Reprinted from **Journal of the Air & Waste Management Association,** *Vol. 40, No. 6,* June 1990

HCl Sorption by Dry $NaHCO_3$ for Incinerator Emissions Control

Kenneth T. Fellows and Michael J. Pilat
Department of Civil Engineering
University of Washington
Seattle, Washington

The sorption of hydrochloric acid (HCl) by thermally decomposed sodium bicarbonate ($NaHCO_3$) was investigated using a fixed-bed reactor containing sorbent particles dispersed in a bed of spherical glass beads. The gas flow rate (68° F and 760 mm Hg) was 0.039 cfm (1.1 liter/min) and the bed had a cross-sectional area of 0.0055 sq. ft. (5.1 sq. cm). The influence of particle diameter (10, 45 and 163 μm), temperature (225, 275, 375, 455, and 550° F), superficial gas velocity (11 and 21 fpm at reactor conditions, 375° F), and inlet HCl gas concentration (415 ppm and 760 ppm in N_2, 275 and 455° F) were studied. Results showed that HCl sorption increased strongly with increasing temperature but was only weakly dependent on particle diameter, superficial gas velocity, and HCl gas concentration.

The implementation of regulations regarding the emissions of hydrochloric acid (HCl) from refuse combustion and hazardous waste incineration has resulted in a need for information on HCl control technologies. HCl sorption by dry alkaline sorbents is one possible option. Sodium bicarbonate ($NaHCO_3$), which has been used for controlling SO_2 emissions, could potentially be effective for controlling HCl emissions. This study was conducted using a bench-scale fixed-bed reactor to obtain data regarding the sorption of HCl by thermally decomposed $NaHCO_3$ as a function of temperature, particle diameter, superficial gas velocity, and HCl gas concentration.

Regulatory Aspects of HCl Emissions

Current federal air pollution control regulations require higher removal efficiencies for HCl than for other pollutants, such as SO_2 or NOx. State and local regulations are also becoming commonplace. HCl concentrations in refuse incinerator flue gas are commonly in the range of 300 to 1000 ppm, whereas hazardous waste incineration emission concentrations range from 200 to 3000 ppm. Hospital incinerators have emissions from 200 to 1500 ppm. At the present time, the United States EPA regulations[1] for hazardous waste incinerators state that HCl removal efficiencies from exhaust gases must be at least 99 percent if the uncontrolled HCl emissions are greater than 4.0 lbs/hr (1.8 kg/hr).[1] Washington State issued a regulation in April, 1987 (WAC 173-434) for solid waste incinerator facilities which limits HCl emissions to 50 ppm or less (corrected to 7 percent oxygen, hourly average) or at least 80 percent reduction in HCl emissions.[2] The Washington State SO_2 regulation is identical to the HCl regulation. The apparent reasoning for having identical SO_2 and HCl regulations is that if adequate measures are instituted to control SO_2, HCl will also be controlled. The Puget Sound Air Pollution Control Agency in the State of Washington adopted a regulation (Section 9.10 of Reg. I) on June 9, 1988 that limits HCl emission concentrations to 30 ppm (corrected to 7 percent oxygen, hourly average) for sources burning 12 tons or more refuse daily or to 100 ppm HCl for sources burning less than 12 tons daily.[3] These regulations illustrate that HCl emissions are coming under increased scrutiny by regulatory agencies.

Implications

The Clean Air Act Amendments bill of 1990, passed by the U.S. Senate in April 1990, would require EPA to set source category emission standards for a list of 191 chemicals (including HCl) applicable to sources which emit 10 or more tons/year. New and existing sources will require maximum achievable control technology (MACT). Current federal HCl regulations apply to sources emitting more than 4.0 lbs/h (17 tons/year). Dry scrubbing of emission gases containing HCl using $NaHCO_3$ is a technology which may be considered in the MACT analysis. This paper presents HCl collection efficiency graphs useful for the estimation of $NaHCO_3$ needed for the baghouse filter cake sorption of HCl.

Chemistry of Dry Sorption

When dry $NaHCO_3$ is injected into a duct containing hot flue gas, it rapidly decomposes to sodium carbonate (Na_2CO_3) via the reaction:

$$2NaHCO_3 + \text{heat} \rightarrow Na_2CO_3 + H_2O + CO_2 \qquad (1)$$

Once the $NaHCO_3$ sorbent particles are substantially decomposed to Na_2CO_3, the sorption inhibiting effects caused by the diffusion of the gaseous products (CO_2 and H_2O) away from the sorbent are greatly reduced. In addition, Na_2CO_3 that has been produced by high temperature (>200° F) decomposition has a greater pore volume, and hence a greater surface area, than does the original $NaHCO_3$ or crystalline Na_2CO_3. Gaseous HCl and Na_2CO_3 react as follows:

$$2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2 \qquad (2)$$

Since decomposition is slow at temperatures less than 350° F, it is possible that gaseous HCl reacts directly with $NaHCO_3$:

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2 \qquad (3)$$

The partially reacted sorbent can then be collected using a baghouse or an electrostatic precipitator where additional HCl sorption can occur.

Review of Literature

Gaseous air pollutants such as HCl, HF, and SO_2 may be sorbed at different rates by a given sorbent depending on a number of parameters (activation energy, gas molecules size relative to sorbent pore size, pore closure or opening due to differences in the size of the reaction products as compared to the reactants, etc.). With regard to pore closure caused by reaction products, theoretical calculations by Dvirka et al. (1988) predict that the expansion coefficient for Na_2SO_4 produced from SO_2 and Na_2CO_3 is 1.26, and the expansion coefficient for 2NaCl produced from 2HCl and Na_2CO_3 is 1.29.[4] This suggests that similar pore closure in the sorbent could occur for both reactions.

Dry sorption of HCl. Uchida et al. (1979) tested the sorption of 1930 ppm HCl by 274 micron $CaCO_3$ particles in a differential fixed-bed reactor using a gas flow rate of 5 cm^3/sec at temperatures from 390 to 1650° F.[5] Simultaneous calcination and reaction occurred at temperatures greater than 750° F. Almost no sorption occurred at 390 or 590° F, but the reaction rate increased rapidly with further increase in temperature. The conversion (mol $CaCl_2$/mol $CaCO_3$) after 860 seconds reaction time was 0.09 at 750° F, 0.23 at 1290° F, and 0.32 at 1650° F. The superficial gas velocity through the sorbent bed was increased from 1 to 2 cm/sec at an unspecified temperature and no change in the reaction rate was observed. The reaction rate (mass HCl sorbed per mass sorbent per second) at 930° F was shown to be directly proportional to HCl gas concentration in the 510 to 1930 ppm range.

Karlsson et al. (1981) conducted a series of experiments using a fixed-bed reactor to react $Ca(OH)_2$ particles (diameter < 90 microns) dispersed in inert sand with 630 ppm HCl in a nitrogen based simulated flue gas at a superficial gas velocity of 11.8 fpm.[6] The HCl concentration in the reactor outlet gas was monitored during the 10–20 hour runs to determine the sorbent conversion at 1 percent breakthrough. Karlsson et al. reported that the conversion of $Ca(OH)_2$ to $CaCl_2$ at 1 percent breakthrough increased from 14 to 28 percent as the temperature was increased from 300° F to 480° F, and increased to 47 percent by raising the temperature to 750° F.

Mocek et al. (1983) tested HCl sorption by predecomposed $NaHCO_3$ particles (250–350 microns) in an integral fixed-bed reactor at 300° F.[7] The absolute HCl gas concentration and total gas flow rate were not specified; the values were presented using dimensionless variables. Nitrogen was used as the carrier gas. The reactor outlet HCl gas concentration was monitored at various times during the experiments. Each experiment was run to a stoichiometric ratio (mol $NaHCO_3$/mol HCl input) of 1.0 and a graph of fractional penetration versus the reciprocal of the stoichiometric ratio was plotted. The reported fractional penetration was 0.05 at a reciprocal stoichiometric ratio of 0.25. The penetration increased to 0.65 at a reciprocal stoichiometric ratio of 0.3 and the gradually increased to approximately 0.98 at a stoichiometric ratio of 1.0, giving a final conversion of 0.41. Reducing the total gas flow rate by approximately a factor of 3 resulted in a final conversion of 0.65. An interesting feature of the data presented by Mocek et al. is the appearance of an increase of 10 to 20 percent in HCl collection efficiency at a reciprocal stoichiometric ratio of 0.3–0.4. This does not appear to be a measurement error because it is present in multiple runs and each dip contains multiple data points.

Dry sorption of SO_2. The effects of temperature, particle diameter, and pollutant concentration on SO_2 sorption by dry sorbents have been investigated using bench-scale fixed-bed reactors. Keener and Davis (1984) found $NaHCO_3$ undergoing simultaneous decomposition and reaction with SO_2 to be most reactive in the 250 to 350° F range with decreasing rate of reaction at higher temperatures.[8] Using a thermal gravimetric apparatus, Kimura and Smith (1987) reported similar results.[9] However, Stern 1975 tested predecomposed nahcolite (70 percent $NaHCO_3$, 7 percent Na_2CO_3) and observed a maximum rate of reaction at 650° F.[10]

Sorbent particle diameter has been shown to affect the SO_2-dry sorption process. Stern reported that the rate of reaction of predecomposed nahcolite with SO_2 increased 125 percent by decreasing the particle diameter from 190 to 90 microns.[10] Keener and Davis found that SO_2 sorption by simultaneously decomposing $NaHCO_3$ had at most a weak dependence on particle diameter.[8]

Pollutant concentration also influences the sorption of SO_2 by dry sorbents. Stern found that the rate of reaction (mass SO_2 sorbed per mass sorbent per time) of SO_2 with predecomposed nahcolite at 500° F was directly proportional to SO_2 concentration.[10] Bares et al. (1970) plotted SO_2 collection efficiency by predecomposed $NaHCO_3$ versus the reciprocal of the stoichiometric ratio (mol SO_2 input to the reactor/mol sorbent) and concluded that collection efficiency was independent of SO_2 concentration in the 510 to 1300 ppm range.[11]

Sorbent dilution in fixed beds. Preventing flue gas channeling through the fixed bed of sorbent particles is necessary for obtaining good gas-sorbent contact. Karlsson et al. reported that $Ca(OH)_2$ conversion to $CaSO_4$ at 1 percent HCl breakthrough became independent of the degree of dilution of the sorbent with sand in the fixed bed at sand-sorbent weight ratios greater than 60:1.[6] Jorgensen and Chang found, for various sorbents, that the conversion at 1 hour was independent of the sand dilution ratio for ratios of 20:1 to 80:1.[12]

Experimental

Test Conditions

A series of experiments were conducted by flowing preheated gas, approximately 760 ppm HCl in N_2, at a flow rate of 0.039 cfm (1.1 liter/min) measured at 68° F and 760 mm Hg, through a fixed bed of $NaHCO_3$ particles mixed with spherical glass beads for a specified time at a constant temperature. The mass of sorbent (0.1 g) and the duration of the runs (30 minutes) were chosen to give overall stoichiometric ratios (mol $NaHCO_3$/mol HCl or mol Na_2CO_3/mol 2HCl) of approximately 1.0. The exhaust gas from the reactor was tested for HCl concentration during four time periods for each run to determine the HCl collection efficiency achieved by the sorbent. Five temperatures were investigated (225, 275, 375, 455, 550° F) as were three particle diameters (10, 45, and 163 μm). Two superficial gas velocities (11 and 21 fpm at reactor conditions, 375° F) and two HCl gas concentrations at two temperatures (415 ppm and 760 ppm HCl, 275 and 455° F) were also studied.

Sorbent

The sorbent used was commercial reagent grade $NaHCO_3$ supplied by the Church and Dwight Corporation of Princeton, New Jersey. Three particle sizes were sieved from the bulk sorbent supplied by Church and Dwight and are referred to as the 10, 45 and 163 micron sorbents. The volume based size distributions of the 10 and 45 micron $NaHCO_3$ are shown in Figure 1. These distributions were measured by Church and Dwight using a Leeds/Northrup "Microtrac" Particle Size Analyzer. The size distribution for the 163 micron $NaHCO_3$ was not measured. The purity of the $NaHCO_3$, determined from alkalinity assays, was 99.7 percent or greater. The BET surface areas of the 10, 45, and 163 micron $NaHCO_3$ sorbents prior to heating in the fixed-bed reactor were 0.41, 0.11, and 0.048 m^2/g, respectively. All particle size, assay, and BET surface area analyses were

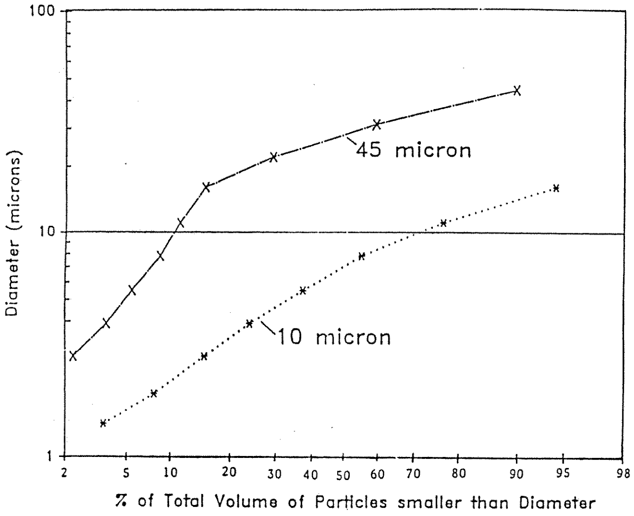

Figure 1. $NaHCO_3$ particle size distributions after processing in University of Washington Laboratory.

performed by Church and Dwight. A low temperature BET surface area analysis procedure was used to prevent thermal decomposition of the sorbent samples. The amount of water in the sorbents, found by heating samples for 2 minute intervals at 130° F until a constant weight was obtained, was less than 0.1 percent.

Apparatus

The apparatus consisted of a heated reactor vessel and a sampling train as shown in Figure 2. The reactor vessel was a pyrex glass cylinder 10 inches long by 1 inch I.D. and consisted of three sections connected by ground glass taper joints. The center section contained a medium sintered glass frit on which the sorbent was placed. The reactor vessel was placed in an insulated box heated by a heat gun capable of providing air heated to 1000° F. In addition, an electrical resistance heating "rope" was coiled around the glass inlet tube to the reactor for a distance of 10 inches to preheat the gas stream. The temperature of the box was controlled to within 5° F of the desired value. The outer surface of the reactor vessel was monitored by a thermocouple. A second thermocouple was located in the gas stream in the outlet tube from the reactor vessel. This location was chosen to reduce the contact of the thermocouple with the corrosive HCl gas. The gas sampling train consisted of six parallel sets of two midget impingers. The first impinger in each set contained 20 mL of water and the second contained silica gel. Gas could be directed to the desired impinger set by means of flow control valves upstream of each impinger set.

The gas, approximately 760 ppm HCl in N_2 was obtained from Scott Specialty Gases. The steel gas cylinder had been "conditioned" to reduce the decline in HCl concentration that occurs with time in unconditioned cylinders. The gas was certified by Scott to be 843 ppm HCl in N_2. The tank was not used immediately and after 3 months the HCl gas concentration had declined to approximately 760 ppm.This 10 percent decline in concentration is similar to that reported by Jerigan et al. (1987) in their work with HCl calibration gases used for testing HCl continuous monitors.[13]

The gas flow rate was measured by a calibrated inlet rotameter, an outlet dry gas meter, and an outlet rotameter. The inlet pressure was monitored and maintained within 2.5 mm of Hg of atmospheric and the pressure drop through the apparatus was approximately 20 mm of Hg. Gas flow was maintained using a vacuum pump downstream of all flow and pressure meters.

Procedure

The sorption experiments were conducted using the following procedure. First, all tubing and the sampling train were purged with nitrogen gas and the reactor box was brought to the desired temperature. The weighed sorbent ($NaHCO_3$), typically 0.090 g, was placed in a cold reactor vessel together with 5.0 g (±0.1 g) of spherical glass beads to prevent gas channeling through the sorbent bed. The sorbent and beads were then stirred to obtain a uniform mixture. The glass beads, composed of Na_2O, CaO, and SiO_2, had an average diameter of 150 μm and a bulk density of 1.5 g/cc. New glass beads were used for each experiment. The reactor vessel was then inserted into the heated reactor box and immediately purged with nitrogen. The purge continued for 6 to 10 minutes until the reactor vessel obtained the desired temperature. Next, the gas flow control valves were adjusted so that the gas flowed through the first impinger set for 6 minutes without passing through the reactor vessel. This provided an initial measure of the inlet gas HCl concentration for that test run. At the end of this inlet gas HCl concentration measurement period, the gas was directed to the reactor vessel and the flow control valves were adjusted so the outlet gas from the reactor flowed through the second impinger set.

Experiments of two different durations were conducted: 12 minutes and 30 minutes. For the 12 minute tests, the second through fifth impinger sets were sequentially operated for 3 minutes each. For the 30 minute tests, the second through fifth impinger sets were run sequentially for 4.0, 6.0, 8.0, and 12.0 minutes, respectively. For the specified gas flow rate, HCl gas concentration, and sorbent mass, the 30 minute tests gave overall stoichiometric ratios (mol $NaHCO_3$ HCl) of approximately 1.0. At the end of the sorption period, the gas flow was directed to bypass the reactor vessel and switched to the sixth impinger set for an additional 4 minutes to measure the final inlet HCl concentration. The reactor vessel was isolated during this time by flow control valves. It was calculated that the mass of HCl gas in the reactor vessel during this time represented less that 0.5 per-

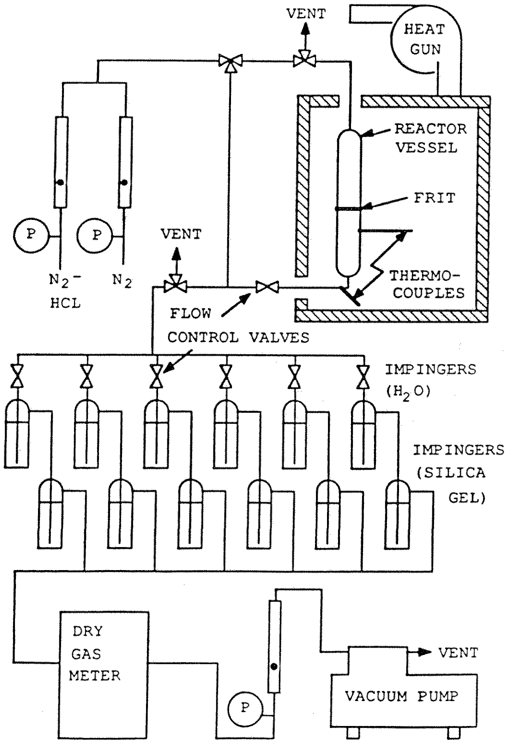

Figure 2. Schematic diagram of apparatus.

cent of the total HCl mass input to the reactor. Following the second inlet HCl concentration measurement period, the reactor was purged with nitrogen for two minutes. The reactor vessel was again isolated by flow control valves and cooled. After cooling, the reactor vessel was removed from the reactor box for later chemical analysis of the sorbent for Cl^-.

Analysis

The six impinger solutions contained HCl in water. The HCl concentrations were measured by taking the pH of the solutions using a Corning General Purpose Combination pH electrode and by titration with 0.01 N NaOH using phenolphthalein indicator. Periodically, the impinger solutions were titrated a second time for Cl^- with 0.01 N $AgNO_3$ using K_2CrO_4 as an indicator. The reacted sorbent was washed from the sintered glass frit in the reactor vessel and titrated for Cl^- with $AgNO_3$. An HCl mass balance calculation was performed for each run using the HCl mass input rate determined from the inlet gas HCl concentration measurement impingers (impinger sets 1 and 6), the HCl mass collected in the 4 outlet gas HCl concentration measurement impingers (impinger sets 2–5), and the HCl mass collected on the sintered glass frit. The HCl mass balance discrepancies were generally less than 5 percent of the total mass input. Furthermore, the discrepancies were random in nature and averaged to −1.6 percent over all of the runs.

Impinger HCl Collection Efficiency

To insure adequate HCl collection efficiencies by the impingers, a modified sampling train consisting of three midget impingers in series, each containing 20 mL of water, was run for 14 minutes with an inlet HCl concentration of approximately 760 ppm at a flow rate of 1.1 liter/minute. Using pH measurement and NaOH titration, the first impinger was shown to have an HCl collection efficiency of over 99.7 percent. Using a 5 ppm HCl inlet concentration, the first impinger collection efficiency was 94.0 percent.

HCl Sorption by Glass Beads and Reactor Vessel

The reactor vessel and sintered glass frit were inert with respect to the gaseous HCl. Tests were conducted at 275 and 455° F in which no sorbent or glass beads were placed in the reactor vessel. 760 ppm HCl in N_2 was flowed through the reactor for 30 minutes. The reactor and sintered glass frit were then washed with 100 mL of water and the resulting solution was titrated for Cl^- using $AqNO_3$. No Cl^- was detected.

The glass beads that were mixed with the sorbent were not completely inert and had HCl collection efficiencies of 1.0, 2.0, 3.5, and 3.9 percent at temperatures of 275, 375, 455, and 550° F, respectively. These values were determined by testing the glass beads in the reactor for 30 minutes with no sorbent using 760 ppm HCl in N_2 at the normal flow rate. The glass beads were then rinsed with water and the resulting solutions analyzed for Cl^- by $AgNO_3$ titration. The experimental results have not been corrected to account for this effect.

$NaHCO_3$ Thermal Decomposition and BET Surface Area

The BET surface area and fractions decomposed for 1.7 g $NaHCO_3$ samples heated at various temperatures were determined. The procedure used to produce these samples was identical to that used in the experimental runs. The sorbent was placed in cold reactor vessel and the reactor vessel was inserted into the preheated reactor box. The reactor vessel was purged with N_2 at 1.1 liter/min for eight minutes. The N_2 flow was then stopped and the sorbent was heated for an additional seven minutes. During this time, the flow control valves remained open to avoid pressurizing the reactor due to the release of CO_2 and H_2O by the sorbent. At the end of this time period, the reactor was removed from the reactor box. The sorbent was immediately removed from the reactor, cooled to room temperature, and placed in sealed sample containers. This process was repeated for different samples at different temperatures. The temperature-time profiles during these runs were typified by exponentially increasing temperatures, asymptotically reaching temperature (±5° F) after ten minutes and five minutes at the specified temperature. The BET surface areas for 45 micron $NaHCO_3$ decomposed at 275, 375, 455, and 550° F are 0.55, 2.60, 2.62, and 2.45 m^2/g, respectively. For the 163 micron $NaHCO_3$ at 275, 375, and 455° F, the BET surface areas are 0.52, 2.24, and 3.52 m^2/g, respectively. No explanation is offered for the exceptionally high surface area of the 163 micron $NaHCO_3$ decomposed at 455° F. Composite samples of the 45 and 163 micron $NaHCO_3$ were 30 percent converted to Na_2CO_3 after heating at 275° F, 90 percent converted after heating at 375° F, and greater than 99 percent converted after heating at 455 and 550° F. Thus, at 375, 455, and 550° F, the $NaHCO_3$ is essentially completely converted to Na_2CO_3 by the time HCl is introduced into the reactor vessel. However, at 275° F, the decomposition is still occurring when HCl is introduced. HCl could be reacting with $NaHCO_3$ or Na_2CO_3.

In the following sections, reference will be made to the "HCl-$NaHCO_3$ reaction" or to "HCl sorption by $NaHCO_3$." These terms are meant to imply thermally decomposed $NaHCO_3$ (Na_2CO_3) for temperaturs of 375° F or greater, and partially thermally decomposed $NaHCO_3$ (a mixture of $NaHCO_3$ and Na_2CO_3) at temperatures less than 375° F.

Results

Effect of Temperature

The HCl collection efficiency by the 45 micron $NaHCO_3$ and the 10 micron $NaHCO_3$ at 225° F increased with increasing temperature up to 450° F as shown in Figure 3. No increase in HCl collection efficiency was observed when the temperature was increased from 455 to 550° F. Since the overall stoichiometric ratio for the experiment was approximately 1.0, 100 percent HCl collection efficiency is theoretically possible for an entire 30 minute test. Each data point represents the average HCl collection efficiency as determined from a given impinger set. Collection efficiency values are plotted at the mid-point of the time intervals during

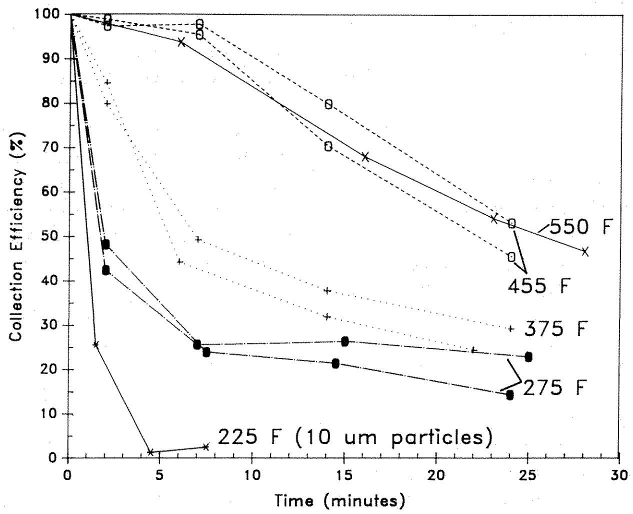

Figure 3. Effect of temperatue on HCl collection efficiency by 45 micron $NaHCO_3$ (10 micron $NaHCO_3$ at 225° F).

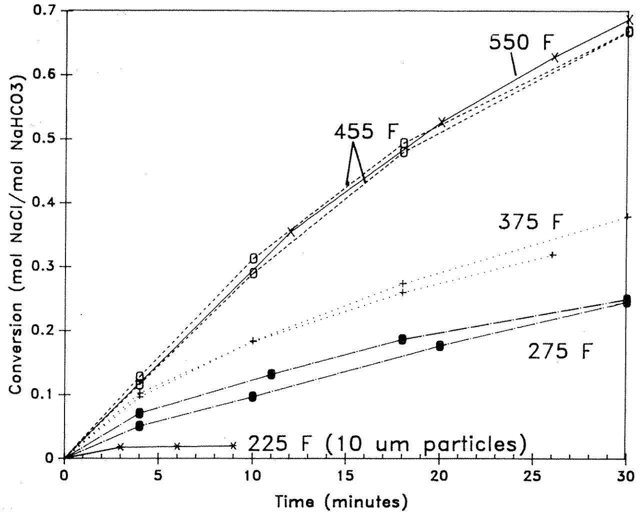

Figure 4. Effect of temperature on conversion of 45 micron $NaHCO_3$ to NaCl (10 micron $NaHCO_3$ at 225° F).

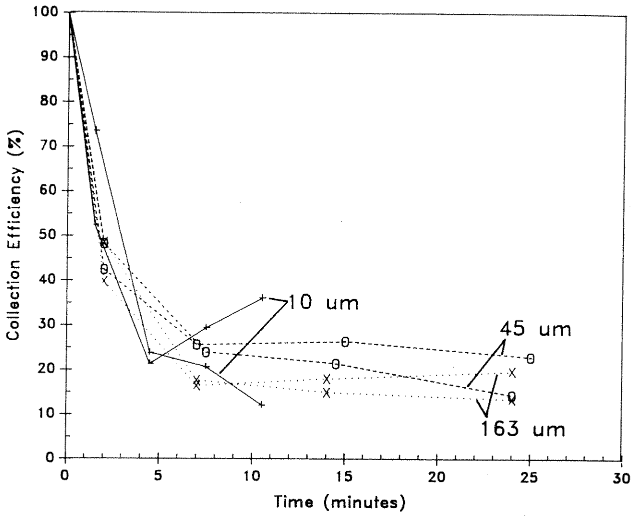

Figure 5. Effect of $NaHCO_3$ particle diameter on HCl collection efficiency at 275° F.

which the impinger sets were in use. Different line types and data point symbols represent tests at different conditions. The superficial gas velocities in the reactor vessel at 225, 275, 375, 455, and 550° F were 9.0, 9.6, 11.0, 12.0, and 13.2 fpm, respectively. The reproducibility of the individual data points was determined from four tests of 45 micron $NaHCO_3$ at 455° F. Results indicate (with 95 percent confidence) that the true mean is within approximately plus or minus 5 percent of the observed value. While other test conditions may have a different degree of reproducibility, these tests give a general indication of the overall error associated with the testing and analysis process.

Figure 4 presents sorbent conversion (mole NaCl/mole $NaHCO_3$) versus time for the same data as shown in Figure 3. It is interesting to note that at 455° F, the HCl collection efficiency was greater than 95 percent even when the sorbent was more than 20 percent converted. Fixed-bed studies of the sorption of SO_2 by $NaHCO_3$ (both simultaneously decomposing and predecomposed) have reported maximum reactivity in the 250–350° F range, with substantially decreased reactivity at higher temperatures. The HCl-$NaHCO_3$ reaction exhibits no such trend.[15–29]

Effect of Particle Diameter

Figure 5 shows that the HCl collection efficiency by $NaHCO_3$ at 275° F increases slightly with increasing particle diameter. The 10 micron $NaHCO_3$ particles were very "sticky" and difficult to disperse to obtain a uniform glass bead-sorbent mixture in the fixed bed. This could account for their slightly lower reactivity and unusual collection efficiency behavior with time. Figure 6 shows that the dependence of HCl collection efficiency on particle diameter at 375° F is very similar in magnitude to that observed at 275° F. The unusual collection efficiency behavior shown by the 10 micron particles at 275° F is also present at 375° F. Mocek et al. (1983) found a similar increase in HCl collection efficiency with time when testing predecomposed $NaHCO_3$. This effect may occur for all particle diameters, but the longer time intervals for which the impingers are operated during the 30 minute tests averages the instantaneous collection efficiency too much to detect it. Recall that at 275° F, the $NaHCO_3$ was simultaneously decomposing during its reaction with HCl, but at 375 and 455° F, the $NaHCO_3$ was nearly completely decomposed before HCl was introduced into the reactor vessel. This factor does not appear to influence the effect of particle diameter on the sorption of HCl.

Effect of Superficial Gas Velocity

The effect of superficial gas velocity (at reactor conditions) on HCl sorption by 45 micron $NaHCO_3$ at 375° F can be seen in Figure 7 and 8. Nearly doubling the superficial gas velocity resulted in a slight decrease in HCl collection efficiency after accounting for the different times required to reach the same stoichiometric ratio. The experimental runs to test the effect of superficial gas velocity were conducted using the same mass of sorbent as in the other tests, but the flow rate was increased from 1.1 to 2.1 liter/minute measured at 68° F and 760 mm of Hg. The run length was chosen as 18 minutes to keep the overall stoichiometric ratio at approximately 1.0.

The stoichiometric ratio (moles sorbent/moles pollutant gas) for a semibatch reactor decreases with 1/time from infinity (x moles of sorbent/0 moles of pollutant gas) at time 0. When x moles of pollutant gas have been made available to the sorbent, the stoichiometric ratio (x moles sorbent/x moles pollutant gas) has a value of 1.0. The reciprocal of the stoichiometric ratio is linear with time and numerically represents what can be called the maximum potential sorbent

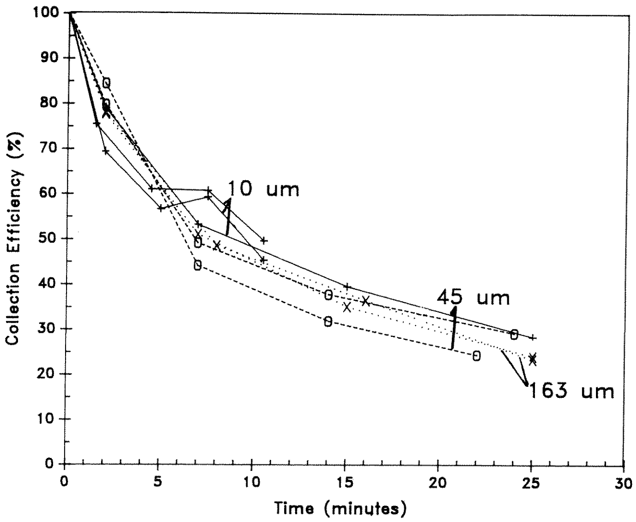

Figure 6. Effect of $NaHCO_3$ particle diameter on HCl collection efficiency at 375° F.

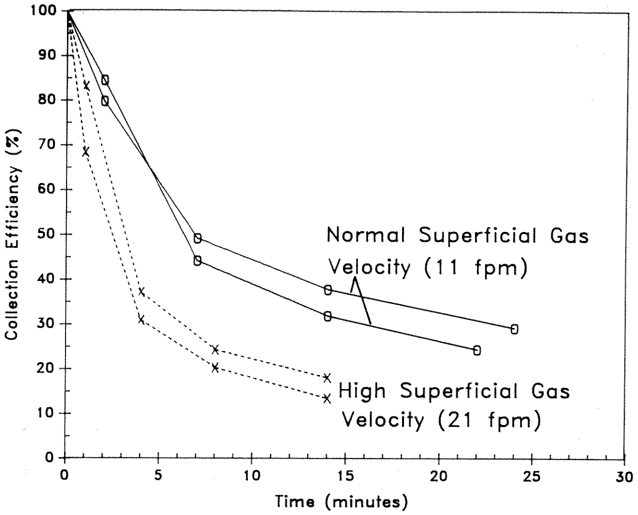

Figure 7. Effect of superficial gas velocity on HCl collection efficiency for 45 micron $NaHCO_3$ at 375° F.

conversion (for values less than 1.0 at least). In other words, the maximum potential sorbent conversion is the conversion the sorbent would obtain if it collected the pollutant with an efficiency of 100 percent. Plotting collection efficiency versus maximum potential sorbent conversion allows a comparison to be made of the sorbent collection efficiencies under different conditions at equal stoichiometric ratios. This plot is shown in Figure 8 for the 375° F runs.

Effect of HCl Gas Concentration

In Figure 9, the plot of HCl collection efficiency versus Maximum Potential Sorbent Conversion at 455° F for HCl gas concentrations of 760 and 402 ppm shows that changes in the HCl gas concentration appear to have little effect on the collection efficiency in this concentration range. At 275° F, a 10 percent reduction in collection efficiency resulted from decreasing the HCl gas concentration from 760 ppm to 428 ppm. This result may have been caused by the release of H_2O and CO_2 from the $NaHCO_3$ decomposing at 275° F, whereas the $NaHCO_3$ tested at 455° F was completely decomposed by the time HCl was introduced into the reactor vessel. The experimental runs to test the effect of HCl gas concentration were conducted using the same mass of sorbent and the same total gas flow rate as in the other tests, but the 760 ppm HCl in N_2 was diluted approximately 1:1 with N_2. The specified HCl inlet concentration was determined from the total mass of HCl collected during the experimental run. The run length was chosen as 60 minutes to keep the overall stoichiometric ratio at approximately 1.0.

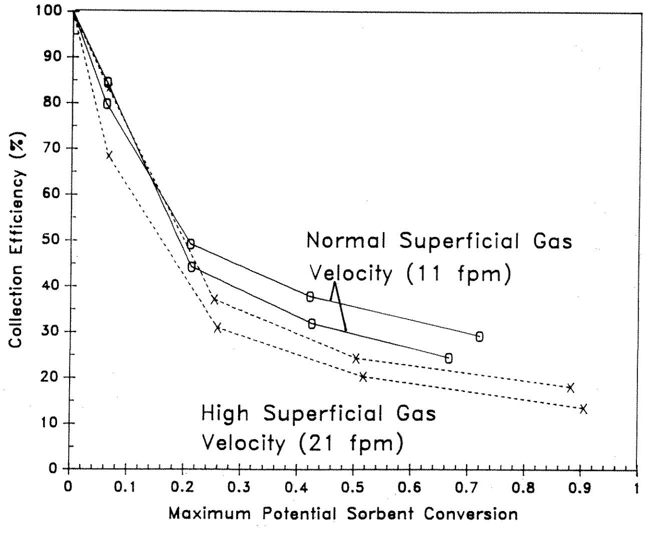

Figure 8. Effect of superficial gas velocity on HCl collection efficiency for 45 micron $NaHCO_3$ at 375° F.

Conclusions

Laboratory measurements of HCl collection efficiencies in a fixed bed of $NaHCO_3$ particles showed that HCl sorption increased strongly with increasing temperature in the 225 to 455° F range, but was only weakly dependent on particle diameter, superficial gas velocity, and HCl gas concentration. Dry sorption of HCl by $NaHCO_3$ has potential as a feasible emissions control process for hospital, municipal refuse, and hazardous waste incinerators, although high sorbent stoichiometric input rates may be required to obtain the 99 percent collection efficiencies required for hazardous waste incinerators. Additional research is warranted to determine the effects of SO_2, CO_2, and H_2O which would be encountered in a real incinerator flue gas on HCl sorption by $NaHCO_3$.

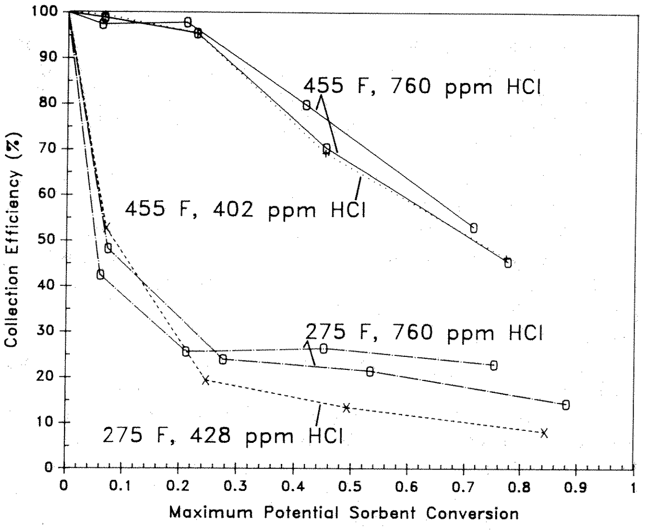

Figure 9. Effect of HCl gas concentration on HCl collection efficiency by 45 micron $NaHCO_3$.

Acknowledgments

The authors wish to thank the University of Washington Valle Scholarship Program and the Church and Dwight Corporation for partial financial support.

References

1. U.S. EPA, 40 CFR 264, Subpart 0, Section 264.343(b).
2. Washington State Regulations, Washington Administrative Code, WAC 173-434, March 16, 1987.
3. Puget Sound Air Pollution Control Agency, Regulation I, Section 9.10, June 9, 1988.
4. M. Dvirka, J. Psihos, J. Cosulich, "Direct injection high temperature acid gas control to prevent the formation of dioxins and furans in waste combustion systems," presented at the 81st Annual Meeting of the APCA, Dallas, Texas, June, 1988.
5. Uchida, et al., "Dry sorption of HCl," *J. Chinese Inst. of Chem. Eng.* **10:** 45 (1979).
6. T. Karlsson, J. Kingspor, I. Bjerle, "Adsorption of hydrochloric

acid on solid slaked lime for flue gas clean up," *JAPCA* **31:** 1177 (1981).

7. K. Mocek, E. Lippert, E. Erdos, "Reactivity of the solid sodium carbonate towards the gaseous hydrogen chloride and the sulfur dioxide," *Coll. Czech. Chem. Comm.* **48:** 3500 (1983).
8. T. C. Keener, W. T. Davis, "Study of the reaction of SO_2 with $NaHCO_3$ and Na_2CO_3," *JAPCA* **34:** 651 (1984).
9. S. Kimura, J. M. Smith, "Kinetics of the sodium carbonate-sulfur dioxide reaction," *AIChE J.* **33:** 1522 (1987).
10. Stern, *Bench Scale Study of Sulfur and Nitrogen Oxides: Adsorption by Nahcolite and Trona*, MS Thesis, Univ. of North Dakota, December, 1975.
11. J. Bares, J. Marecek, K. Mocek, E. Erdos, "Kinetics of the reaction between the solid sodium carbonate and the gaseous sulphur dioxide, III: Study in a integral fixed-bed reactor," *Coll. Czech. Chem. Comm.* **35:** 1628 (1970).
12. C. Jorgensen, C. S. Chang, "Evaluation of sorbents and additives for dry SO_2 removal," *Env. Prog.* **6:** 26 (1987).
13. J. Jerigan, S. A. Shanklin, J. W. Peeler, "Evaulation of HCl Continuous Emission Monitors: Status Report No. 1, Draft," EPA Contract No. 68-02-4442, U.S. Environmental Protection Agency, January, 1987.
14. R. H. Borgwardt, "Kinetics of the reaction of SO_2 with calcined limestone," *Env. Sci. Tech.* **4:** 59 (1970).
15. R. H. Borgwardt, R. D. Harvey, "Properties of carbonate rocks related to SO_2 reactivity," *Env. Sci. Tech.* **6:** 350 (1972).
16. R. H. Borgwardt, K. R. Bruce, "Effect of specific surface area on the reactivity of CaO with SO_2," *AIChE J.* **32:** 239 (1986).
17. T. Dogu, "The importance of pore structure and diffusion in the kinetics of gas-solid noncatalytic reactions: Reaction of calcined limestone with SO_2," *Chem. Eng. J.* **21:** 213 (1981).
18. M. Hartman, O. Trnka, "Influence of temperature on the reactivity of limestone particles with sulfur dioxide," *Chem. Eng. Sci.* **35:** 1189 (1980).
19. W. Hu, J. M. Smith, T. Dogu, G. Dogu, "Kinetics of sodium bicarbonate decomposition," *AIChE J.* **32:** 1483 (1986).
20. J. Marecek, K. Mocek, E. Erdos, "Kinetics of the reaction between the solid sodium carbonate and the gaseous sulphur dioxide, IV: Effect of gas phase composition and of temperature in an integral fixed-bed reactor," *Coll. Czech. Chem. Comm.* **35:** 154 (1970).
21. N. Orbey, G. Dogu, T. Dogu, "Breakthrough analysis of noncatalytic solid-gas reaction: Reaction of SO_2 with calcined limestone," *Can. J. Chem. Eng.* **60:** 314 (1982).
22. D. Schmal, A. C. P. Ligtvoet, A. Brunia, "Some physico-chemical aspects of dry sorbent injection for removal of HCl and HF from waste incinerator flue gases," *JAPCA* **39:** 55 (1989).
23. G. A. Simons, A. R. Garman, A. A. Boni, "The kinetic rate of SO_2 sorption by CaO," *AICHE J.* **33:** 211 (1987).
24. D. Simonsson, "Reduction of fluoride by reaction with limestone particles in a fixed bed," *Ind. Eng. Chem. Process Des. Dev.* **18:** 288 (1979).
25. K. S. Subramanian, T. P. Radhakrishnan, A. K. Sundaram, "Thermal decomposition kinetics of sodium bicarbonate by differential thermal analysis," *J. Thermal Anal.* **4:** 89 (1972).
26. C. Y. Wen, M. Ishida, "Reaction rate of sulfur dioxide with particles containing calcium oxide," *Env. Sci. Tech.* **7:** 703 (1973).
28. J. Wilder, M. J. Pilat, "Suspended phase thermal decomposition of sodium bicarbonate particles," unpublished draft report: University of Washington, Department of Civil Engineering, January, 1987.
29. J. Wilder, M. J. Pilat, "Pilot scale SO_2 control by dry sodium injection using an electrostatic precipitator," *JAPCA*, submitted Oct. 1986, accepted Oct. 1987.

Dr. Pilat is a Professor in the Department of Civil Engineering, University of Washington, Seattle, WA 98195. Kenneth T. Fellows is now an Environmental Engineer with Danes & Moore in Seattle, Washington. This paper was submitted for peer review on September 29, 1988. The revised manuscript was received March 19, 1990.