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THERMOGRAVIMETRIC STUDY OF PROMOTED HYDRATED LIME SORBENTS FOR FLUE GAS CLEAN UP *

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ABSTRACT

A thermogravimetric (TG) technique has been developed for studying the effectiveness of $Ca(OH)_2$ sorbents for removal of SO_2 from humidified simulated flue gas Results obtained with the TG technique were in good agreement with earlier fixed-bed reactor studies, indicating that the TG technique is a satisfactory method for screening sorbents An impregnation procedure was used to investigate the ability of eight inorganic salts to increase the utilization of hydrated lime The alkali halides were most effective, with more than a twofold increase in utilization A second approach to preparing the sorbent—dissolution of the salt in the water used to prepare the hydrate from CaO at 95 ° C—gave less satisfactory results No correlation could be found between the H_2O incorporation and the SO_2 uptake on the sorbents Data from other studies were compared with the TG results, and it was concluded that the manner of combining the additive with the $Ca(OH)_2$ was an important factor in determining additive effectiveness

INTRODUCTION

Calcium- and sodium-based compounds are being investigated as potential sorbents for dry-scrubbing flue gas clean-up processes In particular, calcium-based compounds have been used in conjunction with limestone injection multistage burners (LIMB) and furnace sorbent injection after the burners More recently, it has been suggested that with only minor modifications to the flue gas duct work of an existing coal-fired electric-power-generating facility, high removal efficiencies for sulfur dioxide can be obtained by injecting a dry sorbent into the flue gas [1,2] The flue gas is cooled and humidified by the injection of water either upstream or downstream of the injected dry hydrated lime or other sorbent materials This approach is considered attractive because it could easily be used to retrofit pre-NSPS

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(New Source Performance Standards) utility plants, resulting in lower capital investment as compared with wet limestone scrubbers

Several companies have been developing calcium-based sorbent duct injection processes over the last few years In the confined-zone dispersion process developed by Bechtel Corporation [3], a pressure-hydrated dolomitic slurry is injected through a dual-fluid nozzle in the center of the duct concurrent with the gas flow As the cone of spray moves downstream and expands, the gas within the cone cools and the SO_2 is rapidly absorbed by the liquid droplets According to the developers, pressure-hydrated dolomitic lime is more finely divided and much more reactive than conventionally hydrated lime The in-duct scrubbing (IDS) process [4], developed by General Electric Environmental Services, Inc , is similar to a conventional spray dryer except that the reaction vessel is eliminated, instead, a rotary atomizer sprays slaked-lime reagent directly into the flue gas duct Dravo Corporation is developing a third process called hydrate addition at low temperature (HALT) [5] It involves the injection of a calcium hydroxide sorbent into a duct with humidification and/or temperature control of the flue gas Additives in the water used to prepare the hydrate and the conditions of hydration give the reagent particles a surface chemistry and morphology designed to enhance SO_2 capture

Bench-scale studies have been carried out by a number of investigators with the primary objective of increasing the reactivity and utilization of the calcium hydroxide sorbent Yoon et al [6] have shown in fixed-bed reactor studies that the method of hydration can affect the reactivity of calcium hydroxide prepared from a given limestone The utilization of the calcium hydroxide increased linearly with surface area in tests carried out at 65 °C and 60% relative humidity Borgwardt and Bruce [7] have shown that the high-temperature reactivity (800 °C) of $Ca(OH)_2$ can be correlated with the BET surface area Their results obtained at 65 °C using a differential reactor supported the conclusions of Yoon et al that the reactivity increased with surface area Some fundamental studies carried out by Klingspor and coworkers [8–11] showed that SO_2 did not react with $Ca(OH)_2$ or $CaCO_3$ if less than one monolayer of water was absorbed on the sorbent, i e , below 20% relative humidity Hydrated lime and calcium carbonate were shown to have the same capacity for water vapor adsorption per BET surface area, these studies also showed that the reaction rate for SO_2 conversion increased with the number of monolayers of water vapor adsorbed Other investigations have shown that hydrated calcites and quicklime have similar reactivity [12] Dolomitic hydrates (pressure-hydrated), however, showed higher reactivity on a calcium basis, on a calcium and magnesium basis, the reactivity was similar to calcitic materials, suggesting the magnesium participated in the reaction

Significant increases in the utilization of hydrated lime have been found with $Ca(OH)_2$ sorbents containing inorganic salts Ruiz-Alsop and Rochelle

[13] have investigated the effect of adding these salts to hydrated lime, alkali halides resulted in the highest degree of utilization Similar bench-scale studies [14] of hydrated lime, limestone and sodium bicarbonate showed that relative humidity significantly affected SO_2 absorption by lime and limestone containing additives such as NaCl, $NaNO_3$, NaOH and $CaCl_2$, but had less impact on $NaHCO_3$ reactivity

The present studies were carried out to determine the utility of thermogravimetric (TG) studies as a screening technique for determining the degree of utilization of $Ca(OH)_2$ sorbents containing inorganic salts In addition, it was of interest to compare the utilization of sorbents prepared by three techniques as follows

Sorbent type	Preparation sequence
A	(1a) $\text{CaO} + \text{H}_2\text{O} \rightarrow \underset{\text{dry}}{\text{Ca(OH)}_2}$ (2a) $\underset{\text{dry}}{\text{Ca(OH)}_2} + \text{salt solution} \rightarrow \underset{\text{moist}}{\text{Ca(OH)}_2\ \text{NaCl}}$ (3a) $\underset{\text{moist}}{\text{Ca(OH)}_2\ \text{NaCl}} \rightarrow \underset{\text{dry}}{\text{Ca(OH)}_2\ \text{NaCl}}$ In step (1a), the excess water is removed by the heat of reaction The incipient wetness procedure is used in step (2a)
B	(1b) $\text{CaO} + \text{salt solution} \rightarrow \underset{\text{slurry}}{\text{Ca(OH)}_2\ \text{NaCl}}$ (2b) $\underset{\text{slurry}}{\text{Ca(OH)}_2\ \text{NaCl}} \rightarrow \underset{\text{dry}}{\text{Ca(OH)}_2\ \text{NaCl}}$ In step (1b) an excess of water is used to prevent complete evaporation of the water, decreasing the possibility of sintering of the $Ca(OH)_2$ that can occur during step (1a)
C	(1c) $\text{CaO} + \text{salt solution} \rightarrow \underset{\text{dry}}{\text{Ca(OH)}_2\ \text{NaCl}}$ Step (1c) is identical to step (1a) except for the presence of NaCl in the water of hydration

Dry commercial hydrated lime is prepared according to step (1a) because no costly water removal step is involved

EXPERIMENTAL

Materials

Impregnated hydrated limes were prepared using Longview hydrated lime (LL), available from Southern Industries Corporation, Saginaw, AL The chemical and physical properties of this material are shown in Table 1 Baker reagent grade (Lot 1410-1) CaO was used to prepare hydrated limes, its composition is also shown in Table 1 Calcium oxide (Cat No 20, 815-9)

TABLE 1

Chemical analysis of sorbents

	Sorbent (wt %)	
	Longview lime	Baker CaO
Ca	48 2	69 6
Mg	1 02	0 76
Al	0 06	0 02
Fe	0 15	0 12
Si	< 0 96	< 0 95
Na	0 04	0 07
K	0 39	0 26
Wt loss at 110 °C	< 0 1	< 0 1
Ignition wt loss (%)	26 0	4 0
TG wt loss (%) (300–460 °C)	21 4	3 1
TG wt loss (%) (460–800 °C)	4 4	0 8
Theoretical wt loss [a]	24 3	0
Carbonate carbon	1 21	0 18

[a] Assuming pure $Ca(OH)_2$ and CaO

and $Ca(OH)_2$ (Cat No 23, 923-2) from Aldrich Chemical Company and $CaCO_3$ (C-64) from Fisher Scientific were used as thermogravimetric standards

Apparatus and procedures

The weight increase resulting from exposure of the sorbent to the humidified simulated flue gas (hereafter referred to simply as flue gas) was determined using a modified Perkin–Elmer TGS-2 unit The glass-inlet furnace tube and the thermocouple assembly were replaced by a jacketed glass vessel (12 inches long and 1 inch in diameter) as shown in Fig 1 Humidification of the flue gas (100 ml min^{-1} at 25 °C and 760 mmHg) was effected by mixing the flue gas with an equal volume of N_2 (100 ml min^{-1} at 25 °C and 760 mmHg) that had been saturated with water vapor at 70 °C in spargers After mixing the humidified nitrogen with the flue gas, the calculated composition of the gas stream was 18 2% H_2O, 2466 p p m SO_2, 2 5% O_2 and N_2 as the balance (see Appendix I) The humidity was measured using the Vaisala humidity and temperature indicator HMI 31 equipped with a HMP 32 UT probe The probe was calibrated using a saturated solution of sodium chloride at 25 °C The measured value of the relative humidity was 59 ± 0 5% No CO_2 was included in the flue gas mixture, since only the weight increase due to reaction with SO_2 was desired A heated transfer line from the spargers to the jacketed reaction vessel was used to maintain the water in a vaporized state The sorbent sample (2–4 mg) was

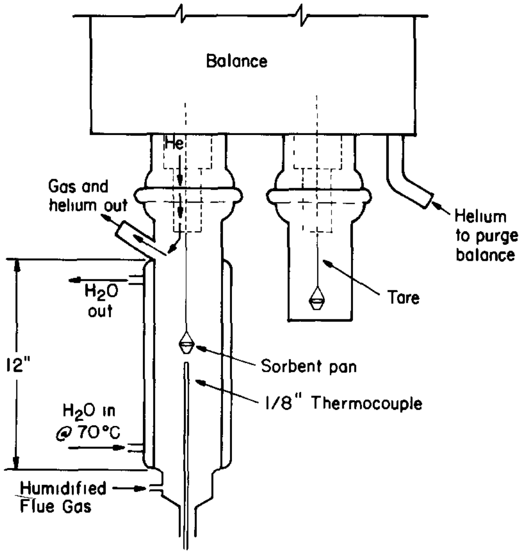

Fig 1 Modified TG unit

dispersed on glass wool that was placed in a quartz bucket The temperature of the reaction vessel was 70 ° C, this temperature was chosen to make a fairer comparison with the data in ref 13

In a typical TG run, N_2 (instead of the flue gas) was mixed with the N_2 gas stream saturated with water vapor to determine the weight increase owing to adsorption of water only on the sorbent (at 59% relative humidity) After exposure of the sorbent for 30 min to humidified N_2, the flue gas was mixed with the N_2 (saturated with water vapor), and the sorbent was exposed to the humidified flue gas for 60 min The weight increase occurring during the 60-min exposure was used to calculate the degree of sorbent utilization It was assumed that the $Ca(OH)_2$ reacted with the SO_2 in the presence of water to form $CaSO_3$ 0 $5H_2O$, this salt was the main product in fixed-bed reactor studies [13] It is unlikely that the nature of the product would depend on the composition and/or concentration of the inorganic promoter Thus, although the assumption of the formation of a different product (such as Na_2SO_4) would result in different values for the percentage utilization, the order of effectiveness of the promoters would remain unchanged The percentage weight increase that would be observed if pure $Ca(OH)_2$ reacted completely was 74 3% The degree of utilization was defined by

$$\% \text{ utilization} = \% \text{ wt increase (expt)} \times \frac{54\ 0}{\% \text{ Ca}} \times \frac{1}{74\ 3} \times 100\%$$

where

54 0 = per cent Ca in pure $Ca(OH)_2$

and

74 3 = stoichiometric weight increase for the reaction

$Ca(OH)_2 + SO_2 \rightarrow CaSO_3\ \ 0\ 5H_2O + 0\ 5H_2O$

The calculation of the degree of utilization for sorbents containing sodium chloride is shown in Appendix II

Surface areas were obtained using the BET equation from the adsorption of N_2 in a Micromeritics 2500 unit A Micromeritics Sedigraph 5000 was used for the particle size distributions, the dispersing liquid (mineral oil plus surfactant) had a viscosity of 4 113 cP and a density of 0 811 g ml^{-1} A Micromeritics AutoPore II 9220 was used to determine pore volume and pore size distribution by mercury intrusion, the contact angle was 130 °, and the surface tension was 485 dyne cm^{-1}

Hydrated limes containing inorganic additives were prepared using three procedures and are classified as Type A, Type B and Type C sorbents according to the procedure described previously

A Impregnation of the LL was carried out at 25 ° C with a solution of the salt dissolved in water The solution/lime ratio was 1 ml of solution to 1 g of lime The slurry was stirred for 5 min and then placed in a microwave oven for 10 min The dried material was crushed and ground using a mortar and pestle

B An aqueous solution of the salt (42 ml) was added to 14 g of Baker CaO at room temperature The slurry was placed in a water bath at 95 ° C for 30 min After being dried in a microwave oven for 10 min, the sorbent was crushed and ground using a mortar and pestle

C 20 g of Baker CaO was added to 12 ml of an aqueous solution of the salt at 50 ° C Rapid stirring of the slurry resulted in a vigorous reaction and the evolution of considerable steam, upon completion of the reaction (about 1 min), the material was dry and was used without further treatment in the TG studies

RESULTS AND DISCUSSIONS

As indicated in the Experimental section, the calculation of the percentage utilization was based on the chemical analysis for Ca in the sample The chemical analysis, however, did not indicate if the Ca was present as $Ca(OH)_2$, or in a form non-reactive towards SO_2 at 70 ° C such as the carbonate Therefore, a TG study using a dry N_2 atmosphere (100 ml min^{-1}) was carried out to determine the percentage of $Ca(OH)_2$ present in the LL and Type A sorbents prepared therefrom The rate of temperature

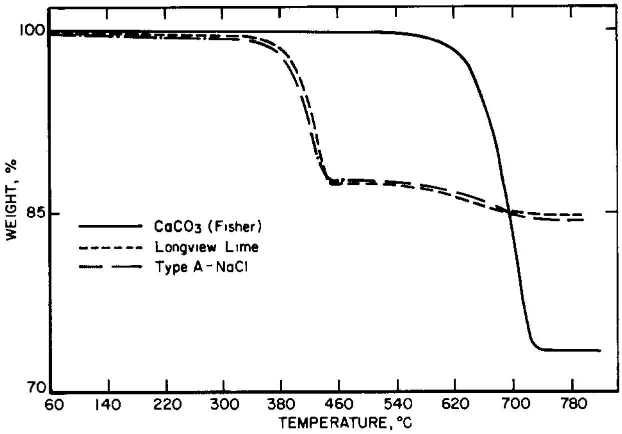

Fig 2 Decomposition curves for selected sorbents between 50 and 800 °C

increase was 10 °C min^{-1} The thermal curve in Fig 2 indicates that the conversion of $Ca(OH)_2$ into CaO occurs between 300 and 460 °C, with an additional weight loss between 540 and 800 °C The percentage of the Ca in LL as $Ca(OH)_2$ was then calculated

$$\% \text{ Ca } (\text{as Ca(OH)}_2) = \frac{54\ 0}{48\ 2} \times \frac{21.4 \text{ (expt wt loss)}}{24\ 3 \text{ (calc wt loss)}} \times 100\% = 98\ 7\%$$

where

54 0 = per cent Ca in pure $Ca(OH)_2$

48 2 = per cent Ca in Longview lime

The weight loss between 540 and 800 °C was probably due to decomposition of $CaCO_3$ to CaO, although the thermal curve for $CaCO_3$ (Fisher Scientific) indicated that no significant decomposition of $CaCO_3$ occurred below 600 °C The shift in decomposition temperature may have been due to the higher dispersion of the $CaCO_3$ in the LL or to the decomposition of impurities such as $MgCO_3$ The thermal curve for a typical Type A sorbent is shown in Fig 2, the calcium hydroxide content for these sorbents, i e, 94–96%, was about the same as that for LL, indicating that an insignificant amount of CO_2 pick-up occurred during the preparation of these sorbents

As shown in Fig 3, the thermal curve for Baker CaO indicated the presence of $Ca(OH)_2$, with a weight loss of 3.9% between 300 and 460 °C and a weight loss of 0 8% between 460 and 800 °C, apparently due to decomposition of $CaCO_3$ to CaO These data indicate that the Baker CaO contained small amounts of $Ca(OH)_2$ and $CaCO_3$, some of which may have formed during the loading of the sample into the TG unit The weight decrease observed between 460 and 800 °C for both the Type B and Type C sorbents indicates the presence of $CaCO_3$, which may have formed during the hydration and drying steps

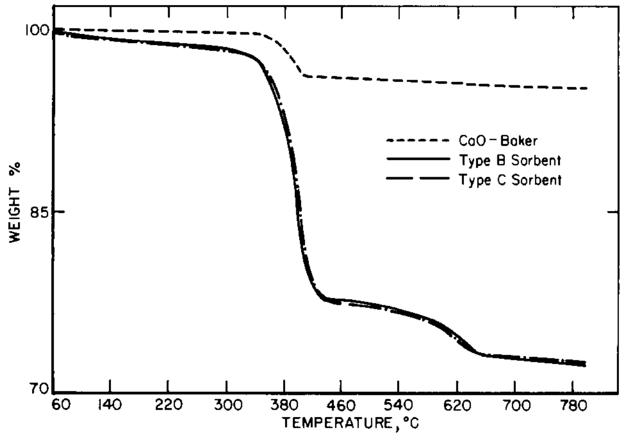

Fig 3 Decomposition curves for selected sorbents between 50 and 800 ° C

The basis for not including CO_2 in the flue gas mixture was that although a dry $N_2 + CO_2$ mixture resulted in no weight increase with LL, an 8 4 wt % increase was found with a humidified $N_2 + CO_2$ mixture Thus, the utilization of Ca for SO_2 pick-up only could not be calculated using the TG technique without analysis of the used sorbent for carbon and sulfur, which is difficult because of the small sample size

The sorption curves for LL are shown in Fig 4 Although the sorbent weight had stabilized after exposure for a few minutes to the humidified N_2, a 30-min exposure was used to ensure equilibration of the sample After exposure to the humidified flue gas, there was typically a rapid weight increase during the first 10 min, followed by a rather abrupt decrease in the rate of SO_2 pick-up A similar weight–time profile was found for all the sorbents used in this study Although a weight increase due to SO_2 pick-up

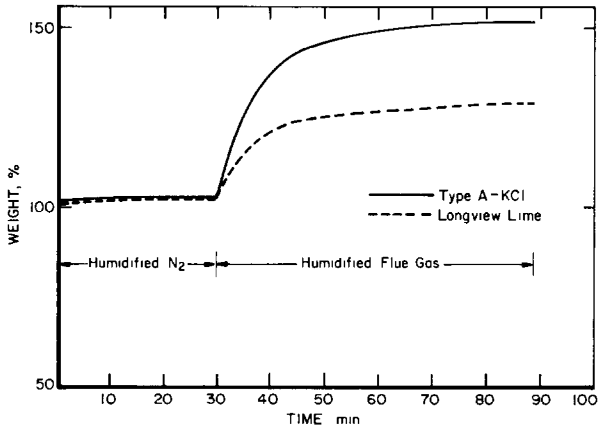

Fig 4 Weight per cent increase for typical sorbents in humidified N_2 and flue gas

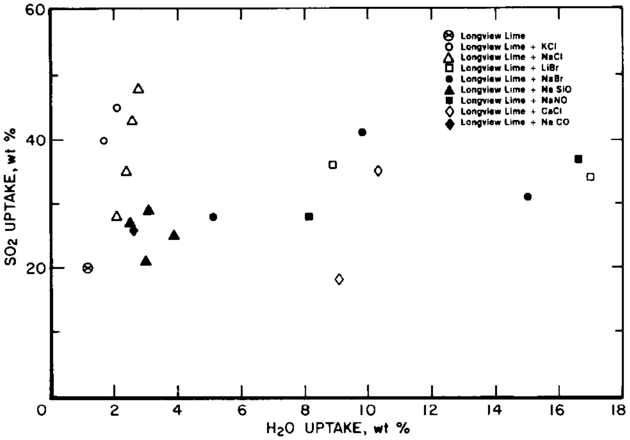

Fig 5 H_2O uptake vs SO_2 uptake for Type A sorbents

was found only when using humidified flue gas, there was no correlation between the SO_2 uptake from humidified flue gas and the weight increase resulting from exposure to H_2O (see Fig 5) The absence of such a correlation indicated that sorption of an excess amount of H_2O on the sorbent did not result in higher utilization of the sorbent The weight increases due to H_2O pick-up and SO_2 pick-up are shown in Table 2, a ranking of Type A sorbents according to percentage utilization is shown in Fig 6

A number of conclusions can be reached after reviewing the data in Table 2

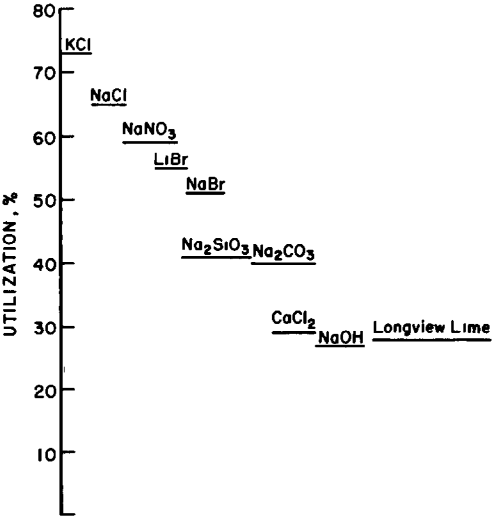

Fig 6 Percentage utilization for Type A sorbents (0 1 mol salt per mol $Ca(OH)_2$)

TABLE 2

Thermogravimetric results

Sorbent	Moles salt/ moles $Ca(OH)_2$	Surface area (m^2 g^{-1})	% Wt increase [a]		% Utilization
			H_2O	Flue gas	
Longview lime	–	17	1.1 [b] (1.0–1.8)	19 [b] (15–20)	28
Baker CaO	–	1	0	0	0
Type A sorbents (Longview lime + salt solution)					
Salt solution					
KCl	0.052	18	1.7	40	65
KCl	0.104	17	2.1	45	73
NaCl	0.033	18	2.1	28	45
NaCl	0.066	20	2.4	35	58
NaCl	0.132	21	2.6	43	73
NaCl	0.198	18	2.8	48	81
LiBr	0.052	19	8.9	36	57
LiBr	0.104	17	17.0	34	55
NaBr	0.026	20	5.1	28	44
NaBr	0.052	20	9.8	41	67
NaBr	0.104	20	17.0	31	51
Na_2SiO_3	0.025	17	3.0	21	33
Na_2SiO_3	0.051	16	3.1	29	46
Na_2SiO_3	0.078	12	2.5	27	44
Na_2SiO_3	0.103	10	3.9	25	41
$NaNO_3$	0.054	18	8.1	28	44
$NaNO_3$	0.108	19	16.6	37	59
$CaCl_2$	0.052	11	10.3	35	55
$CaCl_2$	0.104	9	9.1	18	29
NaOH	0.103	14	7.2	17	27
NaOH	0.206	7	13.3	10	16
Na_2CO_3	0.103	17	2.6	26	40
Type B sorbents (Baker CaO + salt solution at 95 °C)					
No salt	–	18	1.3	22	32
KCl	0.053	19	1.5	35	51
KCl	0.107	17	2.0	46	68
NaCl	0.066	20	1.5	35	53
NaCl	0.132	19	1.5	36	55
$CaCl_2$	0.100	7	5.0	18	26
$CaCl_2$	0.200	6	11.9	30	46
Type C sorbents (Baker CaO + salt solution, > 100 °C)					
No salt	–	15	1.4 (1.2–1.7) [c]	14 (10–19) [c]	20
NaCl	0.110	13	2.3	32	48
NaCl	0.110 [d]	14	3.1	33	49
KCl	0.056	14	3.4	28	41

[a] Average of 2 or 3 runs [b] Average of 5 runs [c] Average of 5 runs [d] 40 g of CaO + 24 ml H_2O used

(1) The alkali halides were the most effective additives

(2) The utilizations obtained for Type A sorbents were 10–25% higher than the utilizations for Type B sorbents with the same salt loading

(3) The low utilization obtained for Type C sorbents was not due to incomplete conversion of CaO to $Ca(OH)_2$ because the thermal curves for the fresh sorbents indicated that most of the Ca in the sample was present as $Ca(OH)_2$ The low surface areas obtained for these sorbents probably accounted for the low utilizations Preparation of these Type C sorbents on such a small scale is probably not a realistic indicator of the performance of these sorbents when prepared commercially

(4) Both Na_2SiO_3 and $CaCl_2$ and perhaps NaOH showed evidence of undergoing reaction with the hydrated lime, as indicated by the decrease in utilization at high salt concentrations as well as by the low surface areas of these sorbents Salts such as $Ca(OH)_2 \cdot CaCl_2 \cdot H_2O$ and [CaO xSiO$_2$ yH$_2$O] can form, resulting in significant alteration of the properties of the hydrated lime [13] Preparation of a type C sorbent using $CaCl_2$ resulted in an extremely vigorous reaction and the formation of a dense, hard material, totally unlike the dry, free-flowing powders obtained with other additives The utilizations obtained for the sorbent containing NaOH were unexpectedly low in view of the positive results found for NaOH-promoted lime in studies carried out by Yoon et al [6]

No SO_2 uptake occurred on these hydrated lime sorbents in the absence of water The importance of working at high relative humidity has been demonstrated by Klingspor and coworkers [8–10]

As shown in Fig 7, there was little difference in the particle size distribution of LL alone and LL that was impregnated with a NaCl solution Sorbents prepared according to Type B or C procedures, however, were considerably smaller in particle size, with 80–90% of the particles less than 10 μm compared with only 50–60% for LL A possible reason for this

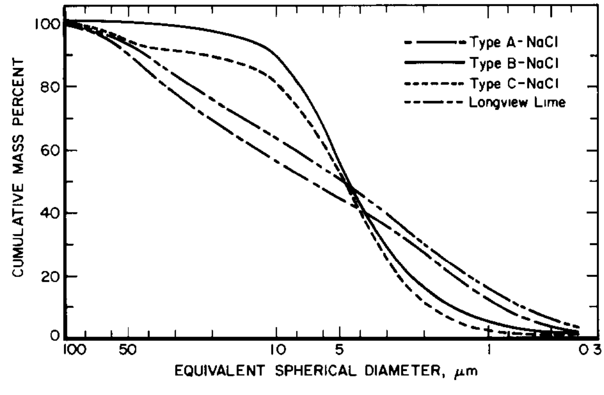

Fig 7 Particle size distributions

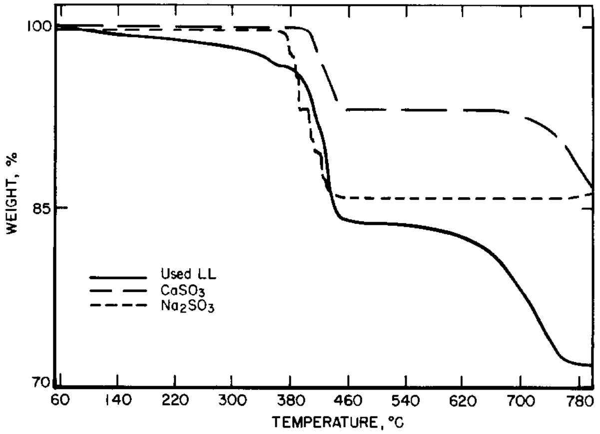

Fig 8 Decomposition curve for used Longview lime, $CaSO_3$ and Na_2SO_3 between 50 and 800 °C

diversity may be a difference in the particle size of the oxides used to prepare the hydrated limes, previous studies [15] have shown that use of a finer quicklime (CaO) resulted in more reactive sorbents (for furnace injection) owing to a corresponding finer hydrate The smaller particle size of Type B sorbents, however, did not result in higher surface areas or increased percentage utilization with these sorbents

Analysis of the used LL sorbent by a TG technique is shown in Fig 8, also shown are the decomposition curves for pure Na_2SO_3 and $CaSO_3$ (in an N_2 atmosphere) Unlike the fresh sorbent, the used LL sorbent showed a small weight decrease at 350 °C, followed immediately by a larger weight decrease between 375 and 460 °C The first decrease (350 °C) was found also for other used sorbents and may have resulted from dehydration of the hemihydrate

$$(CaSO_3\ \ CaSO_4)\ 0\ 5H_2O \rightarrow CaSO_3\ \ CaSO_4 + 0\ 5H_2O$$

The hemihydrate has been identified as a product in flue gas scrubber systems, although TG analysis of this product indicated that dehydration occurred between 400 and 470 °C [16] The larger weight decrease between 375 and 460 °C may have been due to the dehydration of unreacted $Ca(OH)_2$ to CaO and to the decomposition of the reaction products Na_2SO_3 and $CaSO_3$ The large weight decrease between 460 and 800 °C for the used LL sorbent was probably due to the decomposition of calcium sulfite

$$CaSO_3 \rightarrow CaO + SO_2$$

The results obtained with Type A sorbents are in good agreement with the fixed-bed reactor data of Ruiz-Alsop and Rochelle [13], indicating that the TG technique is an effective method for screening sorbents containing various inorganic salts In a similar fixed-bed reactor study, Jorgensen et al studied the effectiveness of NaOH, NaCl, $NaNO_3$ and $CaCl_2$ [14] Each salt was mixed with the $Ca(OH)_2$ in a dry procedure (not by the procedure of water dissolution and mixing with $Ca(OH)_2$ followed by drying) Calcium chloride was the most effective sorbent, followed by NaOH, $NaNO_3$ and NaCl, in decreasing order of effectiveness This order of effectiveness was in sharp contrast to the TG results and may have been due to the different method used in combining the salt and the $Ca(OH)_2$ The deliquescent nature of the NaOH and $CaCl_2$ probably resulted in impregnation of the $Ca(OH)_2$ after exposure to the humidified flue gas, whereas the quantity of H_2O pick-up by the NaCl was insufficient to impregnate the $Ca(OH_2)$ Yoon also found that NaOH and Na_2CO_3 were effective additives but the method used to prepare these sorbents was not clear [5] Finally, McCarthy et al showed that $CaCl_2$ was an effective additive, but again details on the preparation of the sorbent were not stated [15]

The mechanism for the promoting effect of the inorganic salts is unclear Regardless of how the sorbent is prepared, a salt such as NaCl will probably react to some degree with the $Ca(OH)_2$ in the presence of H_2O to form $CaCl_2$ and NaOH Thus, the fact that NaCl is only slightly hydroscopic may be irrelevant when considering the absence of any correlation between the hydroscopic nature of the additive and the degree of utilization Simons and Garman [17] have investigated the rate-controlling mechanisms of sulfation of CaO particles at 700–1200 °C Rate-limiting processes included (1) the filling of the smallest pores and the subsequent loss in internal surface area, (2) the activated diffusion of the SO_2 through the product deposits, and (3) the loss of intraparticle diffusion owing to complete plugging of the largest pores It is not unreasonable to assume similar rate-limiting processes in sulfation of hydrated lime at 70 °C The additives may modify the properties of the $CaSO_3$ $0\ 5H_2O$ product layer, thereby facilitating access of the SO_2 to the unreacted $Ca(OH)_2$ in the interior of the particle [13] Future studies at the Pittsburgh Energy Technology Center will include differential reactor studies with small particles (one micrometer or less) of hydrated lime, with the objective of determining the rate-limiting steps for the sulfation of hydrated lime with and without additives

ACKNOWLEDGMENT

The TG studies were carried out by Michael J Hilterman

APPENDIX I

The humidified flue gas was prepared by mixing N_2 saturated with water vapor at 70 °C with a gas containing 6027 p p m SO_2, 6 10% O_2 and N_2 as the balance The composition of the humidified flue gas is calculated as follows

Vapor pressure of water at 70 °C = 233 7 Torr

Percentage H_2O in N_2 gas stream = 234 Torr/760 Torr = 30.8%

$$\text{Volume of } N_2 \text{ at } 70\,^\circ\text{C} = 100 \text{ ml min}^{-1} \times \frac{343 \text{ K}}{298 \text{ K}} = 115\ 1 \text{ ml}$$

$$\text{Percentage } H_2O \text{ in } N_2 \text{ gas stream} = \frac{\text{ml water vapor}}{\text{ml water vapor} + \text{ml } N_2} = 0.308$$

$$= \frac{x}{(x + 115)}$$

x = ml water vapor = 51 1 ml

Composition of humidified flue gas

Total volume of gas = humidified N_2 stream + SO_2-containing stream

= (51 1 + 115 1) + (115 1) = 281 3 ml

Percentage H_2O = 51 1/281 3 = 18 2% (59 1% relative humidity)

Percentage SO_2 = 0 6027% × 115 1/281 3 = 0 2466%

Percentage O_2 = 6 10% × 115 1/281 3 = 2 50%

Balance of gas is N_2

APPENDIX II

The degree of utilization was calculated assuming only the calcium (and none of the additive) reacted with the SO_2 With sorbents containing sodium salts, however, it is likely that salts such as Na_2SO_4, Na_2SO_4 $7H_2O$, Na_2SO_4 $10H_2O$, Na_2SO_3 and Na_2SO_3 $7H_2O$ could also have formed The purpose of this appendix is to calculate the degree of utilization assuming that all of the sodium in a sorbent containing 0 066 mole NaCl per mole $Ca(OH)_2$ (0 052 g NaCl per g $Ca(OH)_2$) reacted to form Na_2SO_4 $10H_2O$ according to the following reactions

$$2NaCl + 1/2O_2 + SO_2 + 11H_2O \rightarrow Na_2SO_4\ 10H_2O + 2HCl \qquad (1)$$

$$2HCl + Ca(OH)_2 + 4H_2O \rightarrow CaCl_2\ 6H_2O \qquad (2)$$

$$2NaCl + 1/2O_2 + SO_2 + Ca(OH)_2 + 15H_2O \rightarrow Na_2SO_4\ 10H_2O + CaCl_2 \cdot 6H_2O \qquad (3)$$

The percentage weight increase for this reaction (3) is 183% (vs/ 74% for the reaction of $Ca(OH)_2$ to form $CaSO_3$ $0\ 5H_2O$) Thus, if all the $Ca(OH)_2$ and

NaCl reacted with the SO_2, the stoichiometric weight increase can be calculated as follows

Percentage weight increase of sorbent resulting from formation of Na_2SO_4 $10H_2O$ is

$$\frac{0\ 052\ \text{g NaCl}}{1\ 052\ \text{sorbent}} \times 183\% = 9\ 0\%$$

Percentage weight increase resulting from formation of $CaSO_3$ $0\ 5H_2O$ is

$$\frac{100\ \text{g}\ Ca(OH)_2 - 0\ 033\ \text{g used in eqn}\ (3)}{1\ 052\ \text{g sorbent}} \times 74\ 3 = 68\ 3\%$$

The degree of utilization of this sorbent then would have been 35/77 3 or 45% This utilization is at least 50% higher than that for LL (no additive) If salts with formula weights less than the formula weight of Na_2SO_4 $10H_2O$ were formed, then the utilization for the NaCl-impregnated LL is even higher

REFERENCES

1 J Makansi, Power, 130 (1986) 27
2 R Remirez, Chem Eng, 93 (1986) 17
3 J Z Abrams, J H Blake and H W Pennline, Presented at Joint ASME/IEEE Power Generation Conf, Portland, OR, 1986
4 N Z Shilling, Proc 2nd Pittsburgh Coal Conf, Pittsburgh, PA, 1985, p 158
5 H Yoon, J A Withum, W A Rosenhoover and F P Burke, Presented at 1986 Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Raleigh, NC, 1986
6 H Yoon, M R Stouffer, W A Rosenhoover and R M Statnick, Proc 2nd Pittsburgh Coal Conf, Pittsburgh, PA, 1985, p 223
7 R H Borgwardt and K R Bruce, Presented at 1986 Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Raleigh, NC, 1986
8 J Klingspor, A-M Stromberg, H T Karlsson and I Bjerle, Chem Eng Process, 18 (1984) 239
9 H T Karlsson, J Klingspor, M Linne and I Bjerle, A P C A J, 33 (1983) 23
10 J Klingspor, H T Karlsson and I Bjerle, Chem Eng Commun, 22 (1983) 81
11 I Bjerle, J Klingspor and H T Karlsson, Ind J Environ Prot, 4 (1984) 36
12 W R Seeker, S L Chen, J A Cole, S B Greene, J C Kramlich, J B Longwell, A F Sarofim, E T Seiler and J O L Wendt, Kinetics of sulfur and nitrogen reactions in combustion systems, Energy and Environmental Research Corp, DOE DE-AC22-84PC70771, Quarterly Report 1, 1985
13 R N Ruiz-Alsop and G T Rochelle, Presented at American Chemical Society National Meeting, Miami Beach, FL, April, 1985
14 C Jorgensen, J C S Chang and T G Brna, Presented at the 1986 Spring meeting of American Institute of Chemical Engineers, New Orleans, LA
15 J M McCarthy, S L Chen, J C Kramlich, W R Seeker and D W Pershing, Presented at the 1st Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, November 1984, San Diego, CA
16 D L Dorsey and B Buecker, Res Dev, May (1986) 93
17 G A Simons and A R Garman, Am Inst Chem Eng J, 32 (1986) 1491