EFFECT OF DELIQUESCENT SALT ADDITIVES ON THE REACTION OF SULFUR DIOXIDE WITH DRY $Ca(OH)_2$

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ABSTRACT

The effect of deliquescent salt additives in the reaction of SO_2 with dry $Ca(OH)_2$ solids dispersed in a sand reactor was studied. Small amounts of the deliquescent salts (1 to 10 mole %) were added to the $Ca(OH)_2$ by a slurrying, drying process. The reaction rate was studied at relative humidities of 54 and 74 % and other conditions similar to those encountered in bag filters during flue gas desulfurization by spray drying. The reaction solids were characterized by Scanning Electron Microscopy, powder X-ray diffraction, coulter counter size distribution, BET (N_2) surface area, energy dispersive spectrometry, and differential scanning calorimetry. Most of the deliquescent salts tested increased the reactivity of the lime. The most effective additives were: LiCl, KCl, NaCl, NaBr and $NaNO_3$.

INTRODUCTION

Spray drying has become increasingly important in recent years as an alternative to wet scrubbing for sulfur dioxide control. In the spray dryer the sulfur containing flue gas is contacted with a fine mist of an aqueous solution or a slurry of an alkali (typically lime or soda ash). The sulfur dioxide is then absorbed in the water droplets and neutralized by the alkali. Simultaneously, the thermal energy of the gas evaporates the water in the droplets to produce a dry powdered product. After leaving the spray dryer the dry products including the fly ash are removed with collection equipment such as fabric filters or electrostatic precipitators.

Fabric filters are the preferred collection equipment as additional sulfur dioxide removal takes place in the bag house [6, 7]. Typically, under conditions such that 80 % of SO_2 is removed, about 60 to 70 % of the removal takes place in the spray dryer and 10 to 20 % removal takes place in the bag filters [14, 9, 2]. Parametric studies in spray dryer pilot plants have demonstrated that the main variable affecting the SO_2 removal in the bag filters beside the stoichiometric ratio of lime to SO_2 is the approach to the adiabatic saturation temperature of the gases [14, 2, 15, 12, 1]. The approach to the adiabatic saturation temperature in turn is correlated with the moisture content of the solids. Additives that will modify the moisture content of the lime solids in equilibrium with a gas phase of a given relative humidity would then be expected to change the reactivity of the lime towards SO_2.

A few additives have been tested in spray drying systems. $CaCl_2$ has proven effective in increasing the reactivity of limestone and lime towards SO_2 [5]. Adipic acid was also tested [10] with mixed results. Sodium sulfite, Fe^{++} compounds, Ethylenediaminetetra-acetic acid and disodium salt (EDTA) had been used as additives during simultaneous SO_2 and NO_x removal (Niro Process) [4]. The emphasis in the Niro process was to improve the removal of NO_x.

The present work was undertaken to investigate in a systematic manner the kind of additives that could be used to improve lime reactivity towards SO_2. A small fixed bed reactor was used to simulate the conditions encountered in the bag filters during spray drying flue gas desulfurization. Three different kind of additives were tried: buffer acids, organic deliquescents and inorganic deliquescents. The inorganic salts were selected according to their deliquescent properties, or the lowering of the vapor pressure of water over their saturated solutions. Of these three types of additives the deliquescent salts were the only ones that increased

the lime reactivity.

EXPERIMENTAL

Apparatus

The general scheme of the experimental apparatus is given in Figure 3. Simulated flue gas was synthesized by combining nitrogen and sulfur dioxide from gas cylinders. The gas flow rates were measured using rotameters. Water was added by means of a syringe pump and evaporated at 120 °C before mixing with the gas stream. The glass reactor (4 cm diameter, 12 cm height) was packed with a mixture of silica sand and powdered reagent $Ca(OH)_2$ in a weight ratio of 40:1. The addition of sand is necessary to avoid channeling caused by lime agglomeration [5]. The silica sand, obtained from Martin Marietta Aggregates, was 100 mesh. The reactor was immersed in a water bath that maintained the temperature within 0.1 °C. Tubing upstream from the reactor was heated to prevent the condensation of moisture in the walls. Before going to analysis the gas was cooled and the water then condensed by cooling water and an ice bath . The gas was analyzed for SO_2 in a pulsed fluorescent SO_2 analyzer (Thermoelectron Corporation model 40) and the concentration continuously recorded. The reactor was equipped with a bypass, to allow the bed to be preconditioned and then after, to allow the gas flow to be stabilized at the desired SO_2 concentration before beginning the experiment. Prior to each experimental run the bed was humidified by flushing with pure nitrogen at a relative humidity of about 98 % for 10 minutes then later with pure nitrogen at the relative humidity at which the experiment was to be performed for 8 minutes. This was done to better simulate the conditions encountered in the bag filters where the solids are originally slurry droplets.

Preparation of the Samples

An aqueous solution containing the desired additive was prepared. Five ml of this solution were then added to 1 g of lime and slurried. The sample was then placed in a oven to dry at 75 °C for about 14 hours then later sieved to separate the individual lime particles prior to mixing with the silica sand and being placed in the reactor.

Analysis

The fraction of $Ca(OH)_2$ reacted at any given time can be calculated by integrating the SO_2 versus time curve obtained by the recorder on the SO_2 analyzer and doing a mass balance in the reactor. As a backup, the reacted solids are analyzed for sulfite and hydroxide using acid/base and iodine titrations.

Characterization of the reactant

The lime used in these experiments was calcium hydroxide powder reagent. The particle size distribution of the lime was determined by means of a Coulter Counter model T_{AII} using as electrolyte a solution of 4 wt % $CaCl_2$, saturated with $Ca(OH)_2$. The surface area was determined using Brunauer Emmett and Teller (BET) nitrogen absorption isotherms. Table 1 shows the particle size distribution and surface area of the lime used. The surface area was also measured for the lime after being slurried (5 ml water/g lime) and dried overnight at 75 °C. There was a small decrease in the surface area due to this slurrying process. Figures 1 and 2 show Scanning Electron Micrographs of the lime that was used as the reactant. From these pictures it can be seen that the lime particles are in the micron range size, are highly nonspherical and have considerable surface roughness.

The samples of lime with additives that were prepared in the way discussed above were characterized using x-ray powder diffraction, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and BET surface area. According to x-ray diffraction analysis most of the additives precipitate as a separate phase after slurrying with the lime then drying. The exception is $CaCl_2$, where the $Ca(OH)_2.CaCl_2.H_2O$ phase is formed. This finding agrees with the result reported in the literature for the equilibrium of the $Ca(OH)_2$-$CaCl_2$-H_2O system [13]. In the case of $Ca(NO_3)_2$, the formation of the solid phase $Ca_2N_2O_7.2H_2O$ has been reported [13]. This could not be confirmed using x-ray analysis as the diffraction pattern of the $Ca_2N_2O_7.2H_2O$ was not available.

EDS was used to analyze individual particles and it was found that the additives precipitate together with the lime and are, more or less, uniformly distributed through the lime particles. SEM micrographs of the particles of lime with additives showed no significant difference in size or shape from the pure lime particles. The BET surface areas of the lime with different salt additives were also measured. The surface areas ranged from 7.0 to 9.6 m^2/g depending on the additive used. No correlation was found between lime reactivity and surface area.

RESULTS

Effects of Additive Type

The additives tried can be classified as three types: buffers, organic deliquescents and inorganic deliquescents. Column 1 of Table 3 shows the experimental results for these three types of additives, expressed as percentage of lime reacted after 60 minutes of reaction. The experiments shown in column 1 were all run at a relative humidity of 74 % and other conditions as indicated in the table. The buffers added were adipic and glycolic acid in concentrations of 1 and 5 wt % respectively. The addition of buffers proves to be detrimental to the reaction of SO_2 and lime, a conversion lower than the pure lime case was observed. The organic deliquescents tried were monoethanolamine, ethylene glycol, and triethylene glycol all at concentrations of 5 wt %. A small decrease in lime reactivity was found in these cases as can be seen from Table 3. At a 74 % relative humidity all the deliquescent salts tried were successful in increasing the reactivity of the lime, but some salts were more effective than others.

Influence of the relative humidity on effectiveness of additives

Column 2 of Table 3 shows the effect of selected deliquescent salts on the lime reactivity at a relative humidity of 54 %. As can be seen by comparing columns 1 and 2 of Table 3 the effectiveness of some salts change with relative humidity, for example $Ca(NO_3)_2$ was very effective at 74 % relative humidity but behaved poorly at a lower relative humidity. At a lower relative humidity the salts that behave the best were K, Li and Na Chlorides, NaBr, and $NaNO_3$.

Influence of Salt Concentration

A series of experiments were performed to determine the influence of the salt concentration on the SO_2 reaction rate. The salts used were NaCl and $NaNO_3$ in concentrations ranging from 1 to 15 mole %. The experiments were carried out at 54 % relative humidity, and a reactor temperature of 66 °C. As can be seen from Figure 4, the conversion increases with increasing concentration of additive until about 10 mole %. After this the curve levels off. The optimum concentration of additive is then about 10 mole % for 1:1 salts like NaCl and $NaNO_3$.

Effect of Prehumidification at 98 % Relative Humidity

To investigate the effect of prehumidifying the bed on the reactivity of the lime with additives towards SO_2 some experimental runs were made omitting this step. Table 2 shows the results obtained at 54 and 17.4 % relative humidity with and without prehumidification of the bed at 98 % relative humidity. The additives used were NaCl, $NaNO_3$ and KCl. At 54 % relative humidity even when some decrease of the lime conversion was found without the prehumidification, the results are still far superior to the pure lime case. At 17.4 % relative humidity all the beneficial effect in the case of the NaCl appears to be due to the prehumidification of the bed i. e. due to an hysteresis phenomena.

DISCUSSION

Columns 3 and 4 of Table 3 show the deliquescent properties of the salts, expressed as water activity in saturated solutions of the salt at 25 and 100 °C and 1 atm. The water activity is approximately equal to the relative humidity of the gas phase in equilibrium with the saturated solution. When examining the deliquescent properties of the salts it is apparent that if the improvement of reactivity was due solely to deliquescence, $NaNO_3$ and all the chlorides tried, with the exception of the LiCl, should not work at a relative humidity of 54 %. Furthermore, the most deliquescent of all the additives tried, NaOH does not perform as well as some of other less deliquescent salts. We can see that some salts are effective at a lower relative humidity than would be predicted by the vapor pressure of water over saturated solutions of these salts. A possible explanation would be a hysteresis phenomena affecting the amount of absorbed water in the solid phase. Strong hysteresis effects have been reported in NaCl aerosols [17]. From the experimental results presented in Table 2, it can be concluded that even when the hysteresis effects can explain the improvement in reactivity at a very low relative humidity (17.4 %) it can not explain all the improvement observed at 54 % relative humidity. An alternate explanation proposed is that the chlorides and $NaNO_3$ modify the properties of the product $CaSO_3.1/2H_2O$ layer that is formed as the reaction takes place thereby facilitating the access of the SO_2 to the unreacted lime which remains in the center of the particle. NaCl and $CaCl_2$ have been reported to enhance the sulfur dioxide reactivity of limestones in fluidized bed combustion by affecting the the pore structure of the lime during calcination, which then increases the extent of sulfation of the limestone [3].

For an additive to be effective it is necessary that the hydroxide of the cation be very soluble, otherwise the cation will precipitate as the hydroxide and the anion as the Ca salt. For example $Co(NO_3)_2$ is very deliquescent but $Co(OH)_2$ is insoluble so Co precipitates as $Co(OH)_2$ and adding cobalt nitrate becomes equivalent to adding calcium nitrate, which is not very effective.

Table 1

PROPERTIES OF THE $Ca(OH)_2$ USED AS A REACTANT

Particle size (μm)	50 % below 5.6 90 % between 1.5 - 15
BET Surface Area (m^2/g)	9.4 (non slurried lime) 8.8 (slurried lime)

Table 2

EFFECT OF PREHUMIDIFICATION OF THE BED ON LIME REACTIVITY
Inlet SO_2 concentration = 500 ppm
Nitrogen Flow Rate = 4.6 l/min (0°C, 1 atm)
Amount of Lime = 1.0 g

	Lime Conversion after 60 Minutes			
	54 % Relative Humidity 66 °C		17.4 % Relative Humidity 95 °C	
Additive	Prehumidified	Nonprehumidified	Prehumidified	Nonprehumidified
None	11.2	-	4.0	-
10 mole % NaCl	27.0	23.2	9.7	4.0
10 mole % $NaNO_3$	27.2	23.7	11.9	-
10 mole % KCl	37.3	19.3	3.4	-

Table 3

EFFECT OF ADDITIVES ON LIME REACTIVITY AND DELIQUESCENT PROPERTIES OF SALTS
Inlet SO_2 Concentration = 500 ppm
Nitrogen Flow Rate = 4.6 l/min [0 °C, 1 atm]
Amount of Lime = 1.0 g

Additive	Lime Conversion at 60 min. 74 % R.H. 64.4 °C	54 % R.H. 66 °C	a_w at 25 °C	a_w at 100 °C
None	22.4	11.8	-	-
BUFFERS				
5 wt % Glycolic Acid	11.3	-	-	-
1 wt % Adipic Acid	20.3	-	-	-
ORGANIC DELIQUESCENTS				
5 wt % Monoethanolamine	19.6	-	-	-
5 wt % Ethylene Glycol	20.3	-	-	-
5 wt % TEG	20.5	-	-	-
INORGANIC DELIQUESCENTS				
5 mole % Na_2SO_4	28.3	-	-	.902 [8]
5 mole % Na_2SO_3	29.8	16.1	-	-
5 mole % $CaCl_2$(***)	34.6	16.4	.850 [8]	.686(*) [8]
10 mole % NaCl	38.5	27.0	.753 [16]	.735 [8]
10 mole % NaOH	38.8	17.3	.0703 [16]	.004 [11]
5 mole % $Ca(NO_3)_2$(***)	39.4	12.3	-	.553 [8]
10 mole % $NaNO_2$	40.0	-	-	.496(**)
10 mole % $NaNO_3$	41.5	27.2	.738 [16]	.549 [8]
$BaCl_2.2H_2O$	-	19.4	.902 [16]	.71(**)
$Na_2S_2O_3$	-	21.6	-	.52(**)
KCl	-	37.3	.842 [16]	.745 [8]
$NaBr.2H_2O$	-	42.0	.577 [16]	.502 [8]
LiCl	-	43.9	.112 [16]	.085 [8]
100 % SO_2 Removal	48.2	48.2		

(*) Data at 75 °C.
(**) Extrapolated from data reference [8]
(***) Solid phases are $CaCl_2.Ca(OH)_2.H_2O$ and $Ca_2N_2O_7.2H_2O$ respectively.

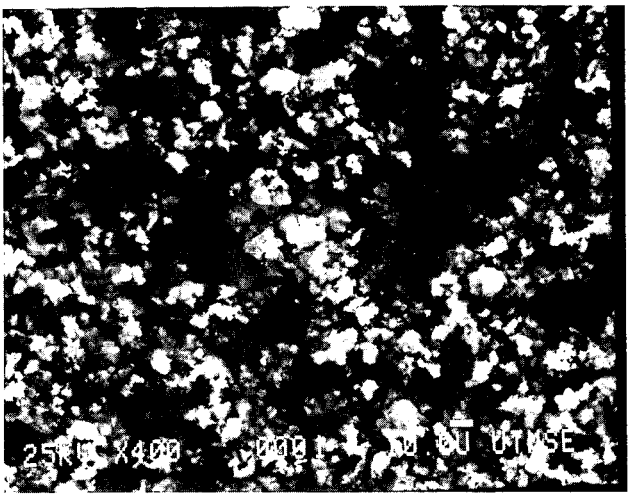

FIGURE 1. $Ca(OH)_2$ SEM MICROGRAPH, 400 MAGNIFICATIONS.

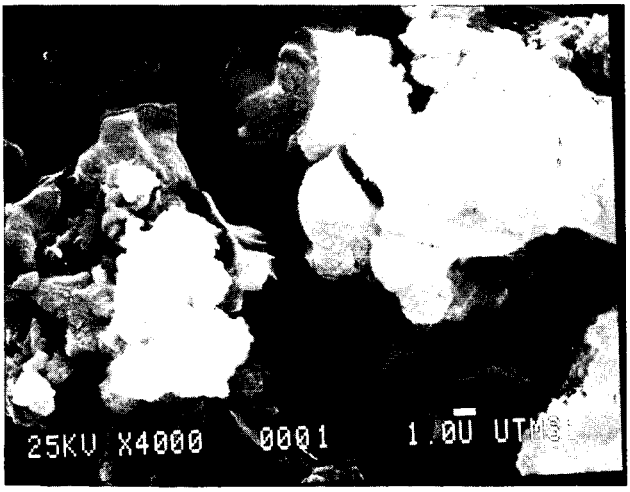

FIGURE 2. $Ca(OH)_2$ SEM MICROGRAPH, 4000 MAGNIFICATIONS

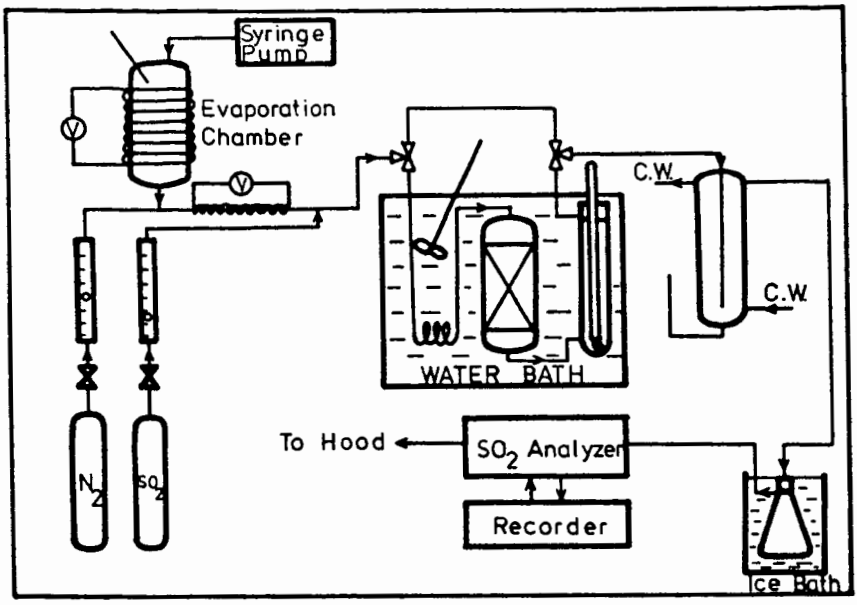

Figure 3. Experimental Apparatus

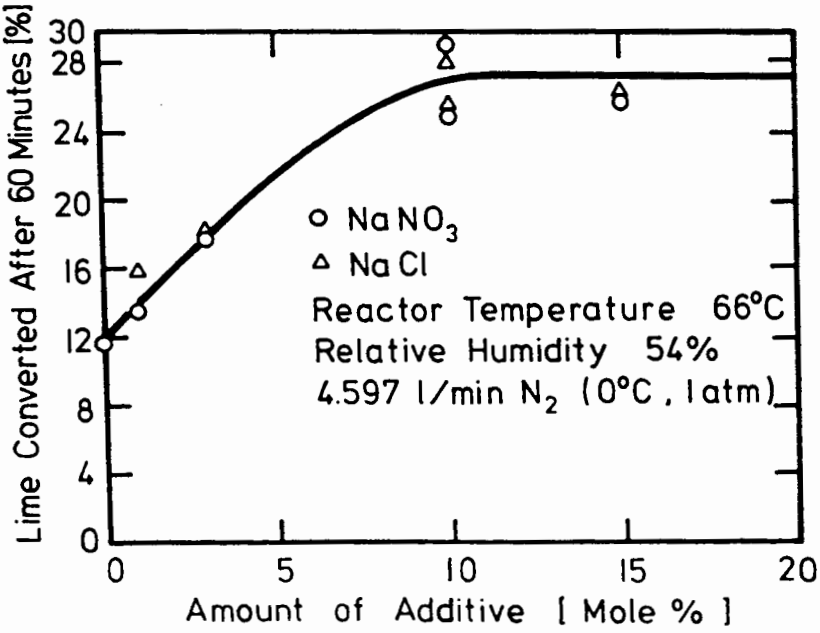

Figure 4. Effect of Amount of Additive on Lime Reactivity.

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