to the result which Daoudi, (1987) got in his Ph.D dissertation. The reasons that the higher reaction temperature (i.e. 1,000 K) reduced the activity of calcium oxide (CaO) were that:

a. The sintering solid reactant powder had a higher reaction resistance at high temperatures than at low temperatures.

b. The melted products had a higher reaction resistance at high temperatures than at low temperatures.

In the cases of calcium carbonate ($CaCO_3$) and calcium hydroxide ($Ca(OH)_2$), as shown in Figures 4.6 and 4.7, the HCl conversion curves presented the same tendency. At a relatively low temperature (700 K), a longer breakthrough time was obtained, and in the later reaction time, the HCl conversion curve dropped faster than at a high temperature

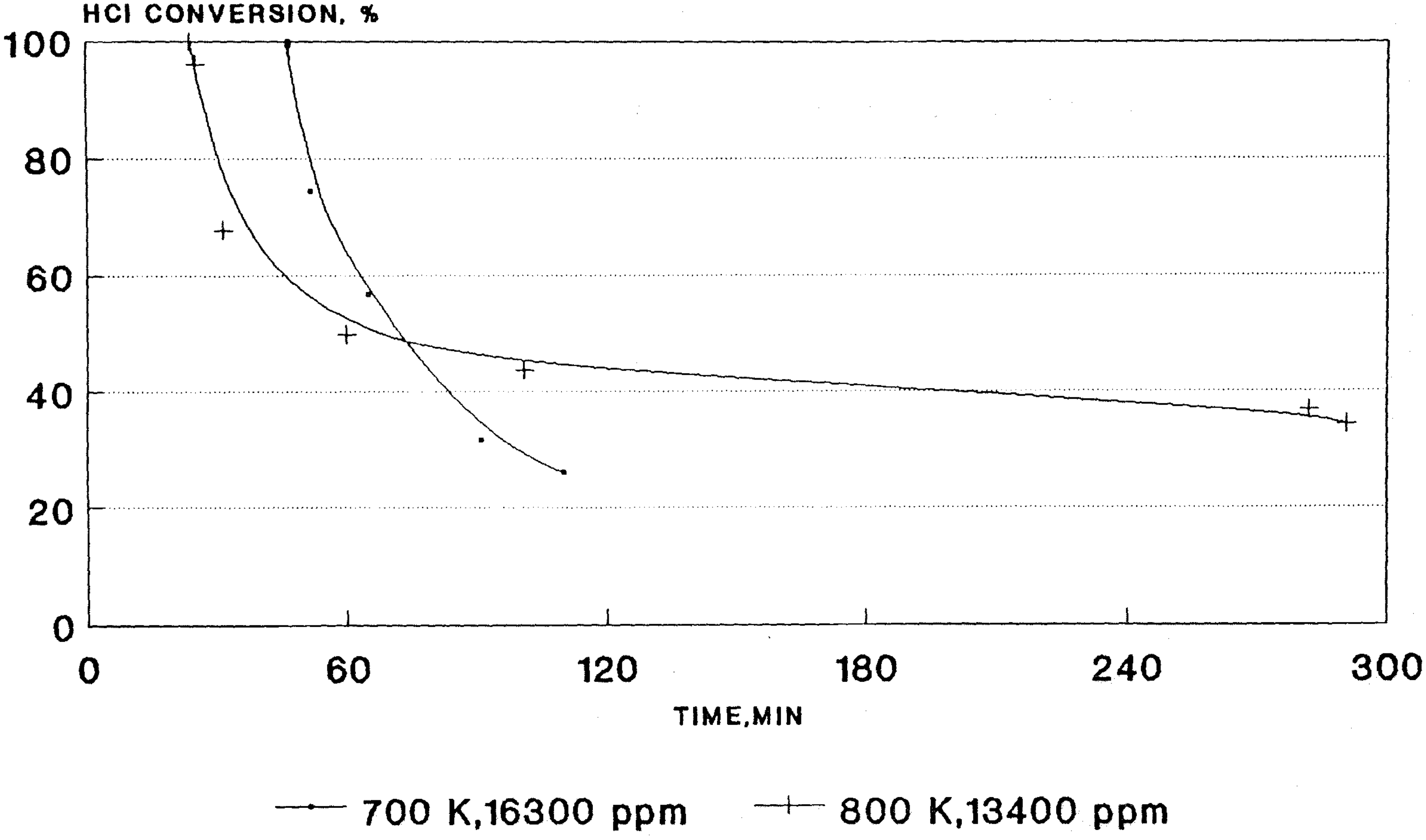
Figure 4.5 Temperature Influence on
HCl Conversion Comparison Curve
CaO Powder at 700 K & 800 K



0.05 Mole, 700 K, 18000 ppm
0.05 Mole, 800 K, 13200 ppm

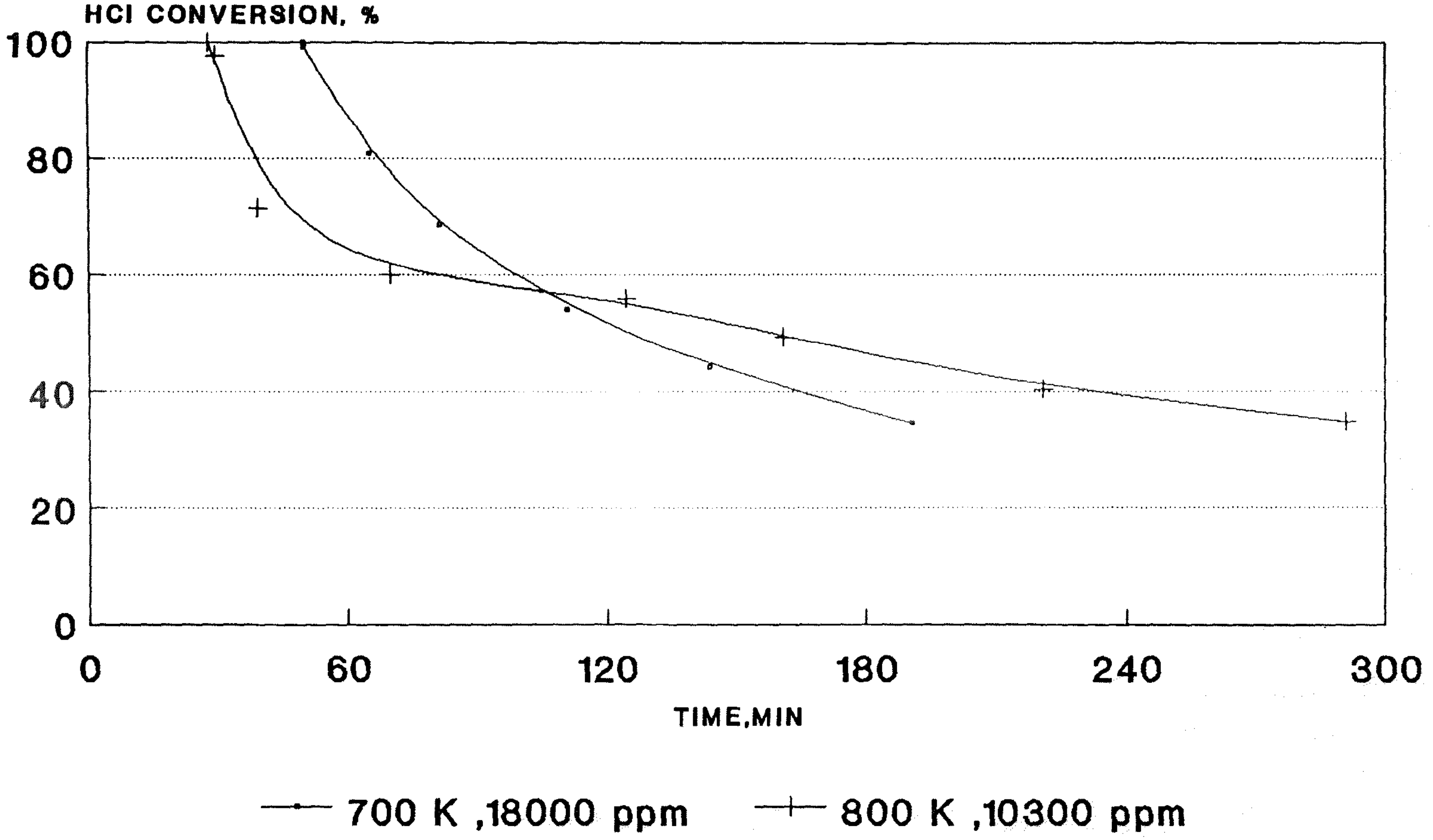
Figure 4.6 HCl Conversion Comparison

Temperature Influence
CaCO3 Powder at 700K & 800K



700 K, 16300 ppm
800 K, 13400 ppm

Figure 4.7
HCl Conversion Comparison
Ca(OH)2 Powder at 700 K & 800 K



0.05 Mole, 700 K, 18000 ppm
0.05 Mole, 800 K, 10300 ppm

(800 K). It was clear that increasing the temperature did not favor these two adsorbents.

Two experiments were then conducted to study the influence of temperature shown in Figures 4.8 and 4.9.

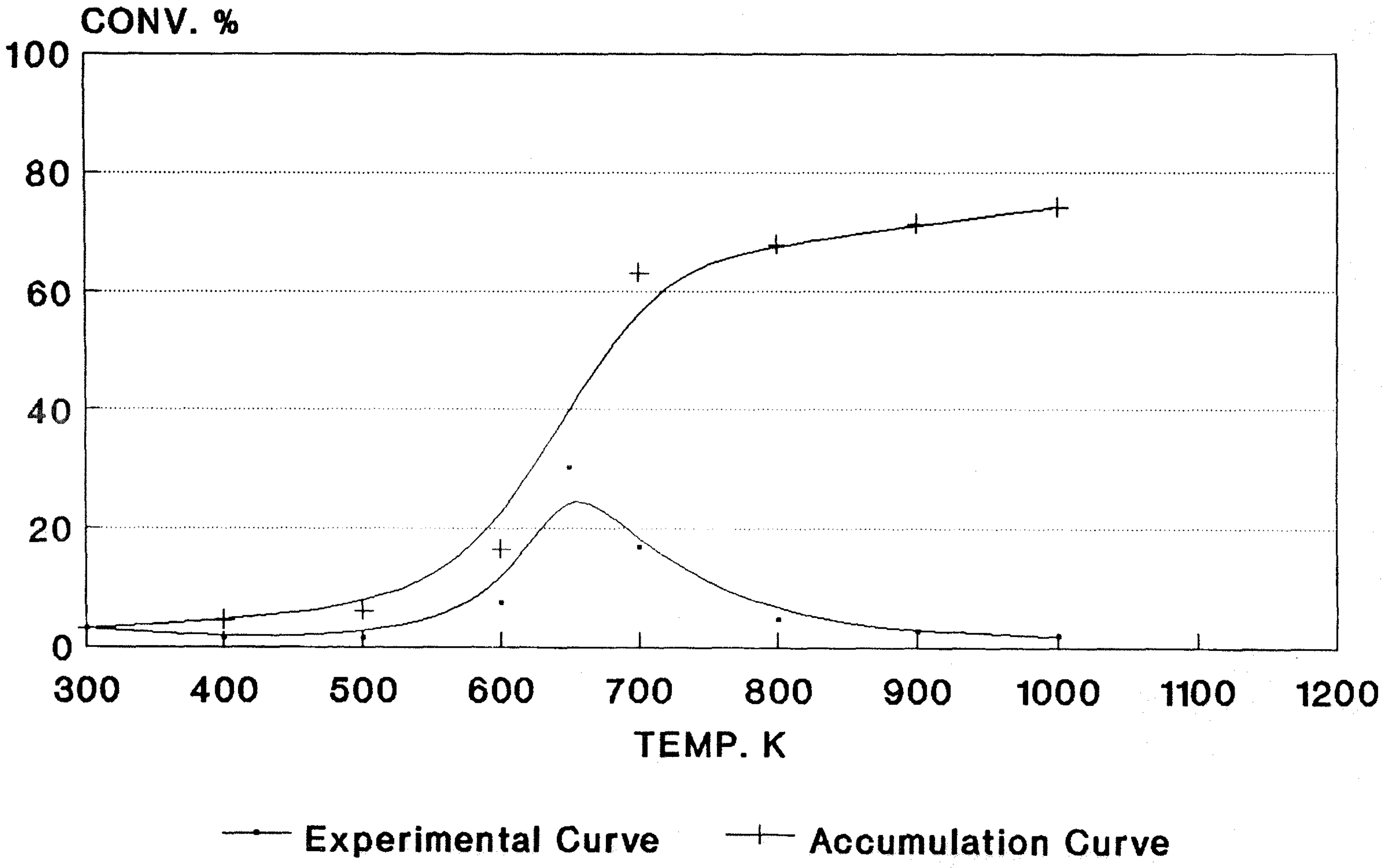
The objective of these experiments was to measure the breakthrough time at each reaction temperature from 300 to 1,000 K at constant flow rate and concentration of HCl. The breakthrough time on each reaction temperature represented the reaction activity at that temperature. With the breakthrough time, we calculated how many moles of HCl gas and solid reactants had been consumed. Figures 4.8 and 4.9 show both integral curve and differential curve for calcium hydroxide ($Ca(OH)_2$) and calcium oxide (CaO) conversion changing with temperatures.

From these curves, the following results are obtained:

(1) The tendency of solid reactant activities changes with increasing temperatures. At a low temperatures, the activity of solid reactants improves with the increasing temperatures because the reaction rate increases with the increasing temperatures. At high temperatures, the activity of solid reactants is reduced with temperature because of the sintering and the melting of adsorbents.

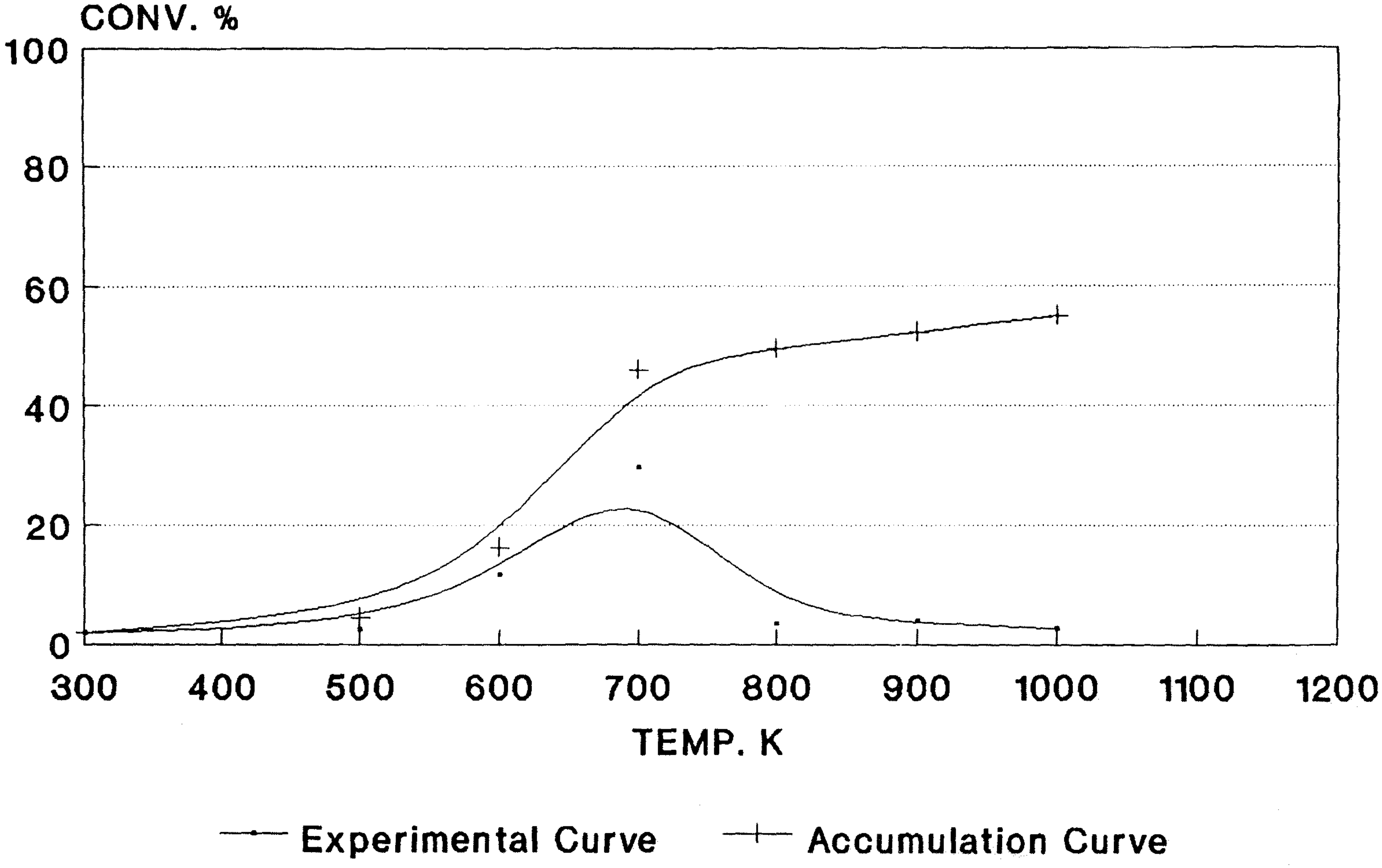
(2) The best reaction temperature range for calcium hydroxide ($Ca(OH)_2$) powder is 600 - 700 K; for calcium oxide (CaO) powder, the best reaction temperature range is 700 - 800 K.

Figure 4.8 Temperature Influence
Ca(OH)2 Conv. vs. Temp. Curve



Ca(OH)2 Powder = 0.05 Mole
HCl Conc. = 20600 ppm

Figure 4.9 CaO Powder Adsorbed HCl Conversion vs. Temperature Curve



CaO Powder = 0.05 Mole
HCl Conc. = 21040 ppm

(3) At temperatures below 500 K , both powder adsorbents react slowly with HCl.

(4) Over 1,000 K, the activities of the powdered solids decrease.

4.1.4 Effects of Different Calcium Compounds on HCl Adsorption

To compare the ability of calcium carbonate ($CaCO_3$), calcium oxide (CaO) and calcium hydroxide ($Ca(OH)_2$) to adsorb HCl gas, we ran six experiments at the best reaction temperature ranges of 700 - 800 K. In these experiments, we used the same amount of solid reactants as the adsorption bed (0.05 mole), the similar HCl feed gas concentration (10,300 - 18,000 ppm), and the same flow rate of feed gas of 800 cc/min. Figures 4.10 - 4.15 show the HCl effluent curves and the calcium utilization curves in each experiment. Three of experiments were run at 700 K; the other three were run at 800 K. These results are compared in Figure 4.16 and Figure 4.17.

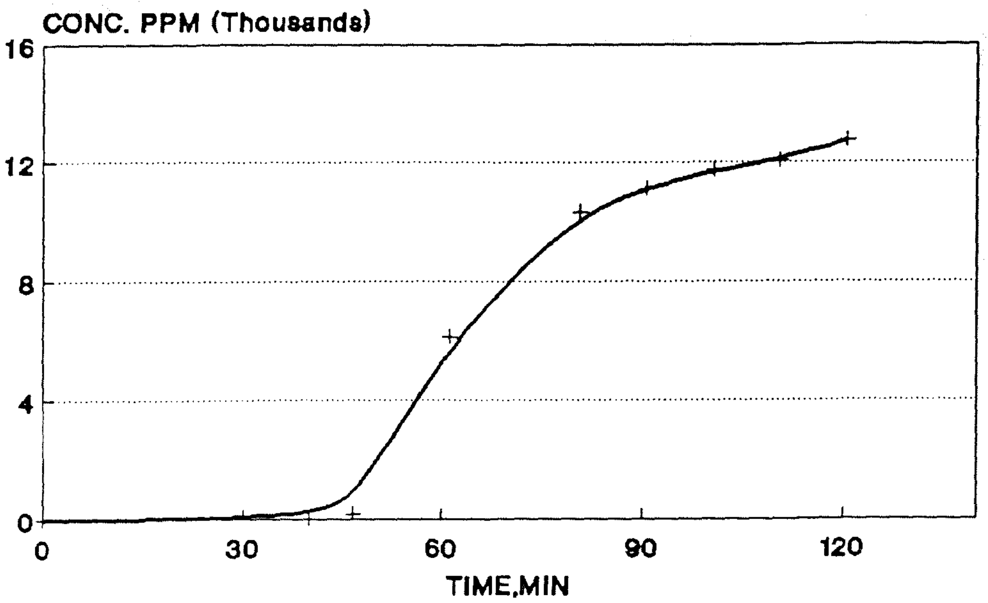
Figure 4.16 shows the HCl conversion curves for the three calcium compounds reacting with HCl feed gas at 700 K. At this temperature, the activity sequence was

$$Ca(OH)_2 > CaO > CaCO_3$$

Figure 4.17 shows the HCl conversion curves at 800 K. At the higher temperature, the activity sequence was

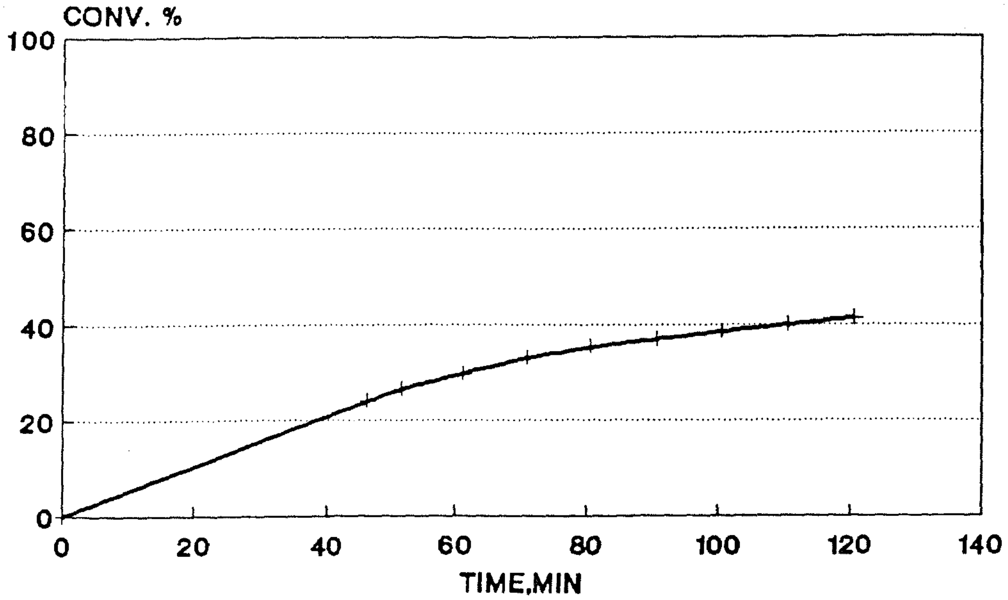
$$CaO > Ca(OH)_2 > CaCO_3$$

Figure 4. 10
(a) HCl Effluent Concentration
CaCO3 Adsorbed HCl at 700 K



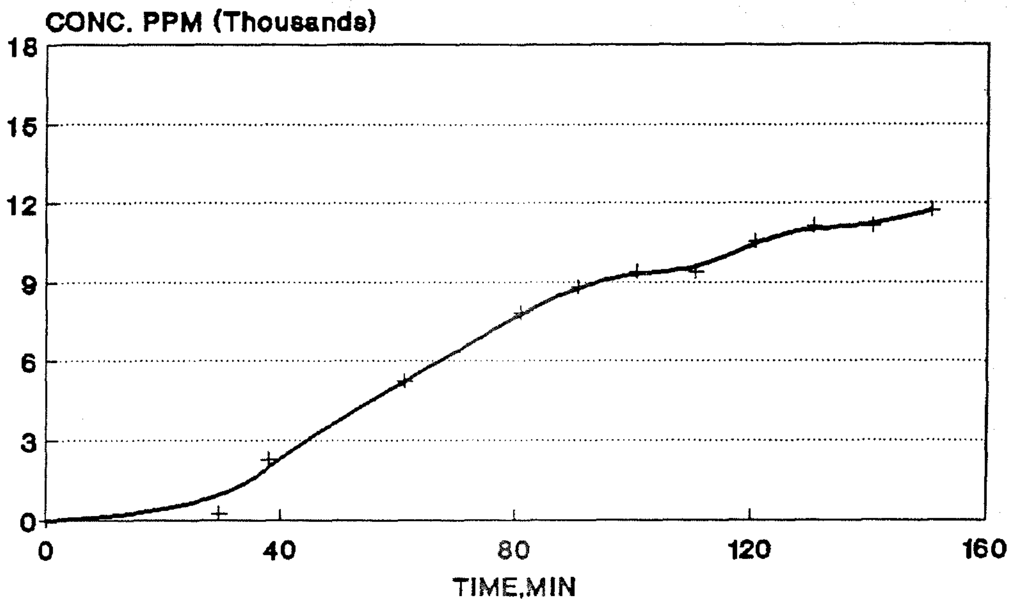
CaCO3 Powder = 0.05 Mole
HCl Conc. = 16000 ppm

Figure 4.10
(b) CaCO3 Conversion Curve
CaCO3 Adsorbed HCl at 700 K



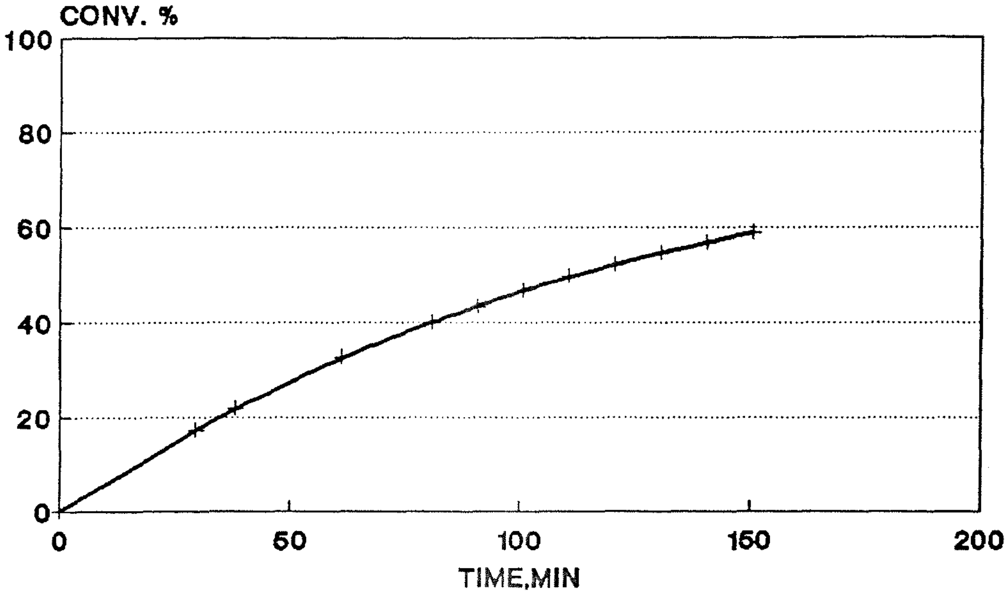
CaCO3 Powder = 0.05 Mole
HCl Conc. = 16000 ppm

Figure 4.11
(a) HCl Effluent Concentration
CaO Powder Adsorbed HCl at 700 K



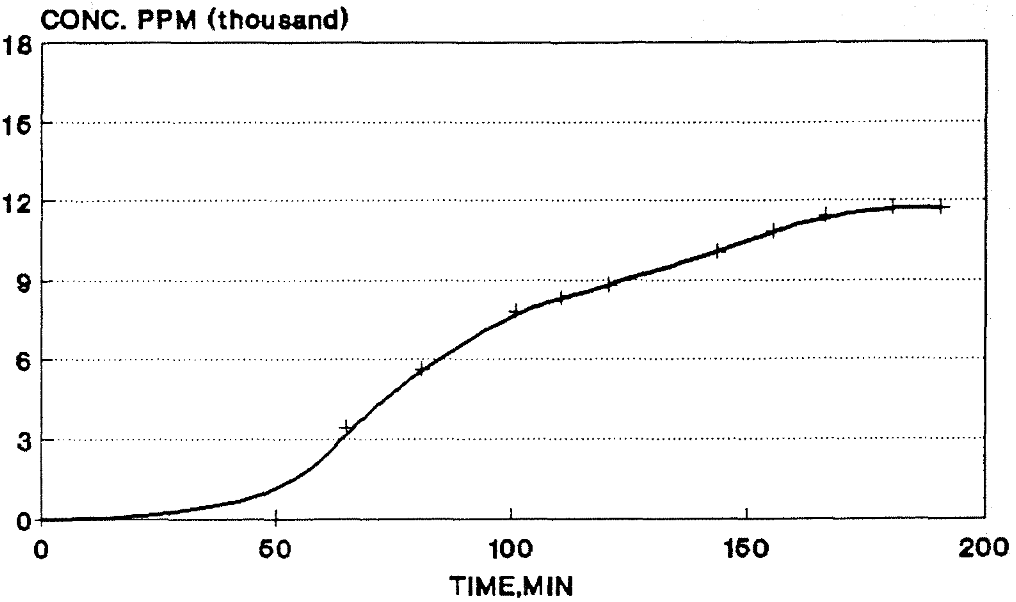
CaO = 0.05 Mole
HCl = 18000 ppm

Figure 4.11
(b) CaO Conversion Curve
Cao Powder Adsorbed HCl at 700 K



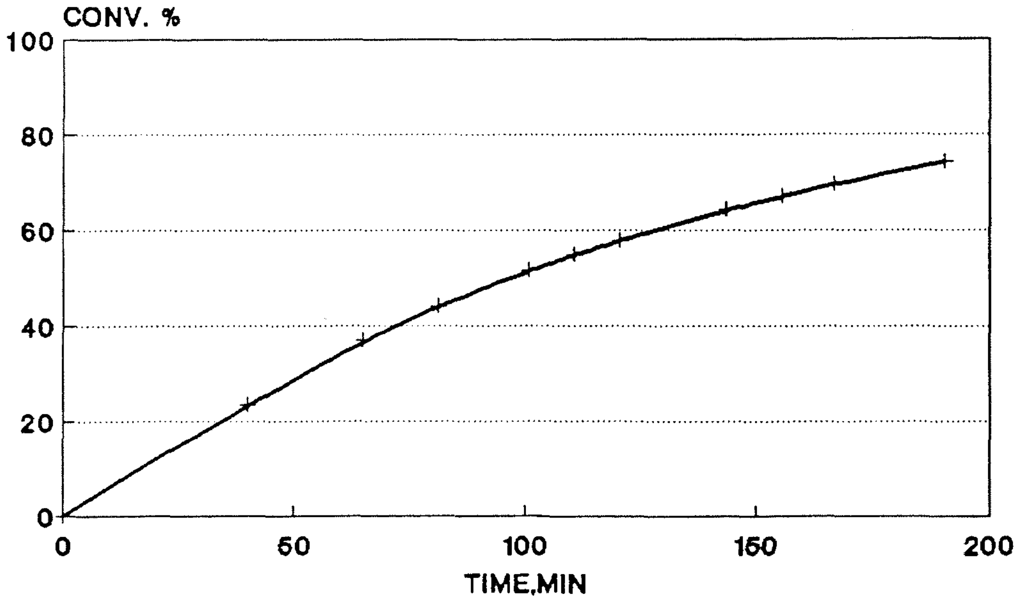
CaO Powder = 0.05 Mole
HCl Conc. = 18000 ppm

Figure 4.12
(a) HCl Effluent Concentration
Ca(OH)2 Powder Adsorbed HCl at 700 K



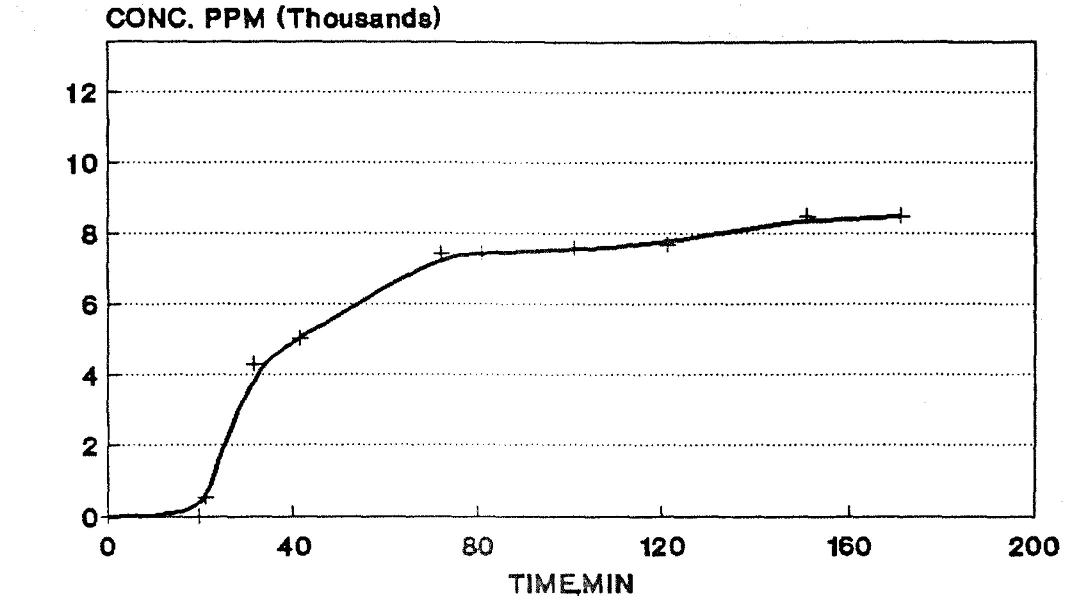
HCl = 18000 ppm
Ca(OH)2 = 0.05 Mole

Figure 4.12
(b) Ca(OH)2 Conversion Curve
Ca(OH)2 Powder Adsorbed HCl at 800 K



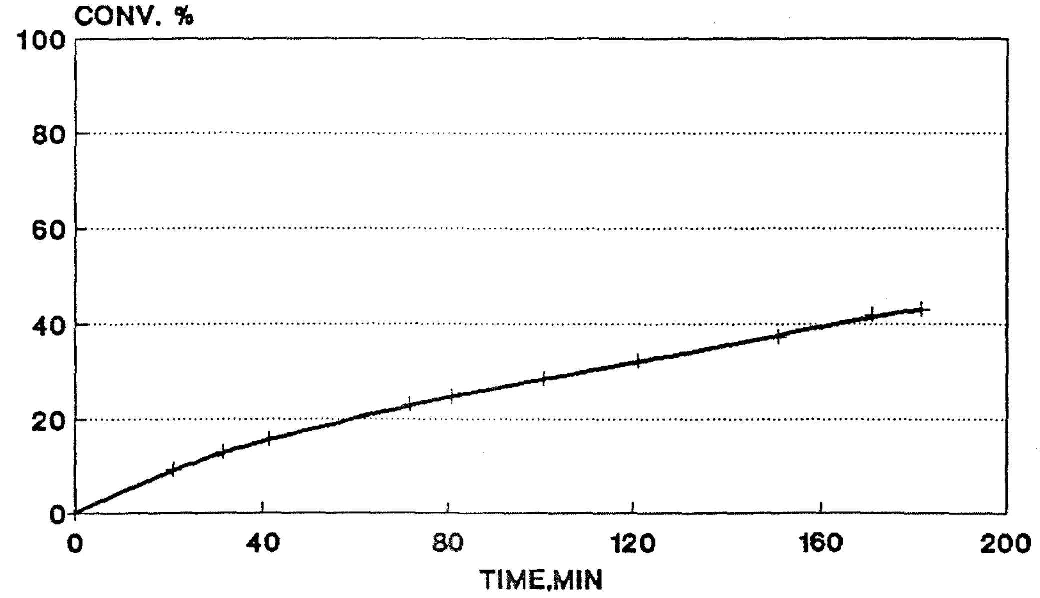
Ca(OH)2 = 0.05 Mole
HCl = 18000 ppm

Figure 4.13
(a) HCl Effluent Concentration
CaCO3 Adsorbed HCl at 800 K



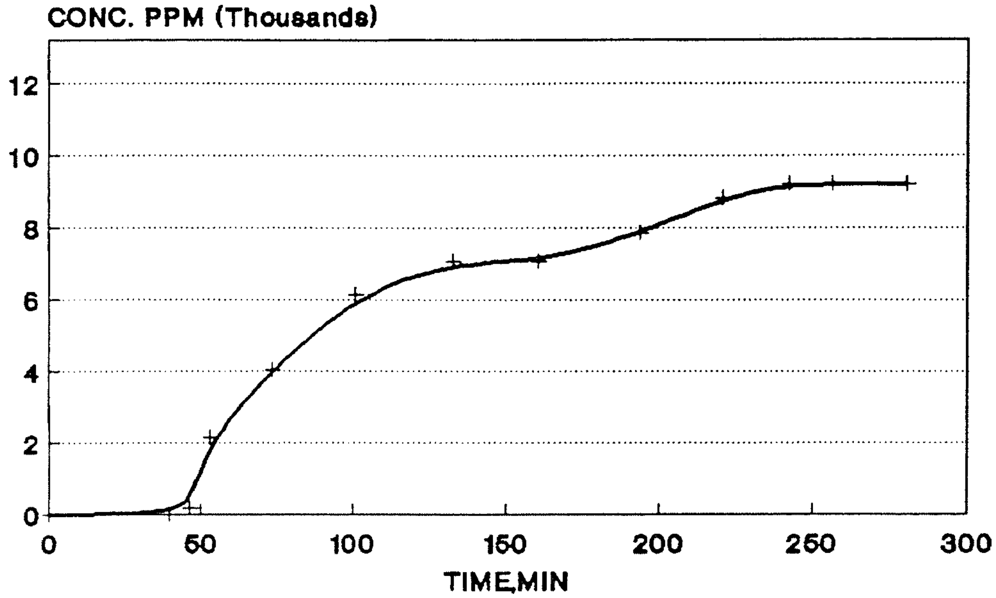
CaCO3 Powder = 0.05 Mole
HCl Conc. = 13400 ppm

Figure 4.13
(b) CaCO3 Conversion Curve
CaCO3 Powder Adsorbed HCl at 800 K



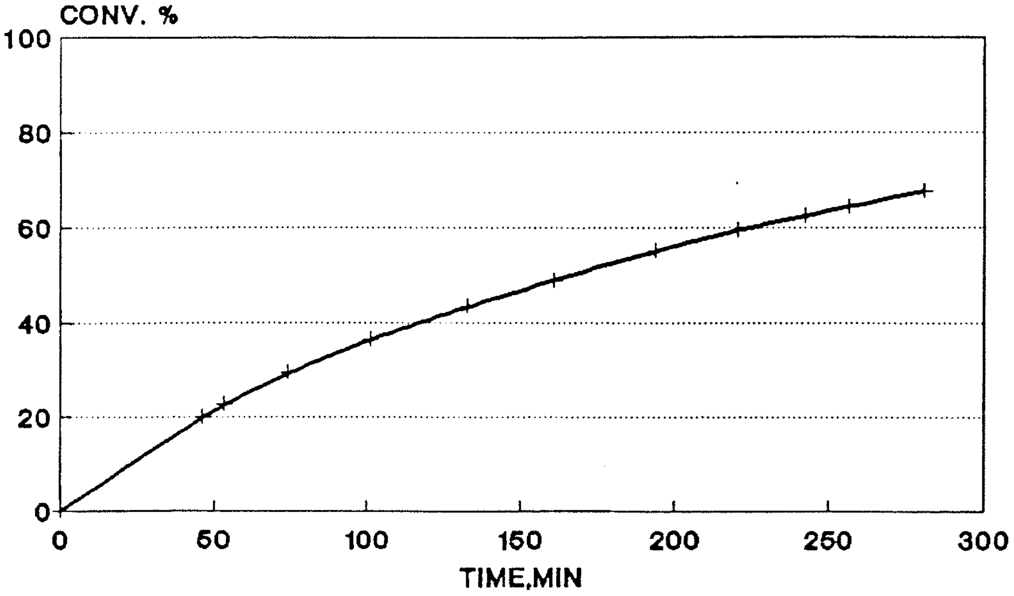
CaCO3 Powder = 0.05 Mole
HCl Conc. = 13400 ppm

Figure 4.14
(a) HCl Effluent Concentration
CaO Powder Adsorbed HCl at 800 K



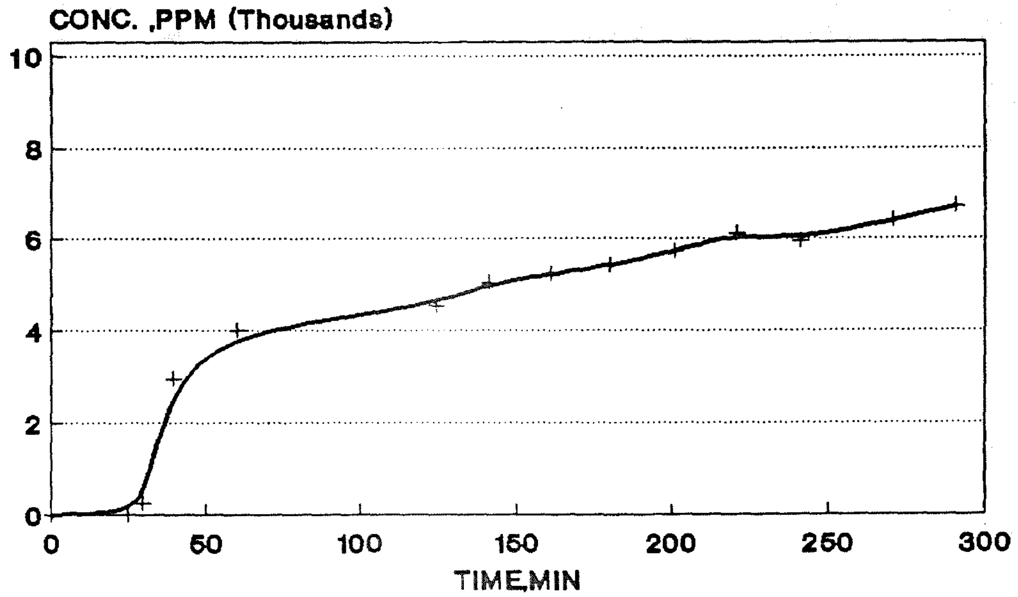
CaO Powder = 0.05 Mole
HCl Conc. = 13200 ppm

Figure 4.14
(b) CaO Powder Conversion Curve
CaO Powder Adsorbed HCl at 800 K



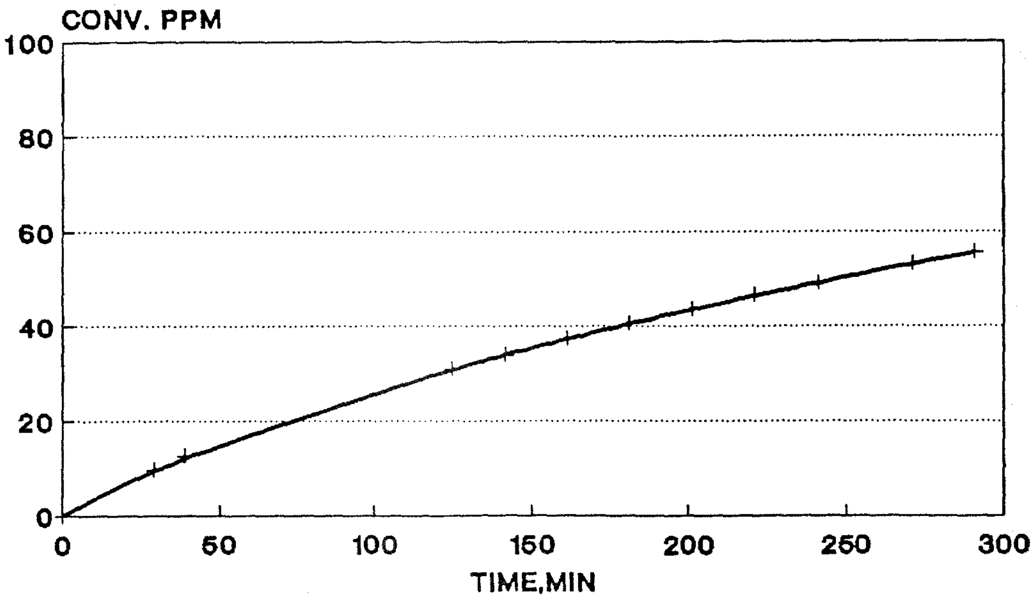
CaO Powder = 0.05 Mole
HCl Conc. = 13200 ppm

Figure 4.15
(a) HCl Effluent Concentration
Ca(OH)2 Adsorbed HCl at 800 K



Ca(OH)2 = 0.05 Mole
HCl Conc. = 10300 ppm

Figure 4.15
(b) Ca(OH)2 Conversion Curve
Ca(OH)2 Powder Adsorbed HCl at 800 K



Ca(OH)2 Powder = 0.05 Mole
HCl Conc. = 10300 ppm

The same activity sequence was obtained by comparing the conversion curves of the calcium compounds in these experiments at the same reaction temperature.

At 700 K, over the same reaction period, calcium hydroxide powder conversion reached 75.5 %, calcium oxide 60 %, and calcium carbonate 40 %.

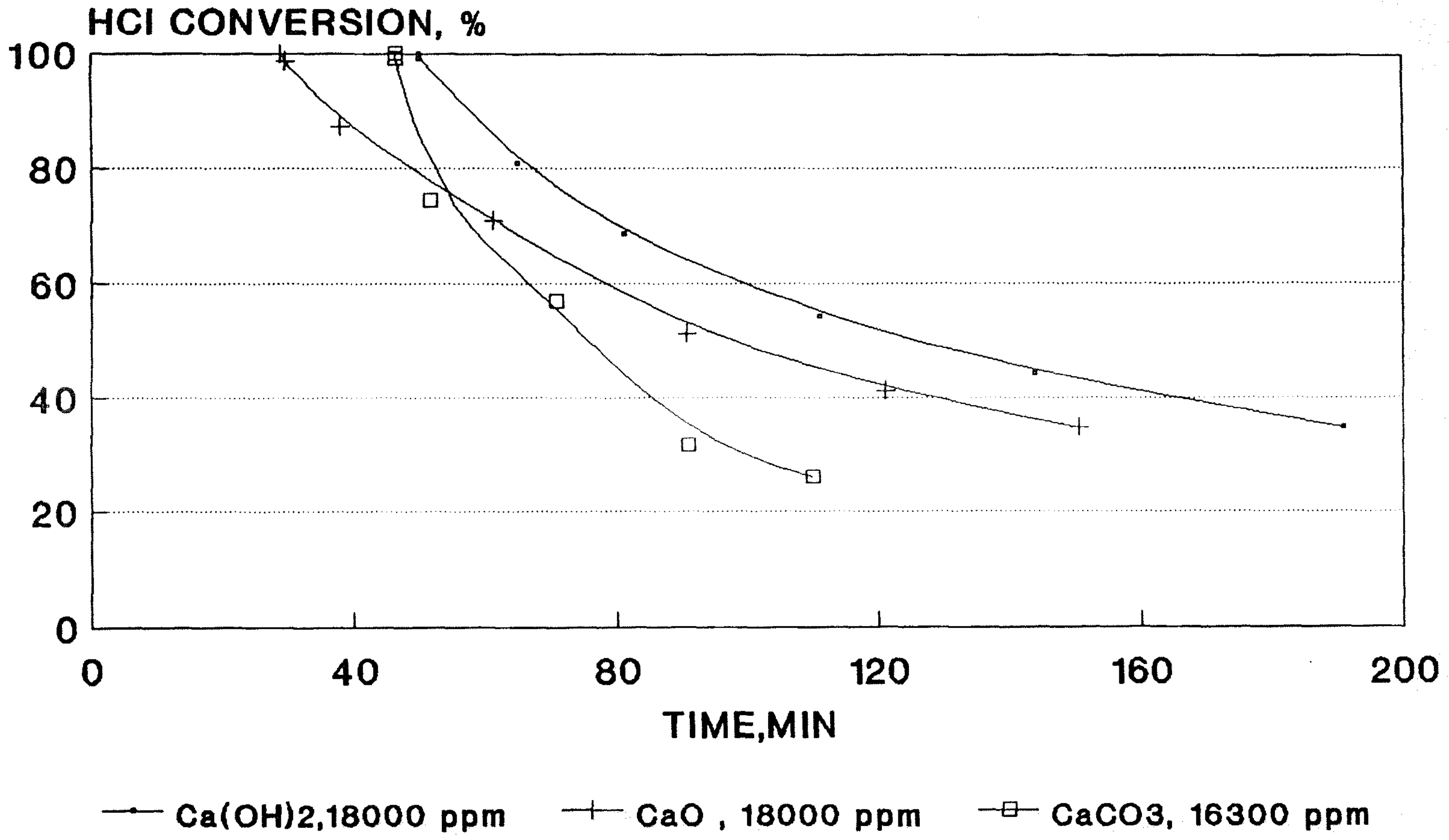
At 800 K, over the same reaction period, calcium oxide powder conversion reached 65 %, calcium hydroxide 58%, and calcium carbonate 45 %.

In general, all calcium compound powders were effective adsorbents. The differences among them were very small. At lower reaction temperatures, calcium hydroxide powder was the best reactant. At a high reaction temperature, calcium oxide was the best reactant. At much higher temperature, (i.e. at 1,000 K), both calcium carbonate ($CaCO_3$) and calcium hydroxide ($Ca(OH)_2$) changed into calcium oxide (CaO). In fact, calcium hydroxide changed into calcium oxide at 750 K, and calcium carbonate changed into calcium oxide at 1,000 K. When calcium oxide was exposed to water at room temperature, it changed back to calcium hydroxide. Consequently, these calcium compounds can be changed into each other at predictable conditions.

4.1.5 Effects of Feed HCl Gas Concentrations Compare for Constant HCl Moles

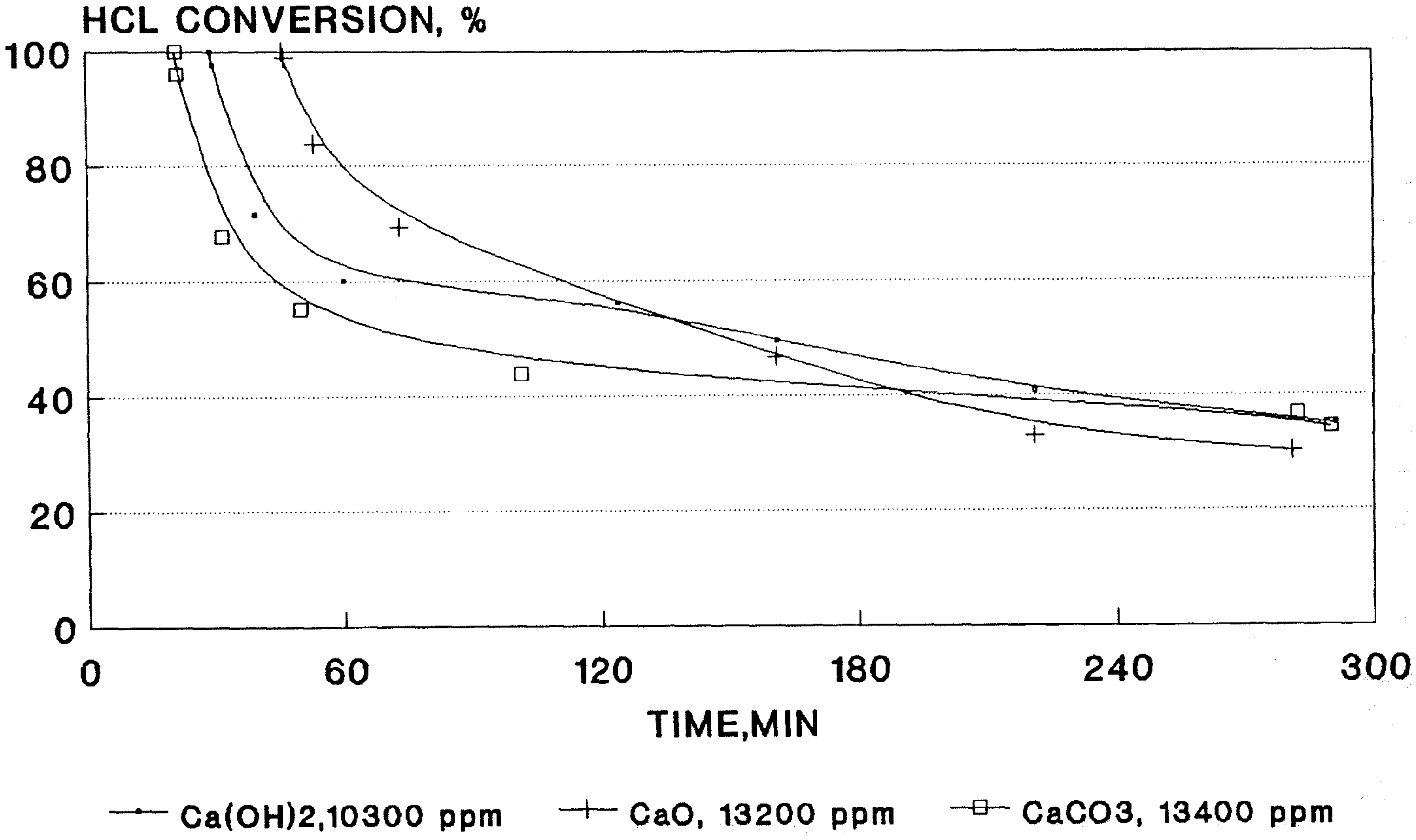
To compare the influence of HCl concentrations, we ran a number of experiments with different HCl concentrations.

Figure 4.16 HCl Conversion Curve
CaO, Ca(OH)2, CaCO3 Powder at 700 K



Ca(OH)2, HCl = 18000 ppm
CaO, HCl = 18000 ppm
CaCO3, HCl = 16300 ppm

Figure 4.17 HCl Conversion Curve
CaO, CaCO3, Ca(OH)2 Powder at 800 K



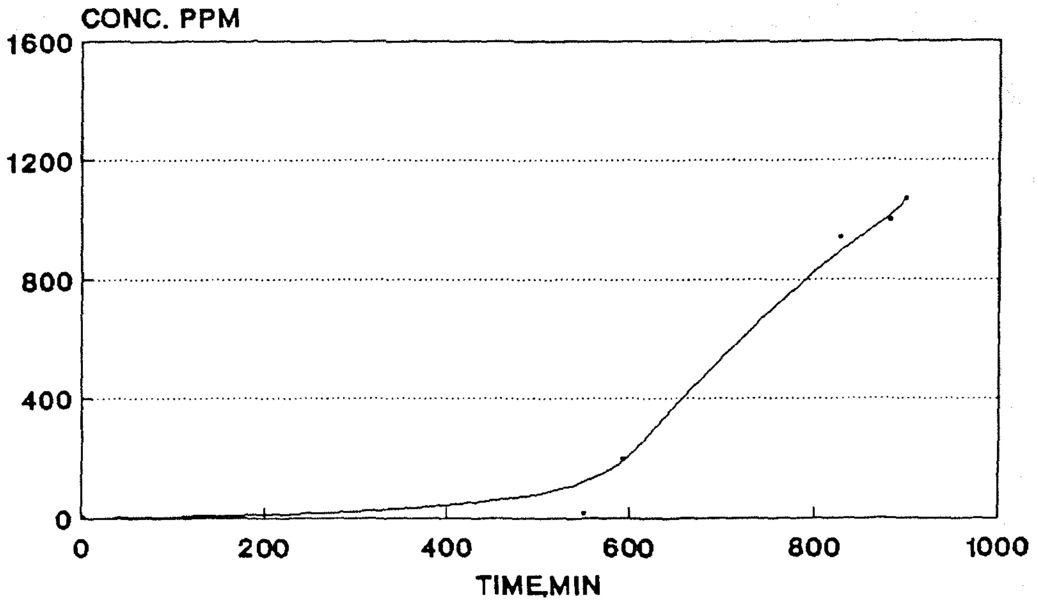
Ca(OH)2 Powder, HCl = 10300 ppm
CaO Powder, HCl = 13200 ppm
CaCO3 Powder, HCl = 13400 ppm

Figures 4.18, 4.19, and 4.20 show three of these experiments in low HCl concentrations. In these experiments, we fixed the flow rate of the feed gas at 800 cc/min and used the three calcium compounds as solid adsorbents. Then, experiments were conducted at the best temperature ranges of 700 K and 800 K, and changed the HCl gas concentration from 1,600 ppm to 20,000 ppm in these experiments. A comparison of these results are shown in Figures 4.21 to 4.26.

In Figure 4.21, two experimental results of calcium carbonate conversion were compared. The only difference in the reaction conditions was the HCl feed concentration of 16,000 ppm vs. 1,600 ppm. There were big differences between the results of calcium carbonate conversion 40%, vs., 7% for same time. Comparing these experiment results with the results shown in Figures 4.22 to 4.26, One can see that the feed gas HCl concentration had an extremely important effect in the adsorption reactions.

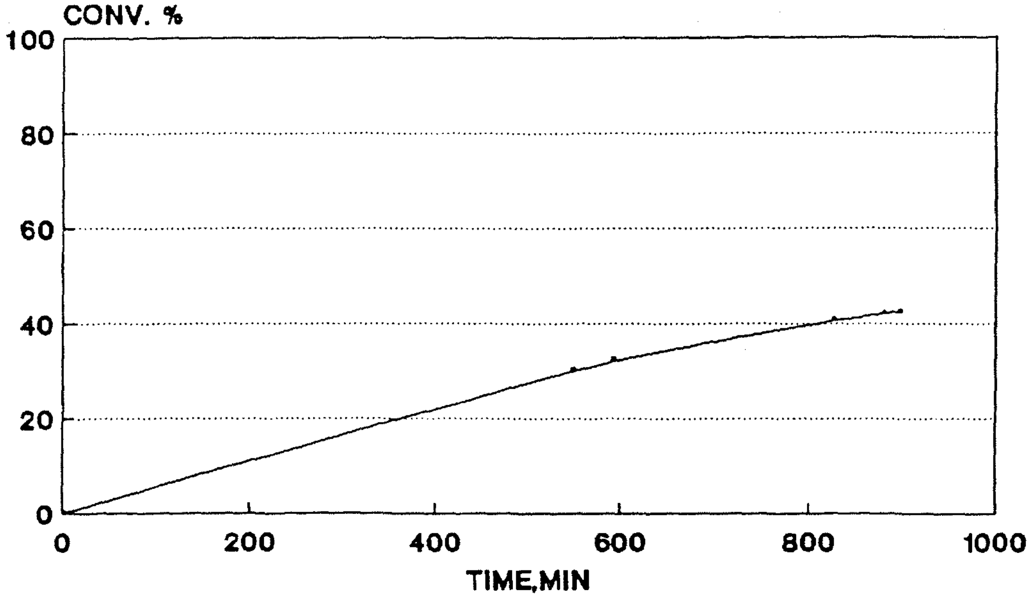
Figures 4.21 to 4.26 show the same trend of HCl concentration effects. The higher the HCl concentration, the higher the solid reactant conversion, but the shorter the breakthrough and the reaction times. The lower the HCl concentration, the longer the breakthrough time. So, for a higher HCl concentration of feed gas, more solid reactants in the reaction bed were needed to make the breakthrough time longer. However, one a equal mole of HCl fed to the system, results are equivalent.

Figure 4.18
(a) HCl Effluent concentration Curve
$CaCO_3$ Powder Adsorbed HCl at 700 K



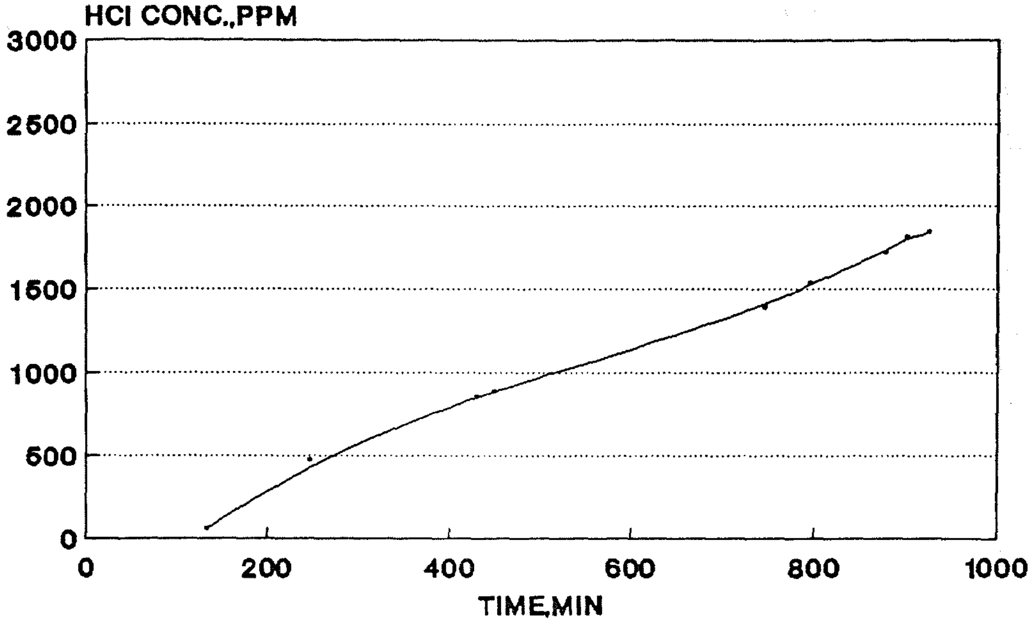
$CaCO_3$ Powder = 0.05 Mole
HCl Conc. = 1600 ppm

Figure 4.18
(b) $CaCO_3$ Conversion Curve
$CaCO_3$ Powder Adsorbed HCl at 700 K



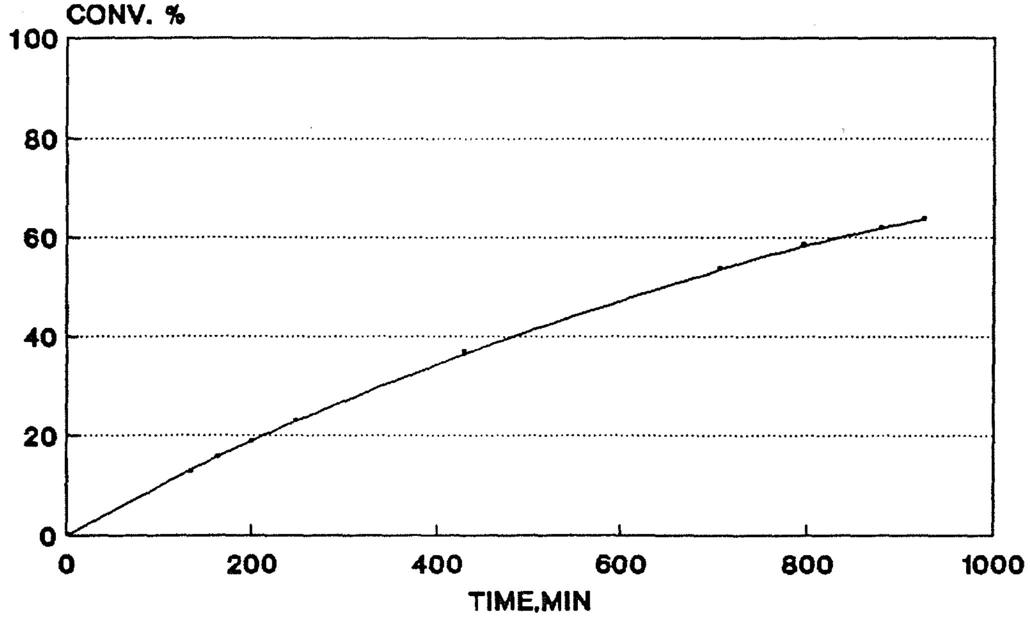
$CaCO_3$ = 0.05 Mole
HCl Conc. = 1600 ppm

Figure 4.19
(a) HCL Effluent Concentration
Ca(OH)2 Powder Adsorbed HCl at 700 K



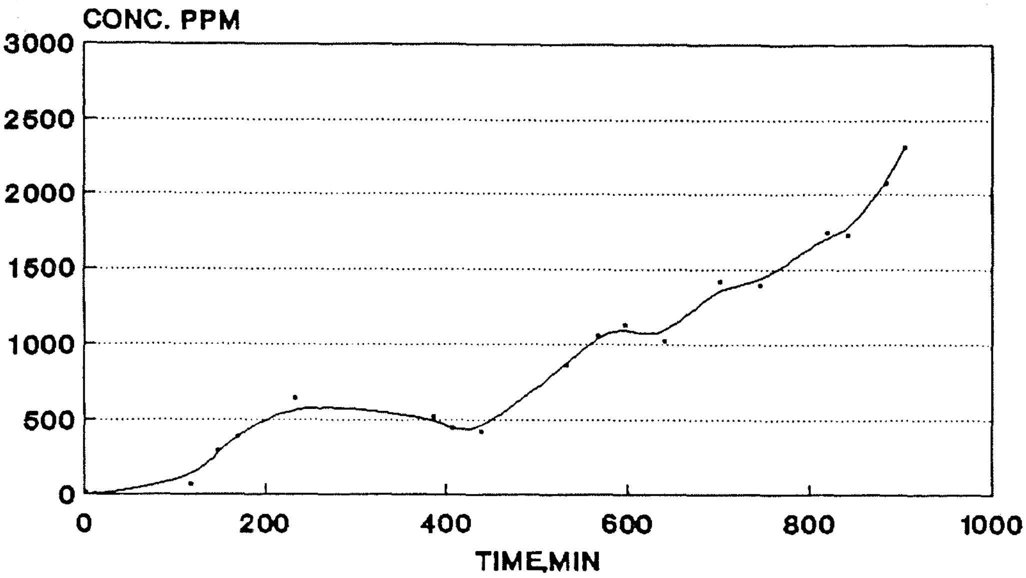
HCl Conc.= 3000 ppm

Figure 4.19
(b) Ca(OH)2 Conversion Curve
Ca(OH)2 Powder Adsorbed HCl at 700 K



Ca(OH)2 = 0.05 Mole

Figure 4.20
(a) HCl Effluent Concentration
CaO Powder Adsorbed HCl at 800 K



CaO = 0.05 Mole

HCl Conc. = 3000 ppm

Figure 4.20
(b) CaO Conversion Curve
CaO Powder Adsorbed HCl at 800 K

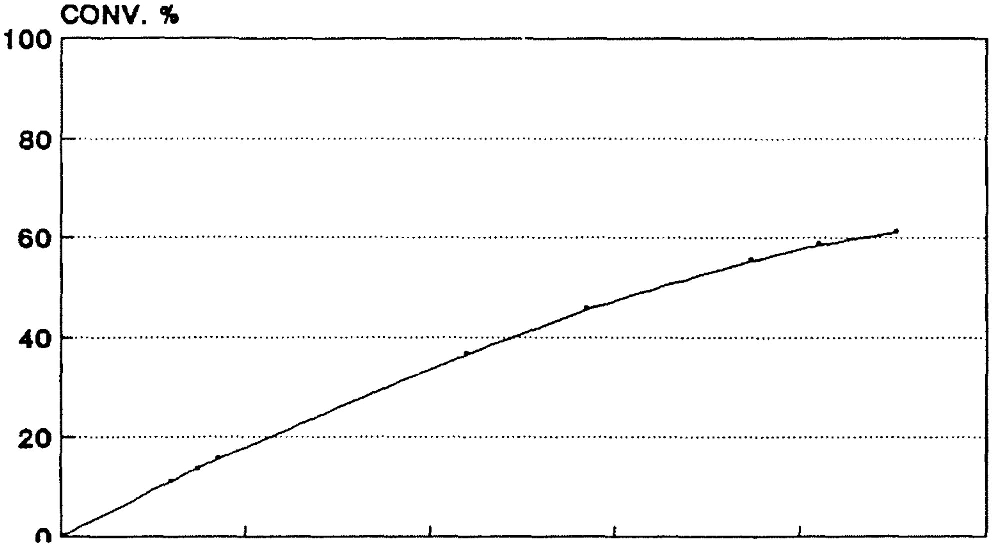
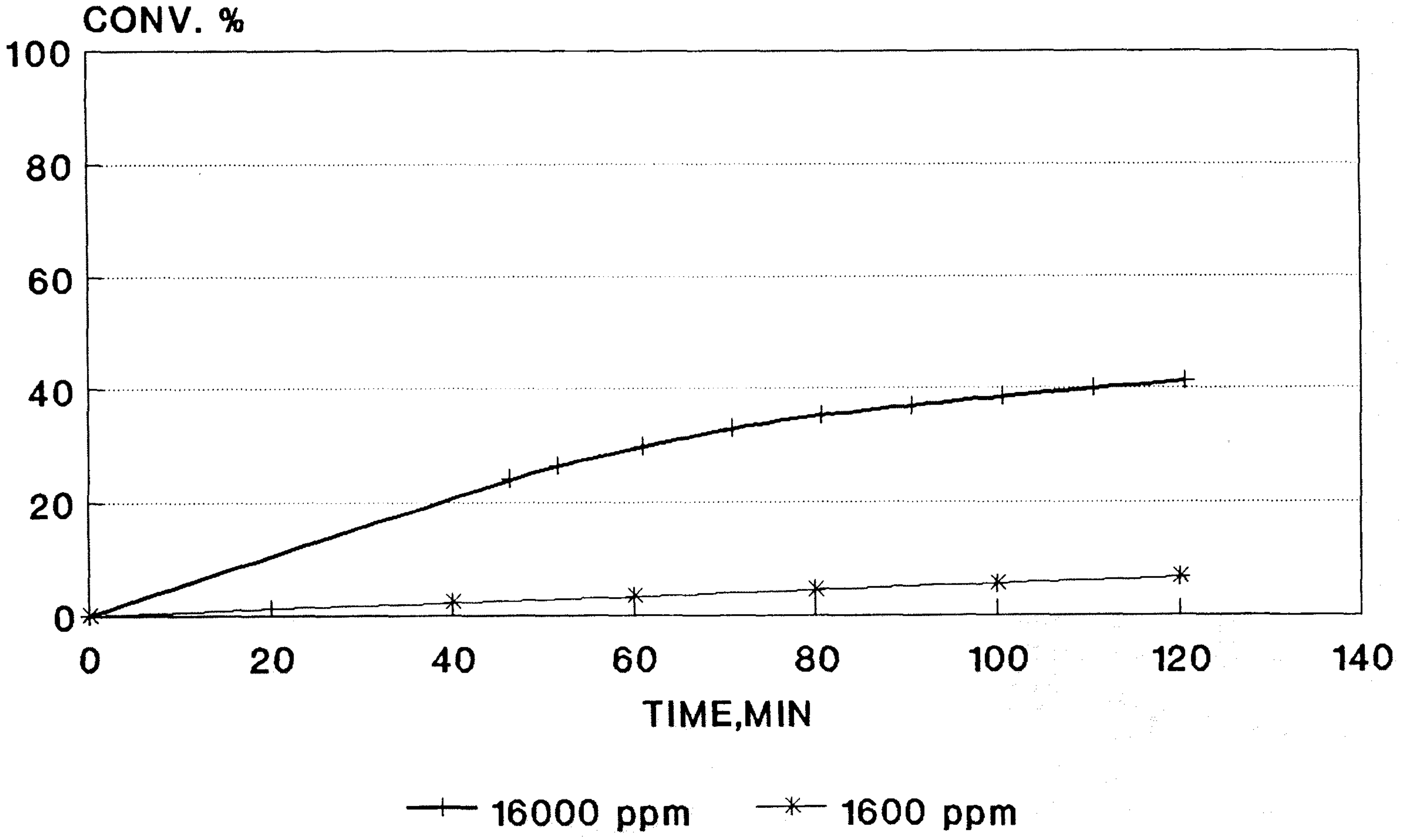
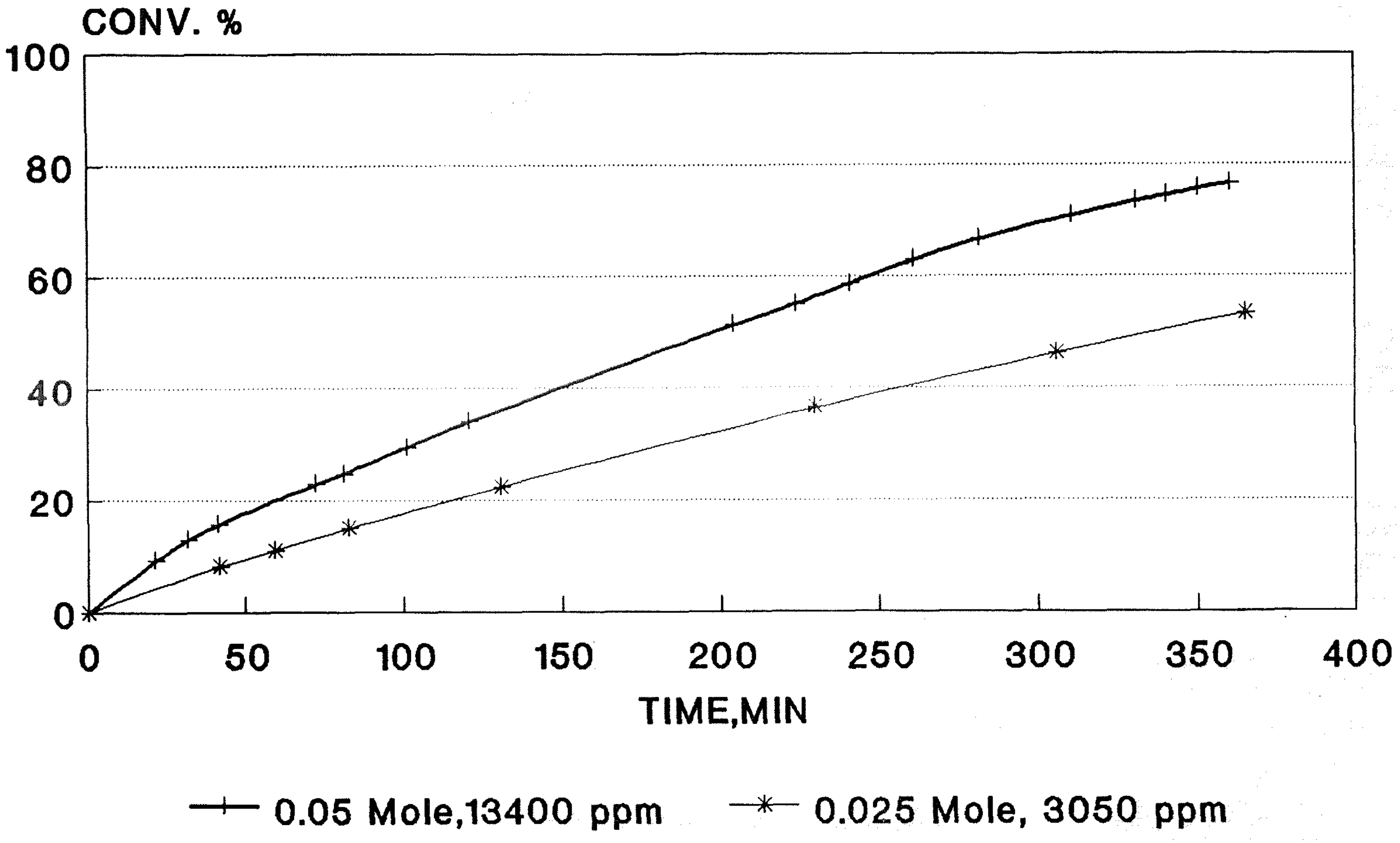


Figure 4.21 Conc. Comparison Curve
CaCO3 Powder Adsorbed HCl at 700 K
HCl Conc. 16000 ppm vs. 1600 ppm



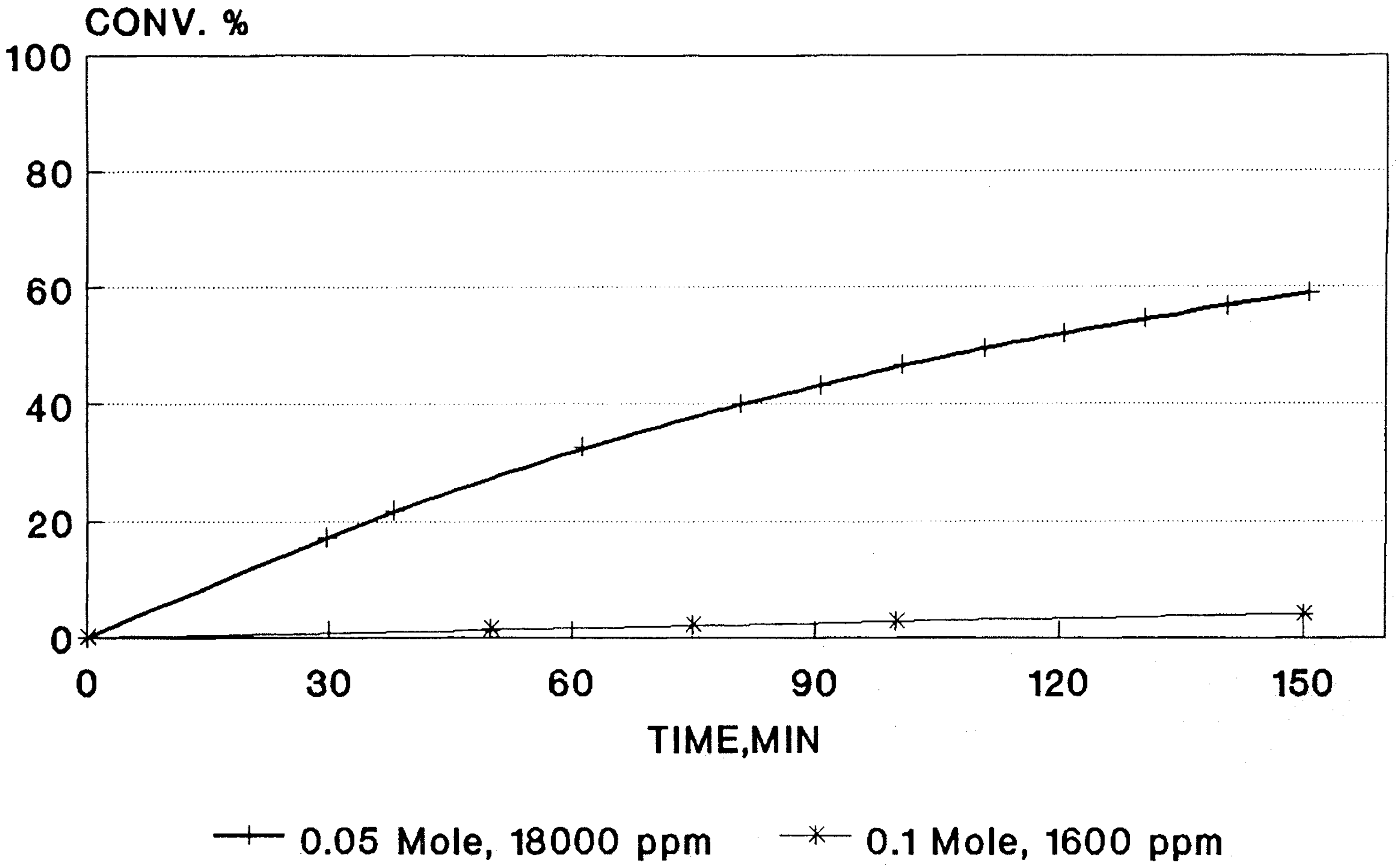
CaCO3 Powder = 0.05 Mole
HCl Conc. = 16000 ppm, 1600 ppm

Figure 4.22 HCl Conc. Effects
$CaCO3$ Powder Adsorbed HCl at 800 K
HCl Conc. 13400 ppm,vs.,3050 ppm



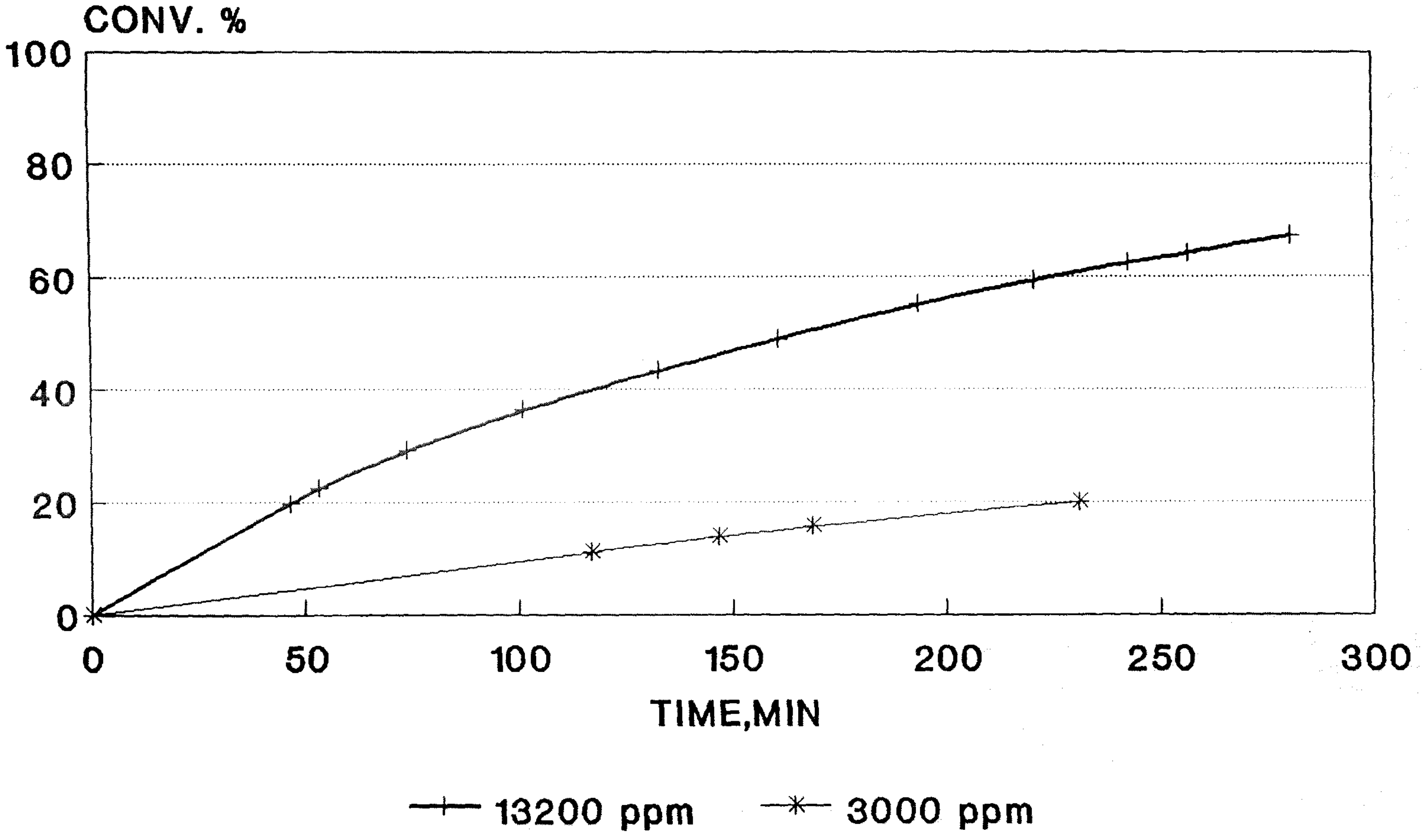
$CaCO3$ Powder = 0.05 Mole, 0.025 Mole
HCl Conc. = 13400 ppm, 3050 ppm

Figure 4.23 Conc. Comparison Curve
CaO Powder Adsorbed HCl at 700 K
HCl Conc. 18000 ppm vs. 1600 ppm



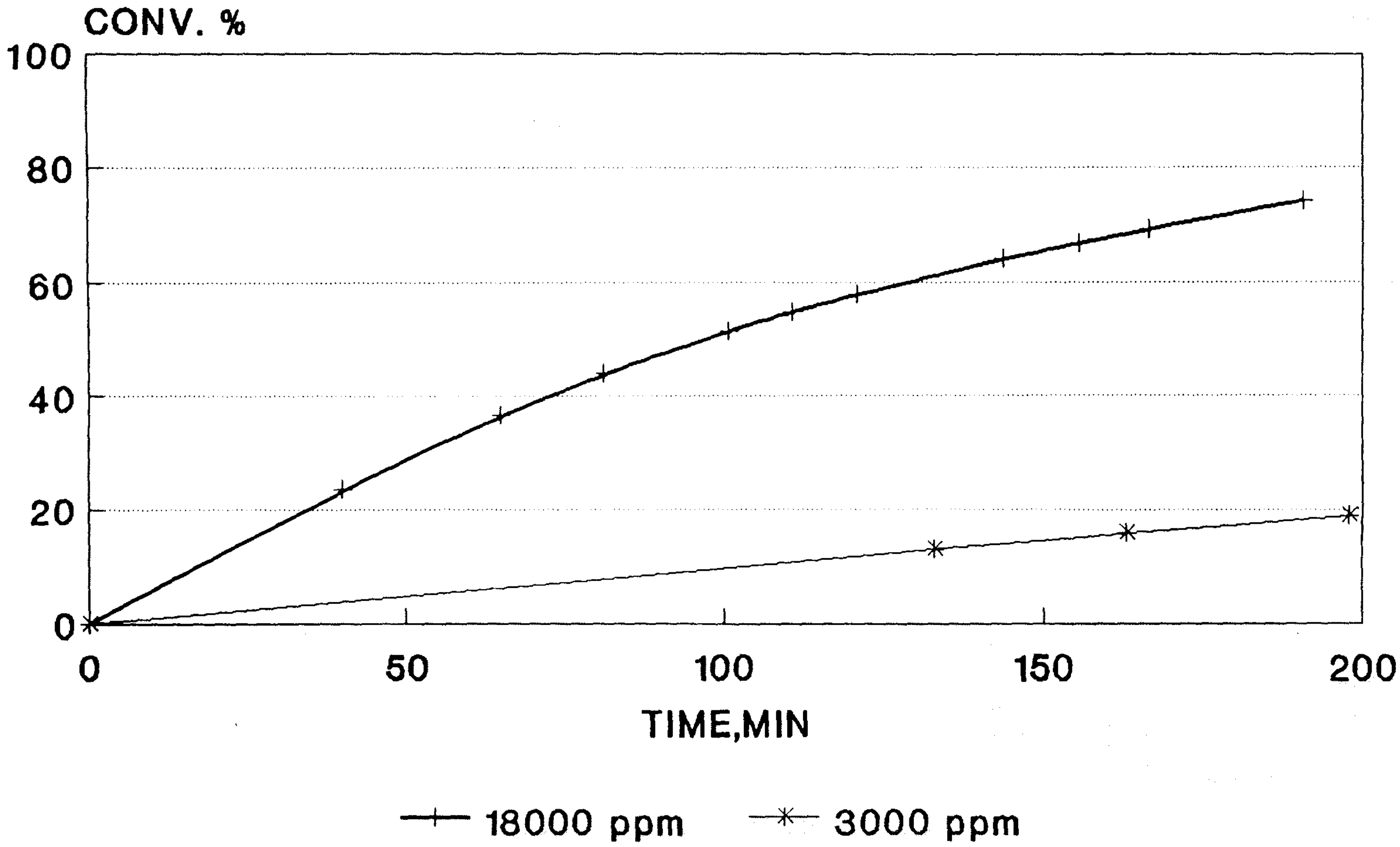
CaO Powder = 0.05 Mole, 0.1 Mole
HCl Conc. = 18000 ppm, 1600 ppm

Figure 4.24 Conc. Comparison Curve
CaO Powder Adsorbed HCl at 800 K
HCl Conc. 13200 ppm vs. 3000 ppm



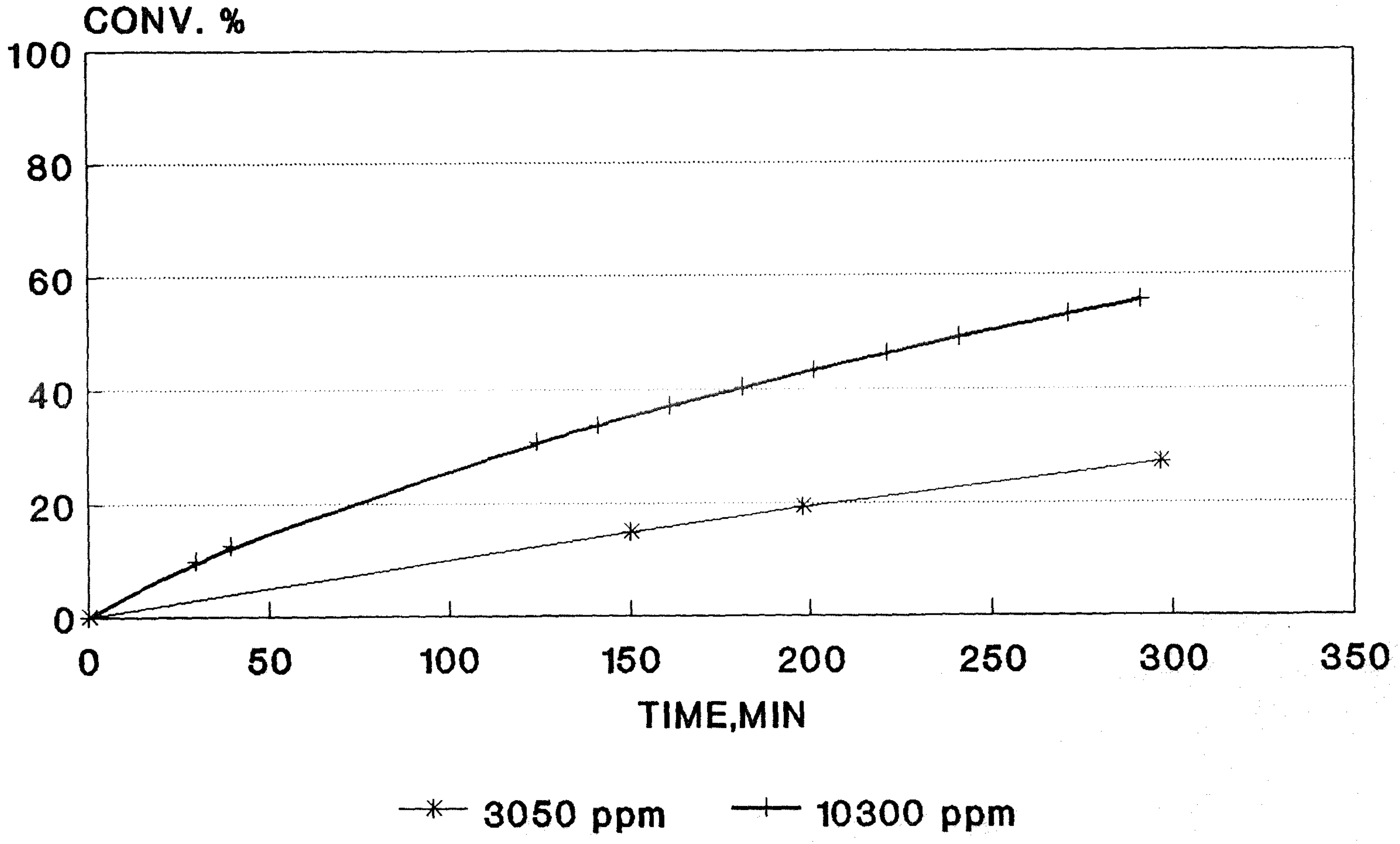
CaO Powder = 0.05 Mole
HCl Conc. = 13200 ppm, 3000 ppm

Figure 4.25 Conc. Curve Comparison
Ca(OH)2 Powder Adsorbed HCl at 700 K
HCl Conc. 18000 ppm vs. 3000 ppm



Ca(OH)2 = 0.05 Mole
HCl = 18000 ppm, 3000 ppm

Figure 4.26 Conc. Comparison Curve
Ca(OH)2 Adsorbed HCl at 800 K
10300 ppm vs. 3050 ppm



Ca(OH)2 = 0.05 Mole
HCl Conc. = 10300 ppm, 3050 ppm

4.2 Effects of Different Particle Size Adsorbents

To study the effects of calcium compound, temperature, and HCl concentration, we chose powder reactants as adsorbents. Powder solid reactants had a much higher surface area than that of the large particle size reactants. In non-catalyst gas-solid reactions, a higher surface area solid reactant adsorbed more HCl gas and got a higher solid reactant conversion and a higher HCl conversion. On the other hand, powder reactants had a much higher pressure drop than those of the large particle size adsorbents. Table 4.1 shows the pressure drop data and the surface area data which we measured in our experiments for different particle size reactants.

In industrial processes, a higher pressure drop results in a higher energy consumption. So, powder reactants are generally not suitable for industrial processes even though they had good activity. In packed bed gas-solid reactions, pressure drops were determined as a function of particle size, gas flow rate and the height of the packed bed. These relationship are presented in Figure 4.27.

To reduce the pressure drop in the adsorption bed, large particle size calcium compounds were evaluated for their ability to adsorb HCl gas. Table 4.2 summarizes these experiment results.

In these experiments, large particle size calcium carbonate Q6-20 and calcium hydroxide Q6-20, where particle sizes are between 0.841 - 3.36 mm, calcium carbonate Q20-60

Table 4.1 Solid Reactants Surface Area Measurements And Pressure Drop Messurements

Material	Surface Area (m*m/g)	Pressure Drop (cm, H2O)	Adsorption Bed Height (cm)
CaCO3 Powder	13.5	12.45	4.0
Q6-20 CaCO3	< 1.0	0.1	3.5
Ca(OH)2 powder	11.7	9.60	2.0
Ca(OH)2 Q6-20	2.7	0.9	3.7
CaCO3 Q100	0.72	27.4	3.0
CaCO3 Q40-200	0.35	21.7	3.0
CaCO3 Q20-60	0.48	3.45	1.5

Flow Rate = 800 cc/min

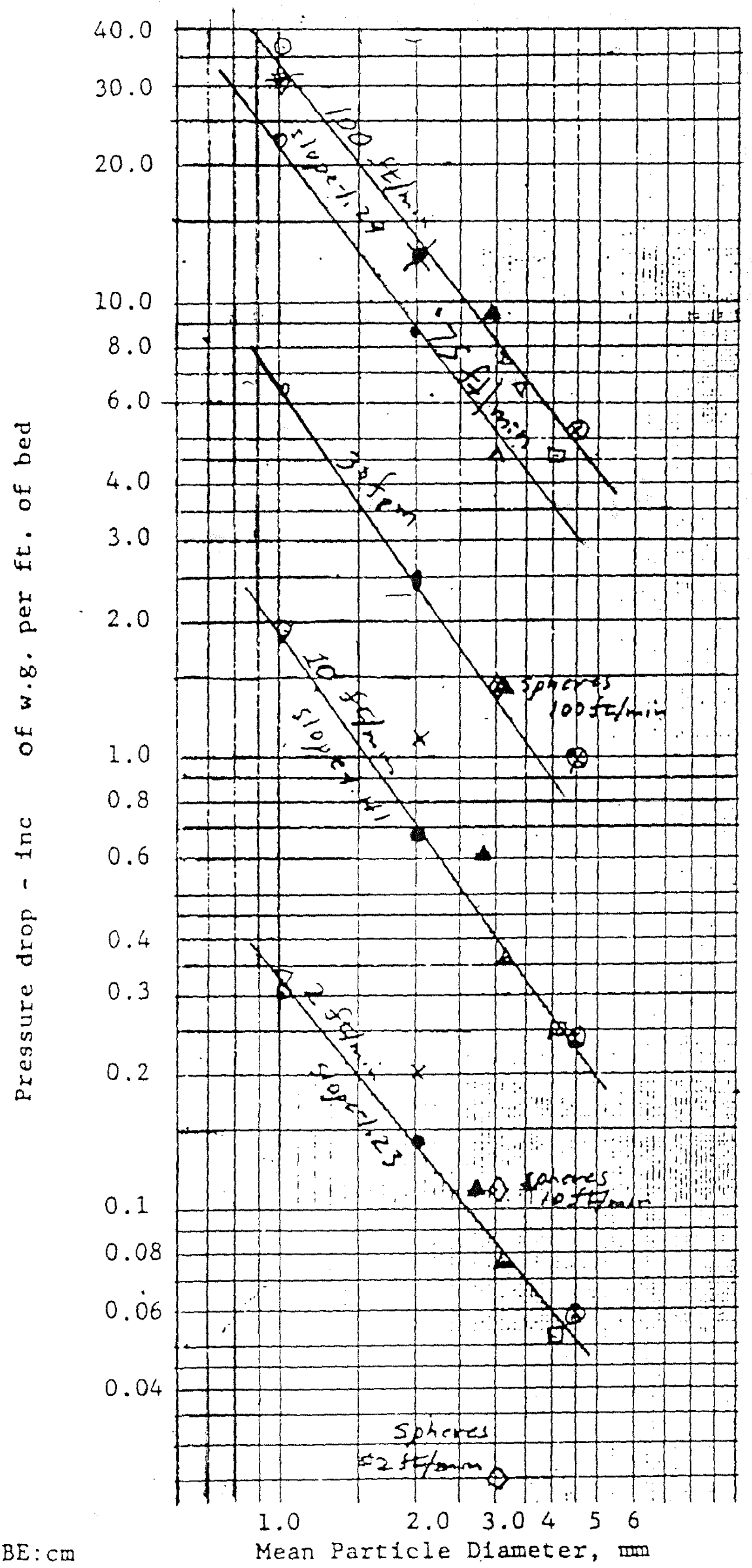


FIGURE 27

Pressure Drop Vs. Particle Size

DBE:cm

(0.250 - 0.841 mm), powdered calcium carbonate, powdered calcium oxide , and powdered calcium hydroxide, where the diameters were less than 400 mesh or less than 0.037 mm, were conducted.

From Table 4.2, one can reach several conclusions:

(1) Large particle size adsorbents have a lower pressure drop in the reaction bed and usually a lower conversion than for the powdered reactants.

(2) Large particle size reactants had less surface area than powder reactants.

(3) Before and after the reactions, the powder reactant bed pressure drop changed considerably. When the powder reactant reacted with high HCl feed gas , a higher product conversion was obtained, and that made the structure of adsorption bed change substantially.

(4) The temperature of the reaction bed determined the pressure drop of the powder adsorption bed. When the reaction temperature was 700 K, a low pressure drop was observed before and after the reaction. When the reaction temperature was 800 K, a significant pressure drop was observed before and after the adsorption.

(5) For large particle size reactants, the activity of adsorption of HCl was improved by raising the reaction temperature. The pressure drop did not change significantly with increasing temperature.

Table 4.2 Different Particle Size Comparison

Exp	HCl Conc. (ppm)	Material (mole)	PDBR (cm, H_2O)	PDAR	SA (m/g)	RBH (cm)	TEMP (K)	CONV. (%)
1	1550	$Ca(OH)_2$ Q6-20 0.2125	0.9	0.9	2.7	3.7	700	24.0
2.	1550	$CaCO_3$ Q20-60 0.1	3.45	3.0	0.48	1.5	700	7.4
3.	1550	$CaCO_3$ powder 0.05	10.50	10.0	13.5	4.0	700	42.4
4.	13200	$CaCO_3$ powder 0.05	12.45	0.2	13.5	3.5	800	76.5
5.	13200	CaO powder 0.05	10.00	0.0	11.7	1.5	800	67.5
6.	10300	$Ca(OH)_2$ powder 0.05	9.60	0.15	11.7	2.0	800	55.6

PDBR - Pressure Drop Before Reaction
PDAR - Pressure Drop After Reaction
SA - Surface Area
RBH - Reaction Bed Height
TEMP - Temperature
CONV - Conversion

Flow Rate = 800 cc/min

(6) At the same reaction temperature, higher surface area reactants had higher activity to adsorb HCl and reached a higher adsorption of HCl. Improving the surface area of the reactants, improved the ability of adsorbing HCl on the adsorbents.

4.3 Improvement the Surface Area for the Large Particle Size Materials

From thermodynamic feasibility studies, one expects calcium carbonate to change into calcium oxide at high temperatures. The conversion temperature is about 1,000 K, and the equation for this reaction is

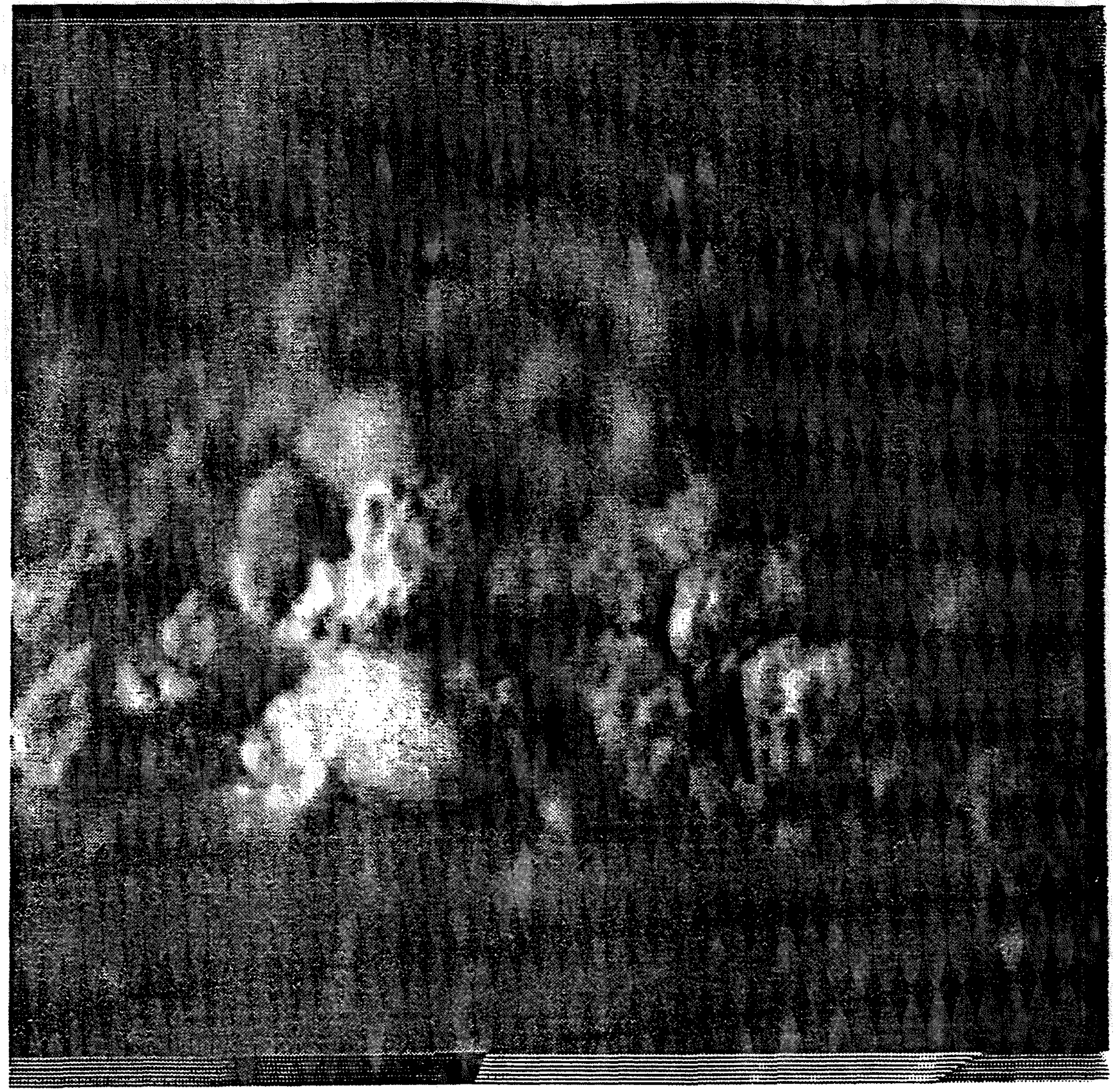
$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

A series of experiments were conducted to determine how much calcium oxide could be formed as a function of temperature. Two measuring methods were used to analyze the adsorption results. One method used a Gas Chromatograph (GC) to measure the concentration of carbon dioxide (CO_2) gas in the exiting gases and to calculate how many moles of CO_2 were produced. One can thus calculate the moles of calcium carbonate that were transformed into calcium oxide and carbon dioxide. The other method was to weigh the reaction material before and after the reaction. The lost weight was the weight of carbon dioxide. Thus, from the adsorption material balance, the moles of calcium carbonate which were changed into calcium oxide were estimated.

Large size particles Q6-20 $CaCO_3$, whose diameters are 0.841 - 3.36 mm, were tested. At 800 K, less than 1 % calcium oxide was formed. At 900 K, about 40 % calcium oxide was formed. At 1,000 K, after long enough reaction time, 100 % calcium oxide was formed.

After all the calcium carbonate was transformed into calcium oxide, cooling down the adsorption bed to room temperature and measuring the pressure drop of the reaction bed, it was found that the pressure drop was as low as that which we measured before the reaction. There were no observable changes of particle sizes. Carefully looking at the surface of the particles, it was found that there were many porosity, just like a honeycomb. Those channels were the pathways for the carbon dioxide to flow out from the internal parts of the particles. A photograph of these particles is shown in Figure 4.28. From the picture, one can clearly see the structure of the particles. To compare the difference between the surface area of this kind of material and that of other particle size materials, samples were analyzed by Engelhard Corporation. Engelhard used a standard BET method to measure the surface area of these samples. The test results are shown in Table 4.1. According to these results, the surface area of these honeycomb structure particles was 2.7 m^2/g, less than that of powder calcium oxide whose surface area was 11 m^2/g, but much higher than that of Q6-20 calcium carbonate whose surface area was < 1 m^2/g. One could expect this honeycomb structure of

Figure 4.28 Photograph of Q6-20 CaO Particles after Treatment



calcium oxide to adsorb more HCl gas than the same size calcium carbonate particles.

Experiments were conducted to test the ability of this honeycomb structure calcium oxide as an adsorbent to react with HCl gas. The conversion of the reactant reached 24 %. Compared to the Q6-20 $CaCO_3$ whose conversion was 7 %. The reactant conversion improved by a factor of three. That implies that one could use the same amount of adsorbent to adsorb much more HCl gas without the pressure drop problems. These reaction processes could be of industrial interest.

Even though the conversion reached 24 %, it was still not as good as was obtained with powders. Because the adsorption occurs on the adsorbent surface, the products covered the surface area to retard further reaction. Looking for a method to further use the unreacted adsorbents, $CaCl_2$ was dissolved into water. A lot of heat was released from the products. The calcium chloride dissolved in the water and the calcium oxide inside reacted with the water to form calcium hydroxide. The calcium hydroxide did not dissolve in the water. They were still the same size particles. Filtering and drying the solid particles in water, it was found that these particles also had lot of holes on their surface just like the honeycomb structure of calcium oxide. Figure 4.29 shows the picture of these particles. We can clearly see the honeycomb structures of the particles.

Engelhard Company helped us to measure this particle surface area by the standard BET method. It was 2.7 m^2/g, much higher than the same size calcium carbonate particles whose surface area was less than 1 m^2/g. Table 4.1 shows the measured results of different particle size surface area. We noticed that the large particle size calcium hydroxide surface area was greater than that of several kinds of particles whose diameters were much smaller than those of this calcium hydroxide. This confirmed that this treatment method provided a method to improve the surface area of large particle size reactants.

Several experiments were conducted to compare the ability of different adsorbents to remove HCl. Figures 4.30, 4.31, 4.32 show the HCl effluent concentration and adsorbent conversion of 0.1 mole Q20-60 $CaCO_3$, 0.2125 mole Q6-20 $Ca(OH)_2$, and 0.05 mole $CaCO_3$ powder reacted with 1550 ppm HCl gas in nitrogen. The reaction temperature was fixed at 700 K; the flow rate of the feed gases was 800 cc/min. The pressure drop results and reaction results are summarized in Table 4.2.

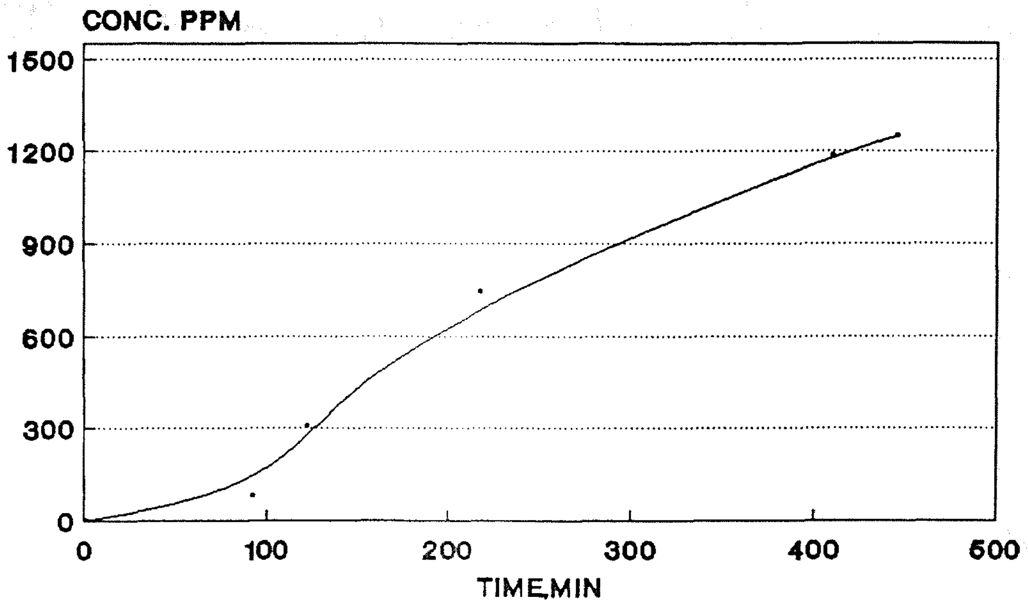
From Table 4.2, one can see that the conversion of Q6-20 $Ca(OH)_2$ was 20%, higher than that of Q20-60 $CaCO_3$ particles, and the pressure drops lower than measured for Q20-60 $CaCO_3$ particles. The experiment results shown that a good method was developed to produce adsorbents which have the potential for use in industrial processes.

The advantages of these kind of absorbents are:

(1) They have higher surface area and lower pressure drops;

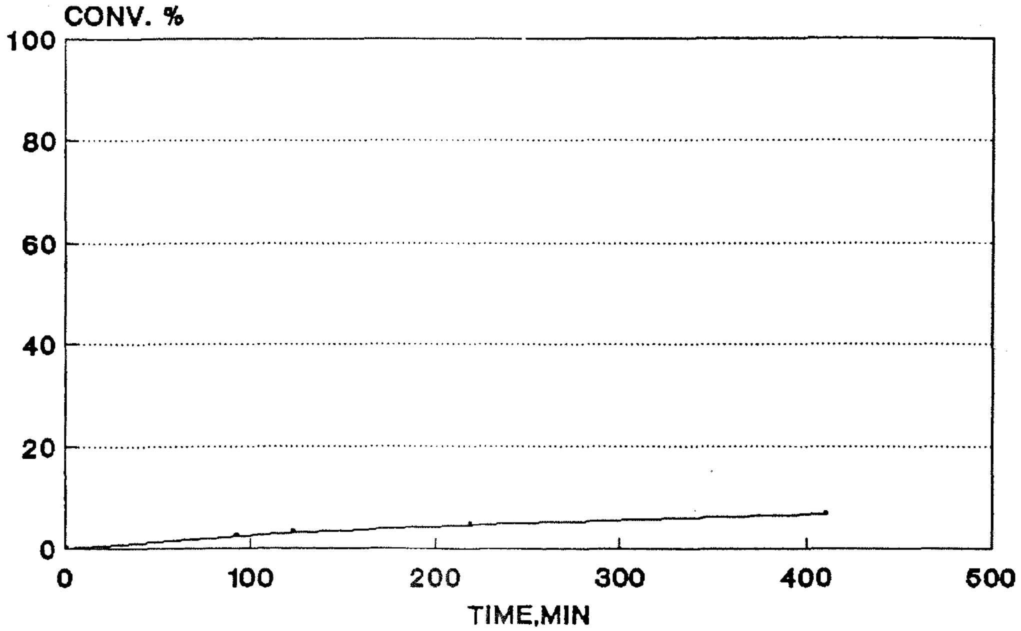
Figure 4.29 Photograph of Q6-20 Ca(OH)2 Particles after Treatment

Figure 4.30
(a) HCl Effluent Concentration
CaCO3 Q20-60 Adsorbed HCl at 700 K



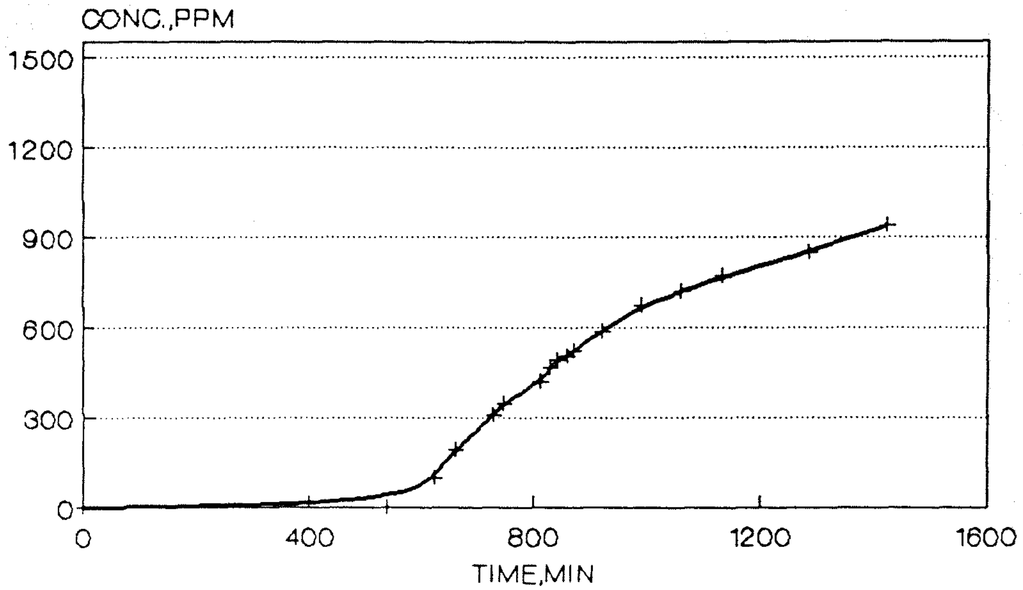
CaCO3 Q20-60 = 0.1 Mole
HCl Conc. = 1550 ppm

Figure 4.30
(b) CaCO3 Q20-60 Conv. Curve



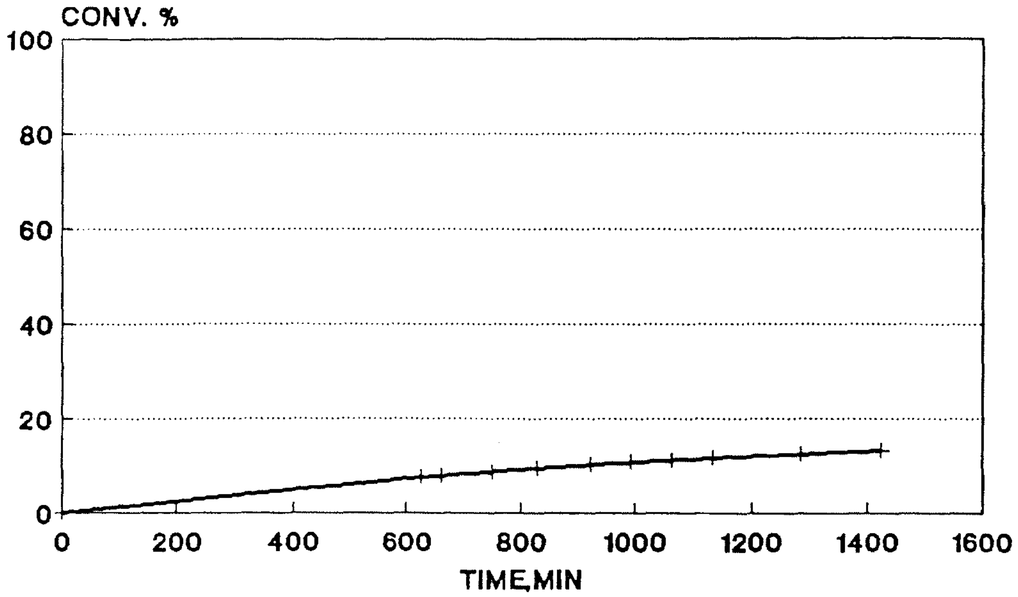
CaCO3 = 0.1 Mole
HCl = 1550 ppm

Figure 4.31
(a) HCl Effluent Concentration
Ca(OH)2 Q6-20 Adsorbed HCl at 700 K



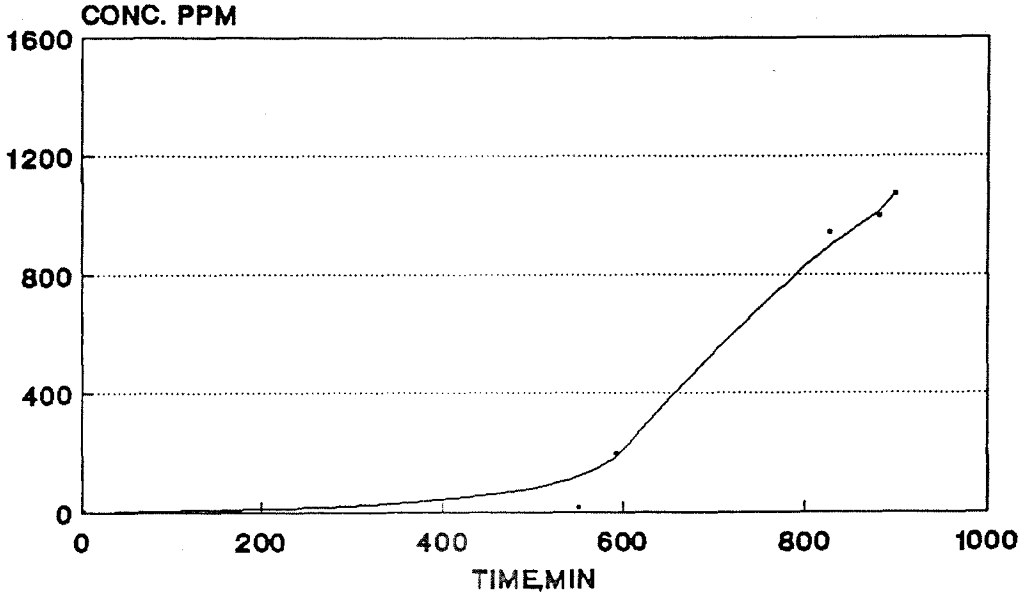
Ca(OH)2 - 15.7450g - 0.2125 Mole
HCl - 1550 ppm

Figure 4.31
(b) Ca(OH)2 Conversion Curve
Ca(OH)2 Q6-20 Adsorbed HCl at 700 K



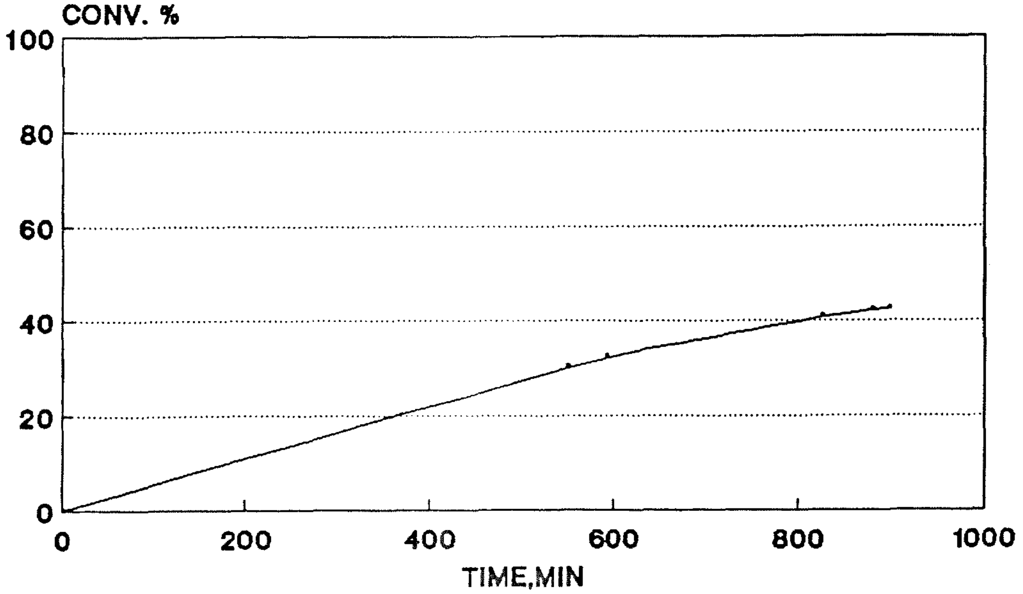
Ca(OH)2 = 0.2125 Mole
HCl = 1550 ppm

Figure 4.32
(a) HCl Effluent Concentration
CaCO3 Powder Adsorbed HCl at 700 K



CaCO3 Powder = 0.05 Mole
HCl Conc. = 1550 ppm

Figure 4.32
(b) CaCO3 Conversion Curve
CaCO3 Powder Adsorbed HCl at 700 K



CaCO3 = 0.05 Mole
HCl Conc. = 1550 ppm

(2) They have good ability to react with HCl gas at lower temperatures;

(3) They are economical materials and easy to get;

(4) They can be used in cycles. The method to change their composition is

$$CaCO_3 \rightarrow CaO \rightarrow Ca(OH)_2 \rightarrow CaO$$

With good industrial process design, the use of this kind of adsorbents can be of considerable interest.

5. CONCLUSIONS

A series of experiments was performed in order to evaluate the ability of calcium compounds to remove HCl gas from hot waste gas stream. Three kinds of calcium compounds and their different size particles were evaluated in these experiments. In Section 4.3, some of the experiments to remove HCl gas, using the higher surface area large particles as adsorbents are described.

The conclusions from this research are:

(1) All of the calcium carbonate ($CaCO_3$), calcium oxide (CaO), and calcium hydroxide ($Ca(OH)_2$) in their solid powder states are effective adsorbents to remove HCl gas from hot waste gas streams. The difference between them is their most active reaction temperature range. At temperature range between 600 K - 700 K, the sequence of activity is

$$Ca(OH)_2 > CaO > CaCO_3$$

At 700 K - 800 K, $CaO > Ca(OH)_2 > CaCO_3$

(2) Different particle size reactants have different available reaction temperature ranges. For the powder calcium compound adsorbents, the available reaction temperature ranges are 600 K - 1000 K. Lower than that temperature range, adsorbents seldom react with HCl gas. Higher than that temperature, sintering of the solid reactants and melting of the products made the adsorption ineffective. For large particle size adsorbents, increasing temperature improved the adsorption ability.

(3) Large particle size adsorbents have lower reaction conversion when they react with HCl gas because of their lower surface area. Increasing the surface area of the large particles improved the reactant conversion.

(4) The effects of HCl gas concentration are significant. The higher the HCl gas concentration, the higher the reactant conversion, but the shorter the reaction time. To adsorb a high concentration HCl gas, larger amounts of adsorbents are needed.

(5) The pressure drop of the adsorbent is influenced by particle size, the adsorption bed height, and the flow rate of the feed gases. The particle size is the main factor to influence the pressure drop of the reaction bed which is very important in the industrial process. The larger the particle size, the lower the pressure drop. The powders have the highest pressure drop even though they have better activity for adsorbing HCl gas. The high pressure drop limited the powder reactants used in industrial processes.

(6) Studying the changes among limestone and its derivatives,

$$CaCO_3 \rightarrow CaO \rightarrow Ca(OH)_2 \rightarrow CaO ,$$

we can get an effective method to improve their surface area of big particle size adsorbents. This improvement is significant in industrial processes because one can improve ability of the solid reactants to adsorb HCl gas without increasing pressure drop of the reaction bed. Furthermore, one can reduce the reaction temperatures. In other words, one can design a simpler, safer and less expensive procedure to remove HCl from hot gas without cooling down the hot gas.

6. RECOMMENDATIONS

The results presented in this thesis indicate that calcium carbonate and its derivatives can be successfully used to quantitatively remove HCl gas. The influence of various operating conditions on HCl removal rate were determined. The improvement the surface area of large particle size adsorbent may allow those of "dry" process in industry.

Research still needs to be conducted in the following areas:

- Further research for large particle size reaction temperature ranges.
- Modeling the relationship among pressure drop and those factors that influence pressure drop.
- Large scale experiments for large particle size adsorbents at high flow rates.
- Careful industrial process design for recycle using calcium compounds.

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