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Using Hydrated Lime and Dolomite for Sulfur Dioxide Removal from Flue Gases

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Sulfation properties of six hydrated lime and three hydrated dolomite sorbents were investigated and compared a thermobalance was used to record the weight increase of the sorbents during the sulfation reaction which is carried out at 338 K. To distinguish between the weight gain by water adsorption and by sulfation, the samples were first exposed to a gaseous mixture consisting of 5% O_2, 10% CO_2, and the balance nitrogen with 55 % relative humidity. After this pre-conditioning, SO_2 was added to the gaseous mixture for sulfation with a concentration of 5000 ppm. The total sulfation capacities and $Ca(OH)_2$ conversion values of hydrated lime sorbents varied between 70.19-123.36 (mg SO_2/g sorbent) and 15.08-23.50 %, respectively. The total sulfation capacities and $Ca(OH)_2$+$Mg(OH)_2$ conversion values of hydrated dolomite sorbents varied between 146.55-226.77 (mg SO_2/g sorbent) and 22.54-30.94 %, respectively. It was found that the total sulfation capacity and conversion values of sorbents were changed depending on the physical properties of sorbents. Regression analysis was applied to relate the total sulfation capacity and conversion values to the physical properties of sorbents and linear empirical equations were developed.

1. Introduction

Although the most commonly used industrial practice for flue gas desulfurization (FGD) is the wet scrubbing processes, dry scrubbing processes, especially dry sorbent injection technology, offer a more economical technology for retrofitting (Gutierrez Ortiz et al., 2008; Maina and Mbarawa, 2011a; Karatepe et al., 2004). Dry scrubbers have significantly lower capital and annual costs than wet systems because they are simpler and demand less water and their waste disposal is less complex (Li et al., 2011; Gutierrez Ortiz et al., 2008; Ogenga et al., 2010; Karatepe et al., 2004).

Dry sorbent injection systems pneumatically inject powdered sorbent directly into the furnace, economizer, or downstream ductwork. The dry waste product is removed using particulate control equipment such as a baghouse or electrostatic precipitator. The flue gas emissions from the coal-fired boiler humidified by fresh water in the duct section. The total SO_2 removal achieved is the sum of the removal in the duct section and the removal in the particulate control device (Gutierrez Ortiz et al., 2008; Karatepe et al., 2004). The contact time in the duct is usually quite short and, therefore, a very reactive sorbent is required (Gutierrez Ortiz et al., 2008; Karatepe et al., 2004; Li et al., 2011)

The most commonly used material for FGD is limestone due to its availability and price (Karatepe et al., 2004; Maina and Mbarawa, 2011a; Maina and Mbarawa, 2011b; Liu et al., 2010; Lee et al, 2005; Li et al, 2010). When limestone is used directly, desulfurization was achieved by the reaction between $CaCO_3$ and SO_2. But this process is not effective to remove a desirable amount of sulphur dioxide from flue gases. Therefore limestone is usually calcined to form CaO which is more reactive than $CaCO_3$.

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Although the reactivity of CaO is better than $CaCO_3$. It's reactivity toward SO_2 should be increased due to stringent desulfurization policies. To achieve this, the calcined limestone is normally hydrated to form $Ca(OH)_2$ which is perceived to be more reactive than CaO towards SO_2 . Many researchers attribute this increase in reactivity to the increase in surface area and porosity of the calcinations of product (Maina and Mbarawa, 2011a; Maina and Mbarawa, 2011b).

The aim of the present study is to investigate and compare the desulfurization efficiences of different hydrated lime and dolomite sorbents.

2. Materials and methods

In the experiments six hydrated lime and three hydrated dolomite samples were used as sorbents. A Shimadzu TG 41 thermal analyzer is used to determine the $Ca(OH)_2$ and $Mg(OH)_2$ contents of these sorbents. Thermal gravimetric experiments were performed at linear heating rate of 10 K/min from room temperature to 1073 K, under nitrogen atmosphere with a flow rate of 40 cm^3/min.

Physical properties of sorbents, such as pore volume, surface area, and mean pore radius, were measured using an Autoscan-33 mercury porosimeter. Sulfation experiments were performed at 338 K. A thermobalance was used to record the weight increase of the sorbents during their reaction with sulfur dioxide. To distinguish between the weight gain by water adsorption and the weight gain by sulfation, the samples were first exposed to a gaseous mixture consisting of 5 % O_2, 10% CO_2, and the balance nitrogen with 55 % relative humidity. After this pre-conditioning, SO_2 was added to the gaseous mixture for sulfation with concentration of 5000 ppm.

3. Results and discussion

The $Ca(OH)_2$ and $Mg(OH)_2$ contents of sorbents determined from their non-isothermal thermogravimetric curves were given in Table 1 together with their physical properties.

Table 1: $Ca(OH)_2$ and $Mg(OH)_2$ contents and physical properties of sorbents

Sample code	$Ca(OH)_2$ (%)	$Mg(OH)_2$ (%)	Pore volume (cm^3/g)	Mean pore radius (μm)	Surface area (m^2/g)
HL1	80.77	----	0.8042	0.1940	8.2925
HL2	79.87	----	0.7441	0.1188	12.5240
HL3	50.12	----	0.5940	0.1139	10.4287
HL4	88.27	----	0.7372	0.1989	7.4116
HL5	85.07	----	0.6500	0.1452	8.9541
HL6	64.42	----	0.9608	0.0935	20.5415
HD1	49.63	29.81	0.5852	0.0574	20.3996
HD2	49.46	38.41	0.8320	0.0545	30.5036
HD3	51.81	36.31	0.6131	0.0384	26.7238

Total sulfation capacity and conversion values of the hydrated lime and hydrated dolomite sorbents were summarized in Tables 2 and 3, respectively.

As can be seen from Table 2 the total sulfation capacities and $Ca(OH)_2$ conversion values of hydrated lime sorbents varied between 70.19-123.36 (mg SO_2/g sorbent) and 15.08-23.19 %, respectively. On the other hand, the total sulfation capacities and $Ca(OH)_2$ + $Mg(OH)_2$ conversion values of hydrated dolomite sorbents were changed between 146.55-226.77 (mg SO_2/g sorbent) and 22.54-30.94 %, respectively (Table 3). The total sulfation capacities of hydrated dolomite sorbents were found to be higher than hydrated lime sorbents. This could be attributed to the high $Mg(OH)_2$ content of the hydrated dolomite sorbents.

It can be clearly seen from Tables 2 and 3, conversion values of hydrated sorbents are rather low. Available solid reactant and the reaction surface area can possibly be reduced significantly with increasing conversion, because the molar volume of reaction products ($CaSO_3.1/2H_2O$and $MgSO_4$) has a larger molar volume than that of reactants ($Ca(OH)_2$ and $Mg(OH)_2$). Therefore, a non-porous protective layer forms on the sorbent surface soon after the start of reaction which prevents further contact of sorbent with reactive gas (Karatepe et al., 2004; Liu et al., 2010; Maina and Mbarawa, 2011a; Maina and Mbarawa, 2011b). The pore closure and a reduction in reaction surface area contribute to decrease in the conversion. Since unreacted part remains the sorbent particle, it is usually obtained low degree of SO_2 removal (Shi et al., 2011; Karatepe et al., 2004). Therefore, the physical properties of sorbents such as specific surface area, pore volume and pore diameter play very important role in SO_2 removal (Karatepe et al., 2004; Lee et al., 2005; Zhang et al., 2010; Ogenga et al., 2010; Li et al., 2011; Maina and Mbarawa, 2011a).

Table 2: Total sulfation capacity and conversion values of hydrated lime sorbents

Sample code	Total sulfation capacity (mg SO_2/g sorbent)	$Ca(OH)_2$ conversion (%)
HL1	88.76	15.08
HL2	123.36	20.55
HL3	70.19	18.85
HL4	103.41	15.77
HL5	117.50	18.59
HL6	112.52	23.19

Table 3: Total sulfation capacity and conversion values of hydrated dolomite sorbents

Sample code	Total sulfation capacity (mg SO_2/g sorbent)	$Ca(OH)_2$ + $Mg(OH)_2$ conversion (%)
HD1	146.55	22.54
HD2	185.34	25.31
HD3	226.77	30.94

The relation between the total sulfation capacities of hydrated lime and dolomite sorbents with their surface areas and mean pore radius are illustrated in Figures 1 and 2. As can be clearly seen from the figures, total sulfation capacities of hydrated sorbents increased with the increase in their surface areas and the decrease in their mean pore radius.

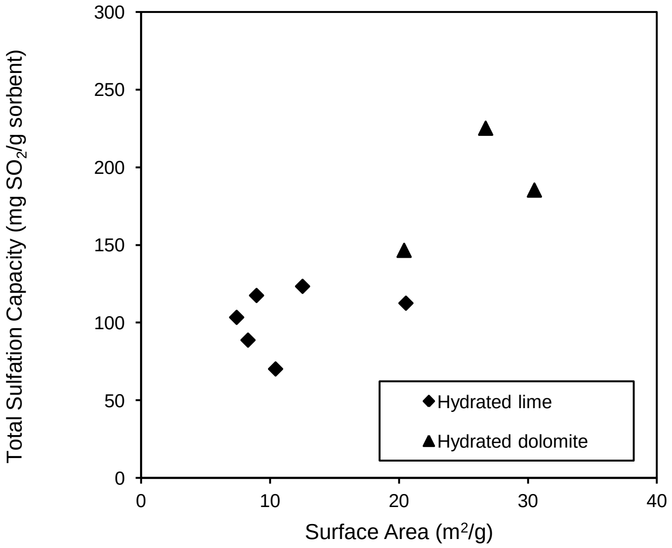

Figure 1: The relation between the total sulfation capacities of sorbents and their surface areas

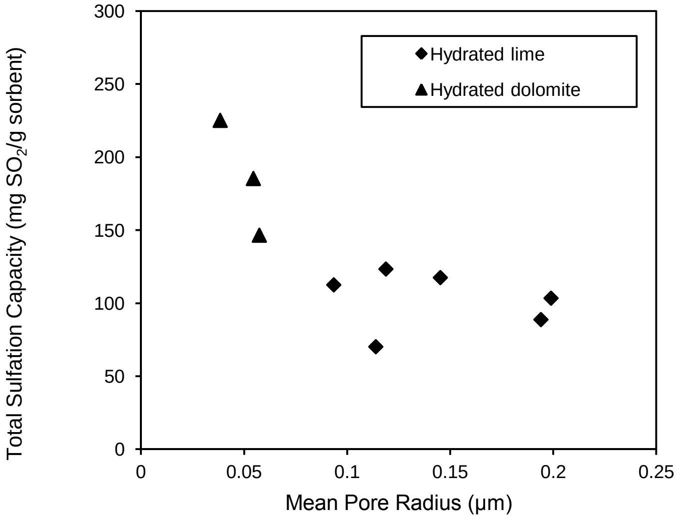

Figure 2: The relation between the total sulfation capacities of sorbents and their mean pore radius

In Figures 3 and 4 the relation between $Ca(OH)_2$ conversion values of hydrated lime sorbents with their surface areas and mean pore radius are shown. It is clearly seen from Figures 3 and 4 that, $Ca(OH)_2$ conversion values increases with increasing the surface area and decreasing the mean pore radius of hydrated lime sorbents.

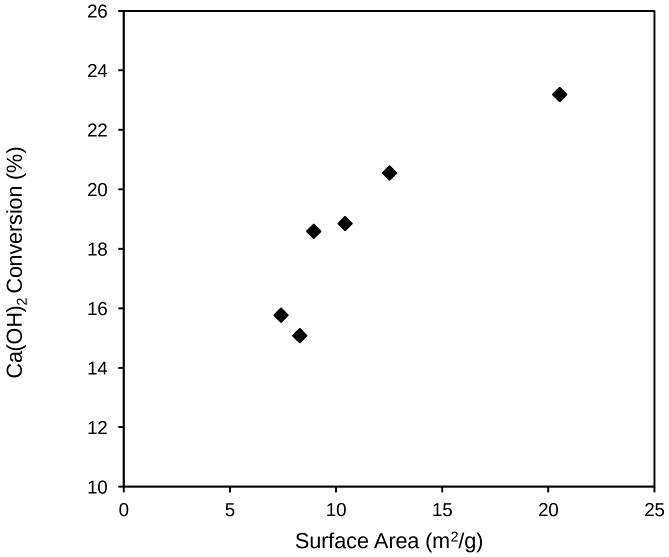

Figure 3: The relation between $Ca(OH)_2$ conversion values of hydrated lime sorbents and their surface areas

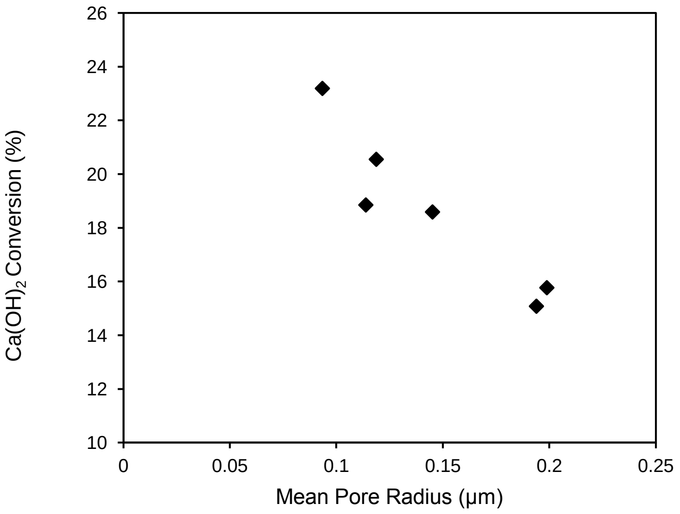

Figure 4: The relation between $Ca(OH)_2$ conversion values of hydrated lime sorbents areas and their mean pore radius

These results suggest that physical properties of sorbents have great influence on their sulfation properties. Following empirical equations were obtained for the total sulfation capacities and $Ca(OH)_2$ conversion values of sorbents related to their physical properties.

$$TSC = 45.54+5.032\ SA-31.7\ R \quad (1)$$

$$CV= 20.901+0.3073\ SA-39.35\ R \quad (2)$$

TSC : Total sulfation capacity (mg SO_2/g sorbent)
CV : $Ca(OH)_2$ conversion values of hydrated lime sorbents(%)
SA : Surface area (m^2/g)
R : Mean pore radius (µm)

The correlation coefficients for Eqs. 1 and 2 were determined as 0.80 and 0.96, respectively. The mean difference between calculated and experimental data for Eqs. 1 and 2 were found to be 18.71 % and 3.16 %, respectively.

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