

Flue Gas Desulfurization by Limestone and Hydrated Lime Slurries

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The sulfation properties of six different natural limestone and hydrated lime slurries were investigated. Sulfation experiments were carried out at the temperatures of 323 K and 298 K in a gaseous mixture consisting of 5% O₂, 10% CO₂, 0.5% SO₂ and a balance of nitrogen by volume. Total sulfation capacities of the slurries were found to vary depending on sulfation temperature, sorbent properties and the sorbent content of the slurry. It was determined that the total sulfation capacities of all slurries shifted to higher values as the CaCO₃ and Ca(OH)₂ contents of sorbents and sorbent content of slurries increases and sulfation temperature decreases. Depending on sulfation conditions and the sorbent properties, the total sulfation capacities of limestone and hydrated lime slurries varied between 14.0-33.1 (mg SO₃/ml slurry) and 17.4-40.4 (mg SO₃/ml slurry), respectively. Regression analysis was used to relate the total sulfation capacity values to the CaCO₃ and Ca(OH)₂ contents of sorbents and linear empirical equations were developed.

1. Introduction

Flue gas desulfurization (FGD) processes are usually categorized as wet and dry or semi-dry systems. In wet FGD processes flue gas is contacted with a slurry consisting of a sorbent in an aqueous medium, such that the flue gas is cooled to the adiabatic saturation temperature. Whereas, dry and semi-dry FGD processes involve injection of a solid sorbent or a sorbent slurry into the furnace or flue gas duct. In wet FGD systems high degree of SO₂ removal is usually achieved with a high level of sorbent utilization (Berman et al., 2000; Song and Park, 2002; Warych and Szymanowski, 2002). However, dry or semi-dry FGD systems usually exhibit lower SO₂ removal efficiencies because of the short contact time between the flue gas and the sorbent (Ersoy-Meriçboyu, 1999). Thus, several wet FGD systems have been developed and are in commercial use, including a variety of scrubbing processes involving limestone or hydrated lime slurries (Ma et al., 2001; Ma et al., 2000).

The aim of the present study is to investigate the sulfation properties of the six different natural limestone and hydrated lime slurries. The effect of temperature, sorbent

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properties and the sorbent content of slurry on the total sulfation capacities of slurries was determined.

2. Materials And Methods

In the experiments six natural limestone samples originating from different localities of Turkey were used. Samples were initially crushed and sieved into a powder with a particle size of $< 250 \mu\text{m}$ and their chemical compositions were determined according to ASTM standards.

Sulfation experiments were performed in a glass reactor which has been immersed in a thermostated stirred water bath. Natural limestones and their hydrated limes were used as sorbents. Powdered sorbents were mixed with enough distilled water to achieve sorbent contents of 1% and 3% by weight. The slurries which were agitated at 700 rpm were sulfated at two different temperatures of 298 K and 323 K. During sulfation a synthetic gaseous mixture consisting of 5% O_2 , 10% CO_2 , 0.5% SO_2 and a balance of nitrogen by volume with a constant flow rate of 100 ml/min was fed into the reactor. The amount of SO_3 absorbed by the slurry during sulfation was determined by iodometric titration method. In this determination, 1 ml of sample was taken from the reactor every 1 hour and titrated with KI-KIO₃ solution using starch as an indicator.

3. Results And Discussion

Chemical composition of the limestone samples used in this study is given in Table 1. Total sulfation capacity results of the slurries prepared from different limestone and hydrated lime samples were summarized in Table 2.

It has been reported that the appropriate operation temperature for wet FGD system is 323 K (Kiil et al., 1998; Takashina et al., 2001). Therefore, all of the desulfurization reactions were performed at 323 K. However, in order to determine the effect of temperature on the desulfurization efficiency, some of the sulfation reactions were also carried out at 298 K (Table 2).

As can be seen from Table 2, for the sulfation temperature of 323 K the total sulfation capacities of the limestone slurries having sorbent content of 1% and 3% by weight changed between 14.0-17.3 (mg SO_3/ml slurry) and 29.6-33.1 (mg SO_3/ml slurry), respectively. On the other hand, the total sulfation capacities of the hydrated lime slurries having the sorbent content of 1% and 3% by weight were changed between 17.4-22.5 (mg SO_3/ml slurry) and 32.9-40.4 (mg SO_3/ml slurry), respectively.

Table 1. Chemical composition of limestone samples

Sample Code	CaO (%)	MgO (%)	SiO ₂ (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	Moisture (%)	Ignition Loss (%)
L1	53.78	0.54	0.68	0.10	0.25	0.08	44.24
L2	52.17	1.05	0.61	0.08	0.21	0.86	44.37
L3	37.45	4.65	12.64	3.54	6.70	0.48	32.71
L4	54.48	0.26	0.22	0.02	0.54	0.10	43.80
L5	54.08	0.76	0.02	0.10	1.20	0.04	43.68
L6	49.91	2.70	3.66	0.46	2.04	0.95	41.53

Table 2. Total sulfation capacities of slurries prepared from limestone and hydrated lime samples

Sample Code	Sorbent Content of Slurry (weight %)	Sulfation Temperature			
		323 K		298 K	
		Sulfation Time (h)	Total Sulfation Capacity (mg SO ₃ /ml slurry)	Sulfation Time (h)	Total Sulfation Capacity (mg SO ₃ /ml slurry)
L1	1	4	17.3	4	21.1
	3	6	33.1	6	48.3
L2	1	4	17.3	----	----
	3	6	31.4	----	----
L3	1	4	14.0	4	17.4
	3	6	29.6	6	39.5
L4	1	4	17.3	4	20.9
	3	6	32.8	6	50.9
L5	1	4	17.0	----	----
	3	6	32.6	----	----
L6	1	4	15.1	4	17.3
	3	6	31.0	6	41.0
HL1	1	4	20.6	4	24.4
	3	6	38.3	6	53.5
HL2	1	4	21.3	----	----
	3	6	37.8	----	----
HL3	1	4	17.4	4	18.7
	3	6	32.9	6	48.4
HL4	1	4	21.3	4	25.6
	3	6	40.3	6	55.7
HL5	1	4	22.5	----	----
	3	6	40.4	----	----
HL6	1	4	18.9	4	22.3
	3	6	35.1	6	52.7

It is known that the CaCO₃ and Ca(OH)₂ contents of sorbents play very important role in the total sulfation capacity values of their slurries. The rate of limestone dissolution depends on the slurry pH and the pH of the slurry is adjusted by the flow of dissolved Ca⁺² ions (Ma et al., 2001; Ma et al., 2000; Song and Park, 2002; Warych and Szymanowski, 2002). In this study, the total sulfation capacities of slurries, prepared from L1, L2, L4 and L5 limestones having the CaCO₃ content of 96.04, 93.16, 97.29 and 96.57%, respectively, were found to be higher than the slurries prepared from L3 and L6 limestones, having the CaCO₃ content of 66.34 and 89.13%, respectively. Similarly, the slurries prepared from HL1, HL2, HL4 and HL5 hydrated limes having the Ca(OH)₂ content of 80.77, 79.87, 88.27 and 85.07%, respectively, could remove more SO₂ than the slurries prepared from HL3 and HL6 hydrated limes having the Ca(OH)₂ content of 50.12 and 61.20%, respectively. These results clearly showed that, the increase of Ca⁺² ion concentration in the slurry resulting from the dissolution of the CaCO₃ and Ca(OH)₂ components of sorbents creates an improvement in the total SO₂ removal efficiency (Song and Park, 2002).

Similar results were also obtained for the sulfation experiments performed at 298 K. The total sulfation capacities of slurries prepared from L1, L4, HL1, HL4 samples were found to be higher than those for the slurries prepared from L3, L6, HL3 and HL6 samples (Table 2). The relation between the total sulfation capacities of slurries having the sorbent contents of 1% and 3% with the CaCO_3 and Ca(OH)_2 contents of limestone and hydrated lime sorbents are illustrated in Figures 1 and 2. The experimental results obtained for the sulfation reactions performed at 323 K clearly showed a strong dependence between the total sulfation capacities of slurries and CaCO_3 and Ca(OH)_2 content of the sorbents and following empirical equations were developed.

$$\text{TSC} = 22.787 + 0.101 \text{ CC} \quad (\text{Slurries with the limestone content of 3\%}) \quad (1)$$

$$\text{TSC} = 23.056 + 0.194 \text{ CH} \quad (\text{Slurries with the hydrated lime content of 3\%}) \quad (2)$$

$$\text{TSC} = 6.499 + 0.101 \text{ CC} \quad (\text{Slurries with the limestone content of 1\%}) \quad (3)$$

$$\text{TSC} = 11.634 + 0.117 \text{ CH} \quad (\text{Slurries with the hydrated lime content of 1\%}) \quad (4)$$

TSC : Total sulfation capacity ($\text{mg SO}_3^{-2}/\text{ml slurry}$)

CC : Calcium carbonate content of sorbent (%)

CH : Calcium hydroxide content of sorbent (%)

The correlation coefficients for Eqs. 1-4 were determined as 0.78, 0.97, 0.80 and 0.91, respectively. The regression analysis of experimental data clearly show that the relation between Ca(OH)_2 contents of hydrated limes and total sulfation capacities of hydrated lime slurries is stronger than the relation between CaCO_3 contents of limestones and total sulfation capacities of limestone slurries. This conclusion shows the significant impact of the sorbent type on the total sulfation capacities of slurries. As can be seen from Table 2, the total sulfation capacities of slurries are increased when the hydrated lime is used as sorbent material instead of limestone. It is known that, the hydrated lime possesses higher desulfurization capacity than limestone due to its higher solubility and higher alkalinity in slurry and better reactivity with SO_2 at low temperature (Ma et al., 2000; Özyüğüran et al., 2006).

The solubility of Ca(OH)_2 in water was determined 0.165% at 293 K, but the solubility of CaCO_3 was found 0.0014% at same temperature (Perry's Handbook, 1998). While the pH value of a fresh prepared limestone slurry is ranged usually between 8 and 9, this value is determined as 12 for hydrated lime slurry (Ahlbeck et al., 1993). It is well known that the increasing the alkalinity will increase dissolution rate of SO_2 and the rate of sulfation reaction, thus the total sulfation capacity increases. The main drawback for using hydrated lime as a sorbent in wet FGD system is the cost of lime which higher due to the calcination process. Therefore, when utilizing hydrated lime as a sorbent material the expenses for calcination, transportation, and slaking must be considered.

A mention earlier, another parameter which effects the total sulfation capacity is the sorbent content of slurry. This effect was also investigated in this study for the sulfation experiments conducted at two different temperatures of 298 K and 323 K. As expected, SO_2 removal efficiency increased with the increase in the sorbent content of slurries since more sorbent content means that more sorbent fed into the reactor for a given inlet SO_2 concentration in the flue gas. Besides, the increment of the sorbent content of slurry made the Ca^{+2} concentration higher in the slurries and this leads to an increase in the internal Ca/S ratio and in the solid-liquid interface area which creates an improvement in the efficiency of SO_2 removal.

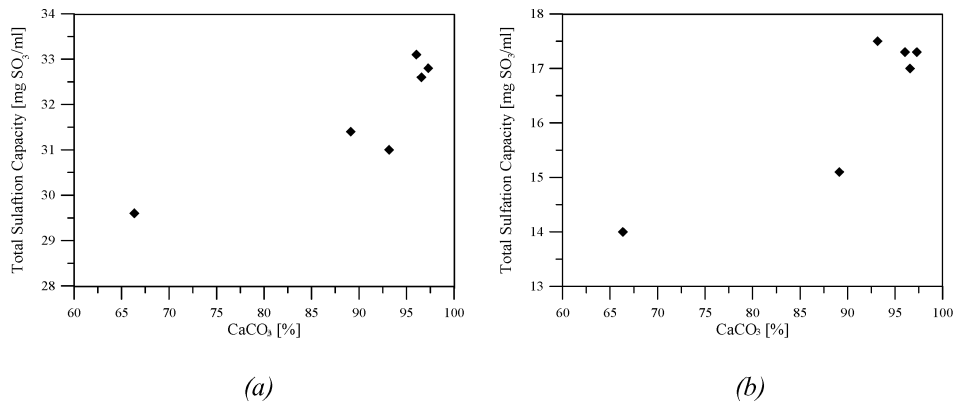


Figure 1. The relation between CaCO₃ content of limestones and the total sulfation capacities of slurries with a limestone content of a) 3%; b) 1%

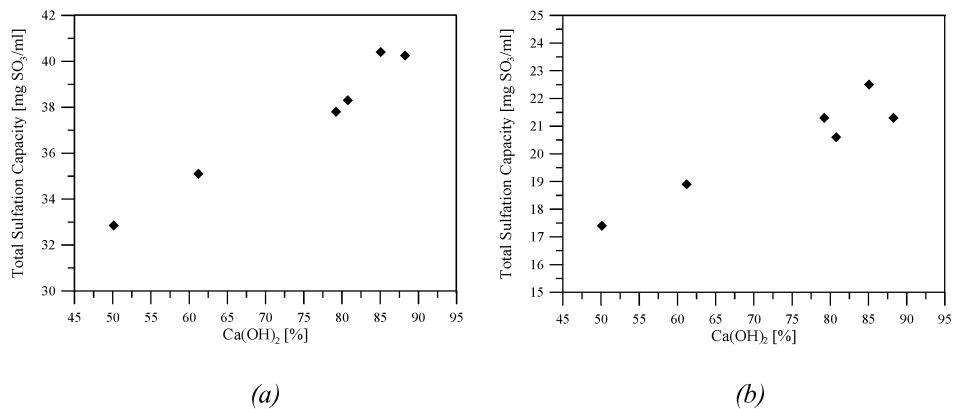


Figure 2. The relation between Ca(OH)₂ content of hydrated limes and the total sulfation capacities of slurries with hydrated lime content of a) 3%; b) 1%

During the sulfation reaction, one mole of CaCO₃ or Ca(OH)₂ react with one mole of SO₂, to form one mole of calcium sulfite dihydrate (CaSO₃·2H₂O). Thus, a 100% stoichiometric limestone or hydrated lime requirement means one mole of CaCO₃ or Ca(OH)₂ for each mole of SO₂ feed. The 150% stoichiometric requirement means 1.5 mole of CaCO₃ or Ca(OH)₂ for each mole of SO₂ feed. Theoretically, higher the stoichiometry, higher the SO₂ absorption. However, it is clearly seen from Table 2 that, although the amount of sorbent in slurry was tripled, total sulfation capacities of slurries did not increase at the same ratio due to the effects of other parameters. This is in agreement with the previously reported studies in literature (Berman et al., 2000; Song and Park, 2002; Takashina et al., 2001).

The experimental data listed in Table 2 indicate that the total sulfation capacities of all slurries are shifted to higher values as the sulfation temperature decreased from 323 K to 298 K. The effect of temperature on the desulfurization efficiency of wet FGD systems depends on how all reactions in the scrubber are affected by the temperature changes. In previous studies (Kiil et al., 1998), it has been reported that the solubilities of calcium carbonate, calcium hydroxide and sulfur dioxide changes depending on the temperature and this phenomena effects the desulfurization efficiency. The solubility of SO₂ in water decreases with increasing temperature; besides, Ca(OH)₂ is rather

insoluble and unlike most soluble metallic hydroxides, its solubility decreases as the temperature increases; on the other hand, CaCO_3 is quite insoluble and its solubility increases only slightly as the temperature is increases (CRC Handbook, 2001).

4. Conclusions

The present study has shown that the total sulfation capacities of limestone and hydrated lime slurries were changed depending on origin and chemical composition of limestones and their hydrated limes. Strong dependence between the total sulfation capacities of slurries and CaCO_3 and Ca(OH)_2 content of sorbents were observed. The total sulfation capacities of all slurries were shifted to higher values as the sorbent content of slurries increases. The SO_2 removal efficiencies of slurries were increased as the sulfation temperature decreased from 323 K to 298 K. Depending on sulfation conditions and the sorbent properties, the total sulfation capacities of limestone and hydrated lime slurries varied between 14.0-33.1 (mg SO_3 /ml slurry) and 17.4-40.4 (mg SO_3 /ml slurry), respectively.

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