CALCIUM CARBONATE SCRUBBING OF HYDROGEN CHLORIDE IN FLUE GASES

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ABSTRACT

A cost-effective reagent for the removal and neutralization of HCl in combustion gas was evaluated. Eleven bench-scale experiments were conducted to evaluate the performance of a process precipitated calcium carbonate sludge vs crushed limestone and caustic. The process parameters investigated were pH, varying HCl and CO_2 partial pressure, and $CaCO_3$/$CaCl_2$ solubility. Removal using $CaCO_3$ sludge more than met the RCRA performance standards by providing 99.9% HCl removal efficiencies. $CaCO_3$ sludge reagent utilization was 42% as compared to 11.5% for the crushed limestone. A cost analysis revealed considerable savings compared to caustic, lime, and crushed limestone reagents.

INTRODUCTION

During the 1970's, there was an expansion in the production of plastics and certain agricultural chemicals which resulted in an increase in chlorinated waste by-products. Since these by-products can be both toxic and hazardous, incineration as the ultimate method of disposal has been widely used [1].

The incineration of chlorinated wastes may be shown stoichiometrically as follows:

$$C_n H_{4m+1} Cl + (N + M)O_2 \rightarrow NCO_2 + 2mH_2O + HCl \quad (1)$$

Due to the environmental hazard posed by the hydrogen chloride, it must be removed from the products of combustion before they are discharged into the atmosphere. RCRA requires hydrogen chloride emissions from hazardous waste incineration to be limited to 4 lb/hr. For discharges in excess of this amount, air pollution control devices are required to remove 99% of the HCl before discharge into the atmosphere [2]. Of the estimated 350 industrial and commercial hazardous waste incinerators in the U.S., approximately 38% use a scrubber for HCl removal [3].

Flue gas scrubbing is usually accomplished by spraying the flue gas with water to quench the gases and then contacting the cooled gas with a liquid scrubbing solution in a packed tower, as shown in Fig. 1. In certain cases the hydrogen chloride is recovered as hydrochloric acid for reuse or recycle. When the acid cannot be used, it is usually neutralized and disposed of as a salt solution. In most cases sodium hydroxide is used as the reagent with a sodium chloride salt solution being produced as follows:

$$HCl + NaOH \rightarrow NaCl + H_2O \quad (2)$$

The advantage in using caustic as the regent is its high solubility in water and its high reactivity in neutralizing the HCl. It has a disadvantage in maintaining a constant pH due to the fact that it is a strong base being used to neutralize a strong acid. It is very difficult to control in the neutral pH range of 6.5–7.0. If the

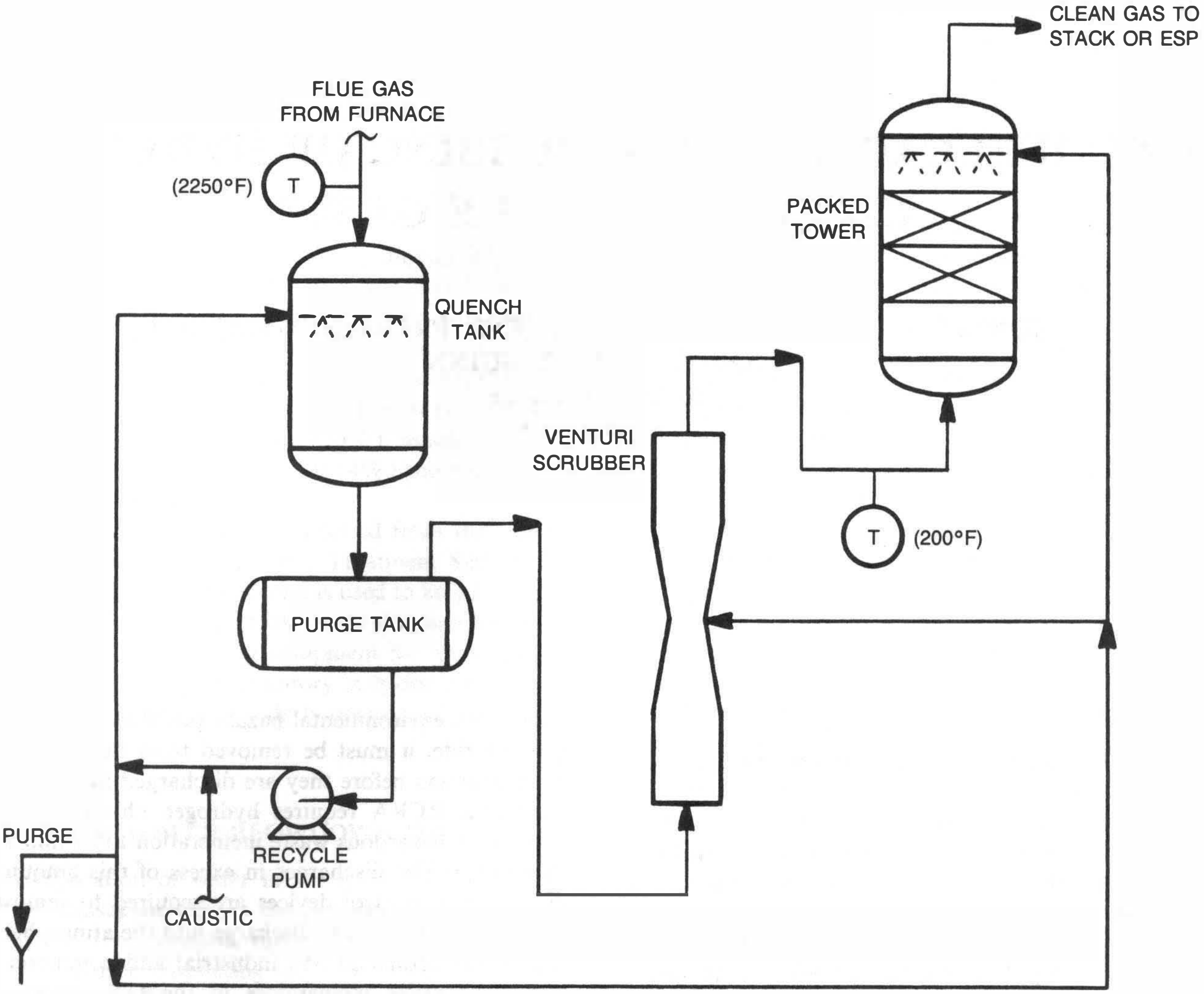

FIG. 1 TYPICAL CONTROL SCHEME FOR HAZARDOUS WASTE INCINERATOR EMISSIONS

pH is allowed to get above 8.5, an undesirable reaction with the carbon dioxide in the products of combustion will occur. This results in unwanted usage of caustic by the following reaction:

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \qquad (3)$$

Another disadvantage with using caustic is its relative cost. At an average cost of about $200/ton ($200/t) [4], the cost of neutralization with caustic can be significant.

Lime is used as a neutralizing reagent in some cases. Lime is slaked to form calcium hydroxide, which is less soluble than caustic, and must be slurried before use. Lime is less expensive at a moderate $60/ton ($66/t) [4], including slaking. Since lime is a weaker base than NaOH, it does not pose the same problems with pH control, as is the case with caustic. The neutralizing reaction is as follows:

$$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O \qquad (4)$$

Another reagent that has been used for removal and neutralization of acid gases is limestone which is calcium carbonate. It is relatively inexpensive at a cost of approximately $25/ton ($28/t) including shipping and grinding. Since it is a weaker base than lime and caustic it does not pose pH control problems. Additionally, since it exists in the carbonate form, it will not react with the carbon dioxide in the flue gas, resulting in consuming the reagent with undesired byproducts. The reaction between HCl and $CaCO_3$ is as follows:

$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2 \quad (5)$$

This reaction can occur in the pH range of 6–7 with no reaction with the CO_2 or inherent problems in controlling pH.

Even with these inherent advantages, limestone has not been widely used for HCl removal and neutralization. The physical characteristics of limestone's low solubility in water has greatly limited its use. To use this material, it must be mined and crushed to be slurried with water for scrubbing and neutralization. The feeding of a slurry poses potential problems for scaling and plugging in the packing and the recirculation piping. In addition, most crushed and slurried limestone solutions have poor reactivity rates, even with a strong acid such as HCl, due to low specific surface area.

The purpose of this investigation was to determine if a form of calcium carbonate that is precipitated directly from solution in a water softening process would offer an enhanced reactivity with hydrochloric acid compared to crushed limestone due to higher specific surface area. Since this material is a waste product, the costs will be primarily associated with handling and transportation expenses. In addition, the parameters of pH, Cl and CO_2 partial pressure, and $CaCO_3/CaCl_2$ solubility, which affect reactivity, were studied.

EXPERIMENTAL APPROACH

Three methods were used to examine the feasibility of using a process precipitated $CaCO_3$ sludge as a reagent for HCl removal and neutralization.

The first employed a computer simulation program which estimated component solubilities and equilibrium conditions. The second approach involved the use of a laboratory-scale reactivity apparatus for measuring the reaction rate of an alkaline reagent with absorbed HCl gas. The third method used a bench-scale HCl scrubber to determine actual operating characteristics and to compare the $CaCO_3$ sludge with limestone and NaOH as neutralizing reagents.

The computer simulation program [5] uses theoretical equilibrium correlations to estimate solid/liquid/gas equilibrium concentrations. Given partial pressure of CO_2 in the gas, concentration of $CaCl_2$ in the liquid, and pH, the program predicted the equilibrium $CaCO_3$ concentration in solution. Using this simulation, the maximum pH at which $CaCO_3$ dissolution could occur was determined as a function of the $CaCl_2$ concentration.

The reactivity apparatus consisted of a 2.0 L reactor equipped with a pH controller. The controller regulated the addition of a mixture of $N_2/CO_2/HCl$ gas bubbled into the reactor. The reactor was initially filled with a known amount of reagent in water. As the reagent dissolved, pH was controlled by the addition of the acid gas. The neutralized product, $CaCl_2$, is very soluble in water, whereas $CaCO_3$ is slightly soluble. The concentration of Ca^{+2} ion in solution as a function of time was used as an indication of the reactivity of $CaCO_3$. The reagents tested were reagent-grade $CaCO_3$, crushed limestone (200–325 mesh particle size), and process precipitated $CaCO_3$ sludge. The reactivity tests represented an initial screening of the $CaCO_3$ reagents to evaluate relative performance potentials.

The bench-scale HCl scrubber apparatus is illustrated in Fig. 2. The synthetic flue gas was prepared by mixing CO_2, N_2, and HCl. The flowrates were controlled with calibrated flowmeters. The gas was sparged through the scrubbing solution in the contactor, where HCl was absorbed, before exiting through a KOH impinger to a vent.

The scrubber solution was held at constant pH in the reaction tank by adding $CaCO_3$ reagent under pH feedback control. The solution was circulated through the contactor and kept at constant level by placing an additional effluent line at the desired level. A liquid blowdown stream was used to maintain constant system volume. The system operating conditions are listed below:

Total gas flowrate	0.10 ft^3/min (2.83 L/min)
Liquid circulation rate	100 ml/min
Contactor liquid volume	50 ml
Hold tank liquid volume	250 ml
Contactor diameter	2.4 cm
Temperature	25° C
$CaCO_3$ sludge wt% solids	10.0 wt%

The tests included operating at pH 4 and 6, HCl gas concentrations of 0.5% and 2.0%, and CO_2 gas concentrations of 0% and 10%. A finer crushed limestone (95% < 400 mesh) and 1.0 N NaOH were used as neutralizing reagents for three of the tests. The operating conditions were chosen to approximate conditions at full-scale incinerator scrubbers [6, 7, 8].

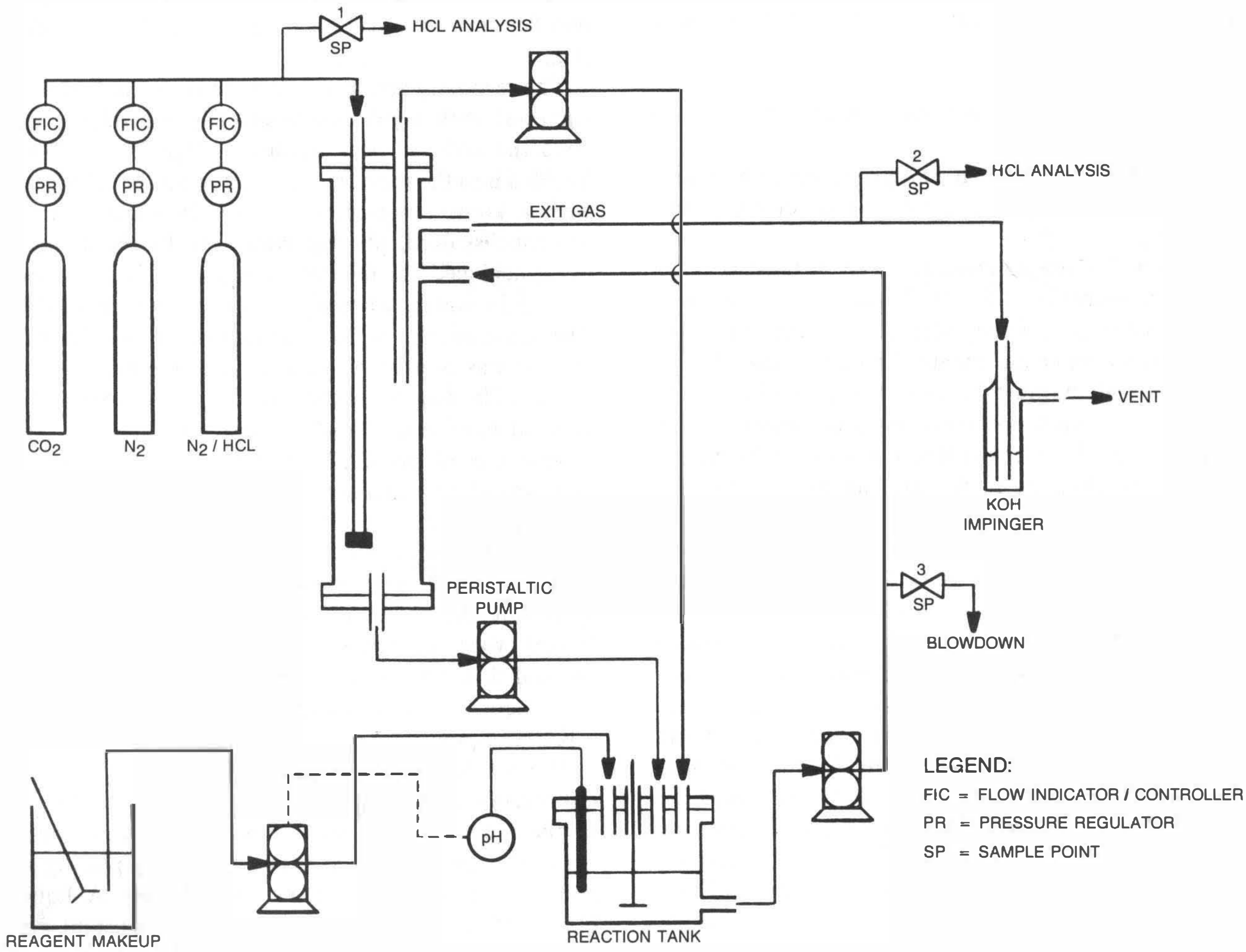

FIG. 2 LABORATORY-SCALE APPARATUS FOR $CaCO_3$ SCRUBBING OF HCL

Operating data collected during each 3-hr test included run time, $CaCO_3$ makeup tank weight, hold tank pH, and temperature. Table 1 shows the sampling and analysis matrix with sample points indicated in Fig. 2. Samples collected during the 3-hr tests included one gas inlet and outlet sample, three liquid hold tank samples, and one final hold tank sample for weight percent solids and specific gravity analysis.

The inlet and outlet gas samples for HCl determination were sparged through three H_2O impingers in series and the impinger liquid was analyzed for Cl^- by ion chromatography. The reaction tank samples were filtered and analyzed for CO_3^{-2} by nondispersive infrared analysis, Ca^{+2} by atomic absorption spectrophotometry, and Cl^- by ion chromatography.

EXPERIMENTAL RESULTS

The computer simulation program, "LIQEQ," predicted the maximum operating pH at which $CaCO_3$ dissolution could occur for a given $CaCl_2$ concentration. These results are shown in Fig. 3. A CO_2 partial pressure of 0.1 atm was used for these cases. From Eq. (5), the steady state $CaCl_2$ concentration can be predicted for any system based on the gas HCl concentration and removal efficiency. For systems operating near the pH on this curve, the $CaCO_3$ dissolution and reactivity will be more dependent on the CO_2 partial pressure.

The reactivity tests compared the reaction rate of HCl with $CaCO_3$ sludge, crushed limestone (200–325 mesh particle size), and reagent grade $CaCO_3$. At pH

TABLE 1 SAMPLING AND ANALYSIS MATRIX

Parameter	Samples/Test	Sample Pt.	Analysis Method
Inlet Gas Hcl	1	1	H_2O Impinger, IC
Outlet Gas HCl	1	2	H_2O Impinger, IC
Reaction Tank Wt% Solids	1	3	Filter, Weight
Specific Gravity	1	3	Weight
Calcium (Ca++)	3	3	AA
Chloride (Cl−)	3	3	IC
Carbonate (CO_3=)	3	3	IR
$CaCO_3$ Slurry Feed Rate	18	-	Reagent Tank Weight

5.0 the $CaCO_3$ sludge was as reactive as the reagent grade $CaCO_3$ and significantly more reactive than the crushed limestone. At pH 6.2 the $CaCO_3$ sludge was more reactive than the reagent grade $CaCO_3$. The reactivity differences are most likely due to differences in specific surface area, which affects dissolution rates significantly. The reactivity test results indicated a potential for $CaCO_3$ sludge as a neutralizing reagent.

The bench-scale HCl scrubber test results are shown in Table 2. Tests CS-1 through CS-8 used $CaCO_3$ sludge as the neutralizing agent. Tests CS-9 and CS-10 were run under the same conditions as test CS-3 with finely crushed limestone (95% < 400 mesh) as the reagent in CS-9, and 1.0 N NaOH in CS-10. Test CS-11 used the fine limestone at a higher pH of 5.9.

For all of the bench-scale scrubber tests the HCl removal efficiencies approached 99.9%. The key operating variable becomes, then, the reagent utilization. Reagent utilization is defined as the ratio of reacted reagent to reagent fed to the system. Utilization is a direct indication of reagent reactivity. Figure 4 shows percent $CaCO_3$ utilization as a function of pH for the different test conditions.

From test CS-12, which was run with 20 wt % limestone reagent at pH 5.9, the low reactivity of the limestone is evident from the low reagent utilization (11.5%). The limestone used for this test was very fine, with a mean particle diameter of 12×10^{-6} m (95% < 400 mesh). A pH of 6.0 could not be maintained with the limestone.

DISCUSSIONS AND CONCLUSIONS

The parameters for evaluation of the $CaCO_3$ sludge were pH, CO_2 partial pressure, and HCl partial pressure. From the bench-scale scrubber results, the $CaCO_3$ sludge demonstrated more reactivity than the crushed limestone. This was evident from the higher reagent utilization for $CaCO_3$ sludge for a given set of conditions.

The system operating pH has a large effect on reagent reactivity. All of the tests at pH 4 had higher utilizations due to the increased solubility of $CaCO_3$ at low pH. The computer simulation illustrated in Fig. 3 supports these results. From the bench-scale scrubber tests it is evident that the operating pH must be limited to 6.0 or less. Even at this sub-neutral pH, HCl removal efficiencies will approach 100%. At pH 4 reagent utilizations are high (> 88%), whereas at the higher pH

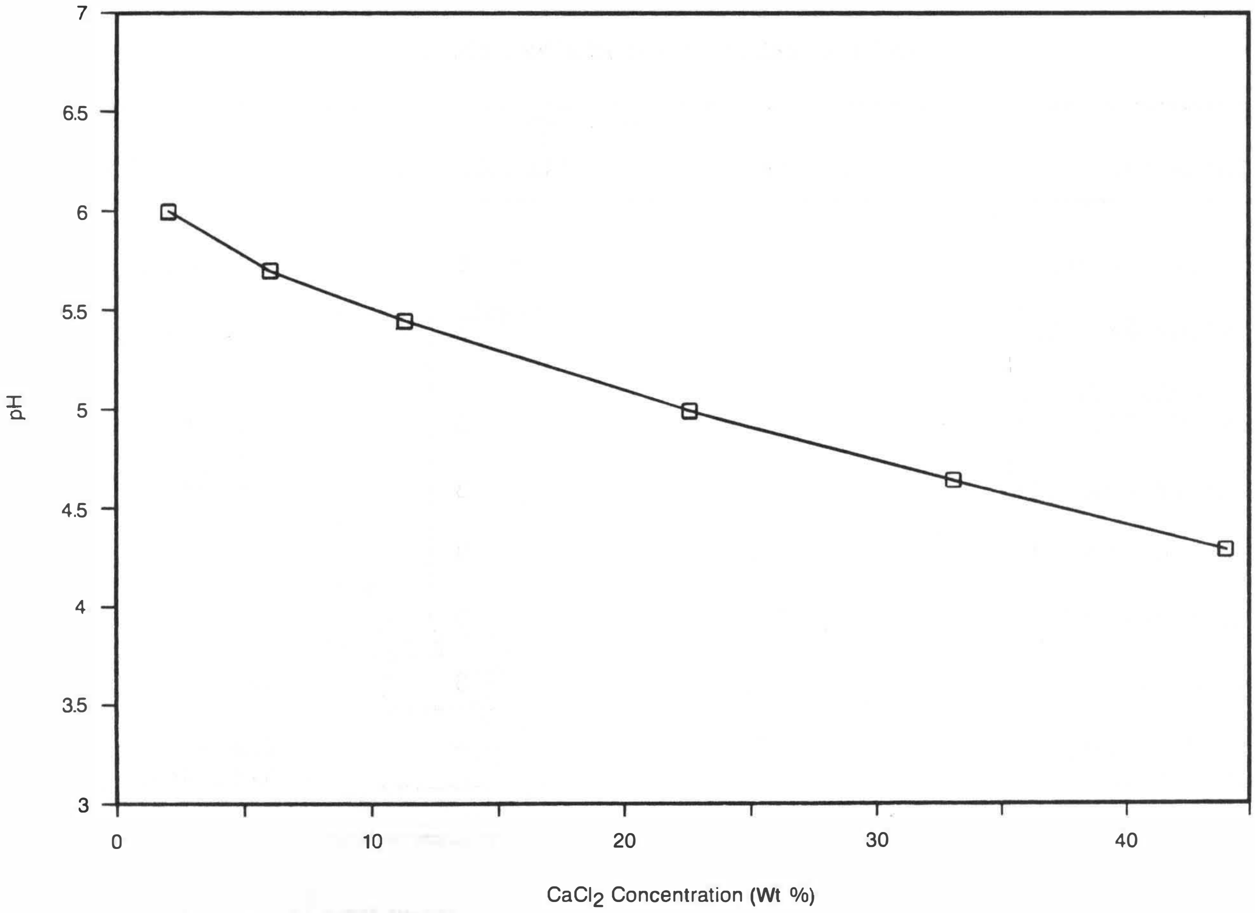

FIG. 3 EFFECT OF $CaCl_2$ ON pH
(Maximum pH for $CaCO_3$ Dissolution)

of 6 the utilization drops to 35% for the $CaCO_3$ sludge. This will allow reagent addition with no possibility of pH control overshoot. It will require, however, that a set point below 6 be maintained to be controllable.

System pH had little effect on HCl removal efficiency. The results in Table 1 show that removal efficiencies of 99.9% are attainable even at a reaction tank pH of 4.0. This is well within the RCRA regulation of 99.0% minimum removal efficiency.

Partial pressure of CO_2 in the gas had a more pronounced effect on reagent utilization for the pH 6 tests with the lower HCl concentration of 0.5%. A minimal effect was seen for the 2.0% HCl tests and for all of the pH 4 tests. The CO_2 effect can be attributed to the low driving force for dissolution of $CaCO_3$ when high liquid CO_3^{-2} concentrations are present. Most incineration flue gas compositions are in the 5–10% range for carbon dioxide concentrations and should not have an adverse effect on reactivity.

From a cost analysis of HCl neutralizing reagents, $CaCO_3$ sludge is more cost effective than caustic, lime [$Ca(OH_2)$], and limestone. Figure 5 shows the annualized reagent costs as a function of HCl load (kg/h) for a scrubber with 99.9% removal efficiency at pH 5. Reagent utilizations used for comparison were 100% for caustic, 95% for lime, 65% for $CaCO_3$ sludge, and 50% for the limestone. Reagent costs used were $200/ton for caustic, $60/ton for lime, $25/ton for limestone, and $10/ton for the $CaCO_3$ sludge. The $CaCO_3$ sludge cost was taken as the limestone cost less processing costs of $15/ton. At lower operating pH the cost effectiveness increases for $CaCO_3$ sludge due to increased reagent utilization.

$CaCO_3$ sludge is an acceptable neutralizing reagent for the scrubbing of HCl incinerator gas for several reasons. It is much more cost effective than caustic as a reagent and provides identical removal efficiencies with better pH control capabilities. $CaCO_3$ sludge pro-

TABLE 2 LABORATORY-SCALE HCL SCRUBBER RESULTS

Test	pH	HCl (%)	CO_2 (%)	Solids (Wt %)	$CO_3^{=}$ (mg/L)	Ca^{++} (mg/L)	Cl^{-} (mg/L)	$CaCO_3$ Util. (%)	HCl Removal (%)
CS-1	4	0.5	0	0.08	118	41100	52000	96.7	99.86
CS-2	6	0.5	0	2.02	161	31000	46700	73.0	99.90
CS-3	4	2	0	0.33	409	38600	64900	90.9	99.92
CS-4	6	2	0	6.12	433	18000	35700	42.3	99.92
CS-5	4	0.5	10	0.14	92	37300	60700	87.8	99.92
CS-6	6	0.5	10	6.02	313	15200	37400	35.7	99.95
CS-7	4	2	10	0.29	330	39300	75300	92.4	99.89
CS-8	6	2	10	6.47	646	15100	50300	35.5	99.93
CS-9	4	2	0	0.29	NA	NA	48500	86.0	99.87
CS-10	4	2	0	0	NA	NA	30600	100.0	99.92
CS-11	5.9	2	0	17.7	NA	NA	NA	11.5	99.95

* Crushed limestone used as reagent (95% < 400 mesh)
**1.0 N NaOH used as reagent
NA = Not analyzed

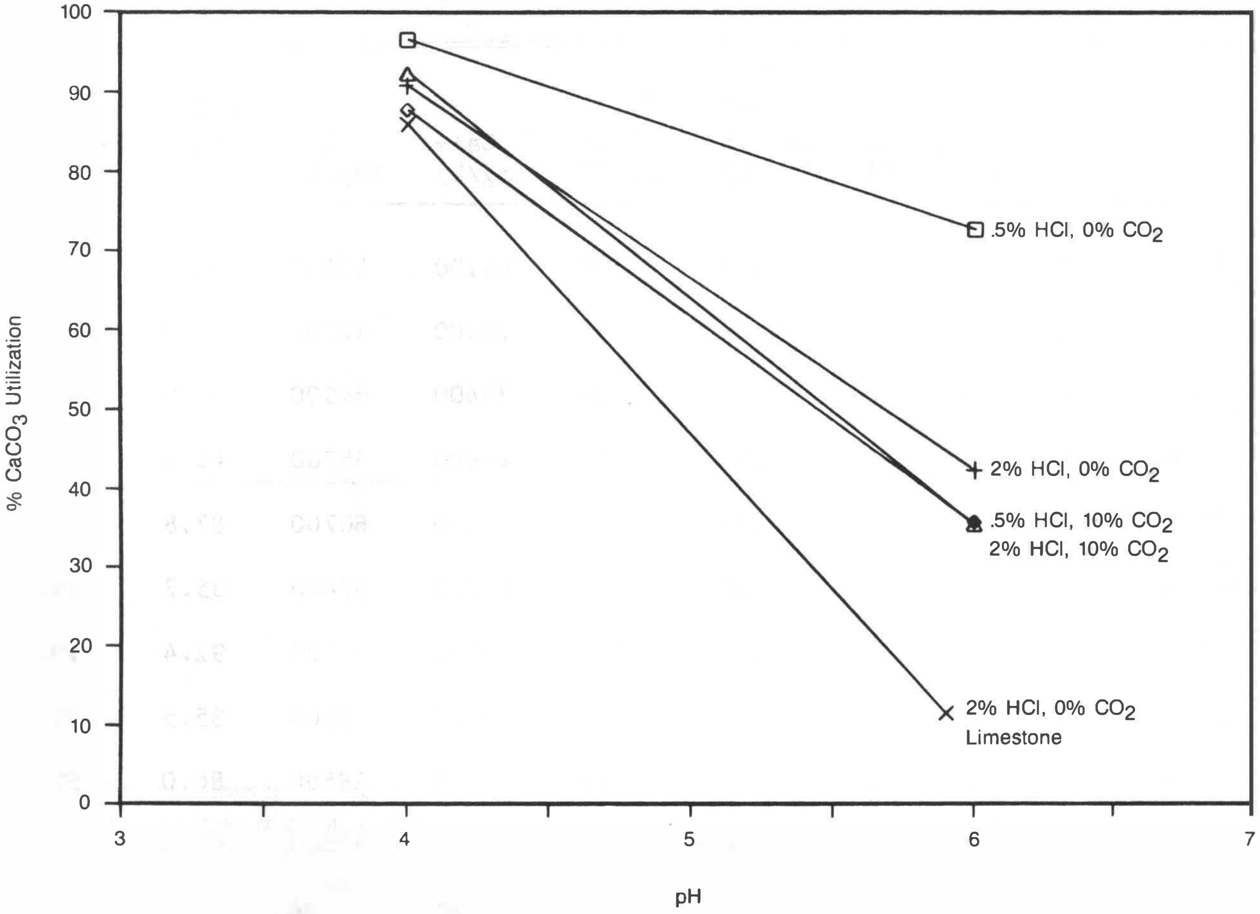

FIG. 4 pH VS $CaCO_3$ UTILIZATION

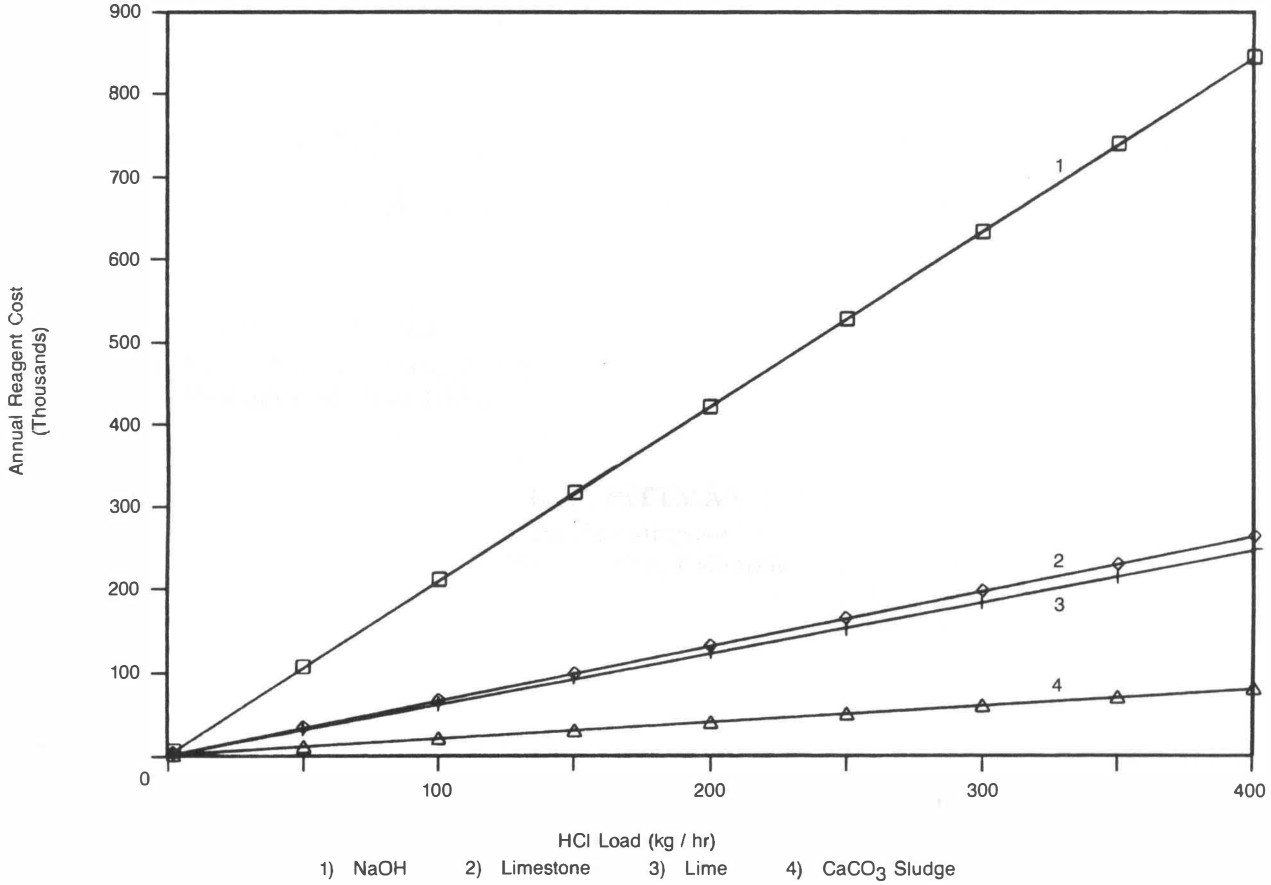

FIG. 5 HCL SCRUBBER REAGENT COSTS
(Operation at pH 5.0 with 99.9% HCl Removal)

vides more reactivity and higher reagent utilization than the crushed limestone and there is no additional processing involved. The $CaCO_3$ sludge can be slurried and used with no pretreatment.

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