

Effect of Magnesium and Calcium Salts on the Sulfation Capacity of Trona Slurry

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The sulfation experiments of the slurries prepared by using natural trona ($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$) originating from the Beypazarı-Ankara region of Turkey were performed at different conditions. A statistical design technique was applied by the use of a two-level factorial design matrix to interpret experimental results. Sulfation conditions were selected according to a two-level factorial design matrix considering the following variables: sulfation time (3 and 7 h), sorbent content of slurry (1 % and 3 %) and sulfation temperature (298 and 323 K). It was found that the sorbent content of slurry has the strongest effect on the total sulfation capacity in comparison with sulfation time and temperature. The effects of different magnesium and calcium salts on the total sulfation capacities of trona slurries were also investigated. The total sulfation capacities of slurries were increased from 11.45 to 33.00 (mg SO_3 /mL slurry) and from 21.25 to 25.80 (mg SO_3 /mL slurry) with the addition of magnesium and calcium salts, respectively.

1. Introduction

The processes that can be applied to remove sulfur oxides from the flue gases are classified as wet and dry processes. In wet systems different slurries are used to absorb sulfur oxides present in flue gases; however, in dry systems adsorption occurs on the surface of sorbent particles. Wet methods are more commonly used in the industry due to their high (95%) desulfurization efficiency (Bandyopadhyay and Biswas, 2008; Dou et al., 2009; Gomez et al., 2007; Kallinikos et al., 2010).

In wet flue gas desulfurization (FGD) processes, sulfur dioxide removal efficiency depends on the reagent concentration of the scrubber loop. Therefore wet processes are modified by changing composition of the scrubbing liquor in order to increase the efficiency of absorption, the utilization of sorbent and the operating effectiveness of the FGD system as a whole (Chang et al., 1986; Frandsen et al., 2001; Glomba, 2010; Souza et al., 2010; Ukawa et al., 1993).

In this study, the effects of sulfation conditions such as sulfation time, sorbent content of slurry and sulfation temperature and also the effects of different magnesium and calcium salts on the total sulfation capacities of trona slurries were determined.

2. Materials and Methods

Trona sample used in the experiments was initially crushed and sieved into a powder with a particle size of $<250 \mu\text{m}$. According to ASTM standards, the chemical composition of trona was determined as 45.91 wt% Na_2CO_3 , 37.85 wt% NaHCO_3 , 0.185 wt% SiO_2 and 15.37 wt% moisture.

Sulfation experiments were performed in a glass reactor which has been immersed in a thermostated stirred water bath. Powdered sorbent was added to 300 mL distilled water in different amounts to achieve sorbent contents of 1 % and 3 % by weight. The experimental conditions were selected according to a two-level factorial design matrix considering sulfation time (3 and 7 h), sorbent content of slurry (1 % and 3 %) and sulfation temperature (298 and 323 K) as variables. In order to investigate the effects of different magnesium and calcium salts on the total sulfation capacities of trona slurries, MgO , $\text{Mg}(\text{OH})_2$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, CaO , CaCO_3 and $\text{Ca}(\text{OH})_2$ were used as additives. 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 h and titrated with KI-KIO₃ solution using starch as an indicator.

3. Results and Discussion

3.1 Effect of sulfation conditions on the sulfation capacities of slurries

Total sulfation capacity results of the slurries obtained at different conditions were summarized in Table 1.

Table 1: Total sulfation capacities of slurries obtained at different conditions

Sorbent content of slurry (weight %)	Sulfation temperature (K)	Sulfation time (h)	Total sulfation capacity (mg SO_3 /mL slurry)
1	298	3	10.05
		7	10.85
	323	3	10.25
		7	10.75
3	298	3	16.26
		7	28.70
	323	3	14.00
		7	28.00

As can be seen from Table 1, the sulfation reactions of the slurries having sorbent content of 1 % at the temperatures of 298 and 323 K were completed in 3 h and total sulfation capacities of slurries were determined as 10.85 and 10.75 (mg SO_3 /mL slurry), respectively. On the other hand, for the slurries having the sorbent content of 3 %, the sulfation reactions of slurries performed at 298 and 323 K were completed in 7 h and

the total sulfation capacities of slurries were reached to 28.70 and 28.00 (mg SO₃/mL slurry), respectively.

Interpretation of the experimental results given in Table 1 was achieved according to 2³ factorial design technique by considering sorbent content of slurry, temperature and time as variables. The actual and coded values of these variables were given in Table 2.

Table 2: Actual and coded values of the variables

Level	Upper Level	Lower Level	Base Level
a ₁ (C)	3	1	2
Sorbent content of slurry (%)			
X ₁	+1	-1	0
Coded			
a ₂ (T)	323	298	310.5
Temperature (K)			
X ₂	+1	-1	0
Coded			
a ₃ (t)	7	3	5
Time (h)			
X ₃	+1	-1	0
Coded			

The regression equation used to estimate the sulfation capacities of the slurries and comprehend the effects of experimental variables and their interactions on the sulfation capacities is a multi-factor linear model of the following type:

$$Y = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_4X_1X_2 + A_5X_1X_3 + A_6X_2X_3 + A_7X_1X_2X_3 \quad (1)$$

The design matrix and results of experiments were listed in Table 3.

Table 3: Design matrix and results of experiments

Trial No	X ₁	X ₂	X ₃	Total sulfation capacity (mg SO ₃ /mL slurry)
1	-1	-1	-1	10.05
2	-1	-1	1	10.85
3	-1	1	-1	10.25
4	-1	1	1	10.75
5	1	-1	-1	16.26
6	1	-1	1	28.70
7	1	1	-1	14.00
8	1	1	1	28.00

The results given in Table 3 were analyzed statistically to identify and measure the main and interactional effects quantitatively by using analysis of variance which is the most effective technique in factorially designed experiments. The variance test of the parameters for the trona sample showed that some of the variables are not statistically significant. Therefore, their respective terms are not included in the following regression equation:

$$Y = 16.1075 + 5.6325X_1 + 3.4675X_3 + 3.1425X_1X_3 \quad (\text{mg SO}_3/\text{mL slurry}) \quad (2)$$

The correlation coefficient for equation 2 was determined 0.993 and the mean difference between calculated and experimental data was found to be 1.0%. The relationship between the coded values (X_k) and actual values (a_k) can be given as follows:

$$X_1 = (a_1 - 2) \quad \text{or} \quad X_1 = (C - 2) \quad (3)$$

$$X_2 = (a_2 - 310.5) / 12.5 \quad \text{or} \quad X_2 = (T - 310.5) / 12.5 \quad (4)$$

$$X_3 = (a_3 - 5) / 2 \quad \text{or} \quad X_3 = (t - 5) / 2 \quad (5)$$

where C is the sorbent content of slurry (%), T is the temperature (K) and t is the time (h).

The regression equation (Eq. 2) clearly shows that since the coefficient of sorbent content of slurries is the highest among all the variables, the effect of this variables on the sulfation capacities of slurries is the strongest. As expected, SO₂ 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 SO₂ concentration in the flue gas. Besides, the increment of the sorbent content of slurry made the Na⁺ concentration higher in slurries and this leads to an increase in the internal Na/S ratio and in the solid-liquid interface area which creates an improvement in the efficiency of SO₂ removal.

During the sulfation reaction, one mole of trona react with two mole of SO₂. Therefore, the stoichiometric sorbent requirement means one mole of trona for two of SO₂ feed. Theoretically, higher the stoichiometry, higher the SO₂ absorption. However, it is clearly seen from Table 1 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 (Dou et al., 2009; Glomba, 2010; Özyüğüran et al. 2006).

The sulfation capacity of slurries were also increased with increasing sulfation time. However, the effect of this variable on the sulfation capacity of slurries is less than that of the sorbent content of slurries. The increments observed in the sulfation capacities of slurries depending on sulfation time were found remarkably higher for the slurries having the sorbent content of 3%. These results clearly show that the higher the sorbent content of the slurry makes the sulfation time longer.

It can be seen from Equation 2, that sulfation capacities of the slurries were also influenced from the interactional effect of sorbent content of slurry and sulfation time (X_1X_3). In other words, if one of the variables is changed with respect to another one, it will have a considerable effect on the total sulfation capacity of slurries.

It has been reported that the appropriate operation temperature for wet FGD system is 323 K (Takashina et al., 2001; Zhong et al., 2008). Therefore, all of the desulfurization reactions were performed at 323 K. In order to determine the effect of temperature on the desulfurization efficiency, the sulfation reactions were also carried out at 298 K (Table 1). The results given in Table 1 clearly showed that the total sulfation capacities of the slurries having sorbent content of 1 % and 3 % are not changed with the temperature. Therefore, any term relating with this variable was not included in the regression equation.

3.2 Effect of calcium and magnesium salts on the sulfation capacities of slurries

Sulfation reactions that performed to determine the effect of magnesium and calcium salts on the total sulfation capacity were carried out at 298 K for the trona slurries having the sorbent content of 1 % by weight. At the first step, optimum ion concentration was determined by using MgO as an additive. The sulfation capacities of the slurries having 1000, 2000, 3000, 4000 and 5000 ppm Mg^{+2} ion concentration were determined as 15.05, 20.50, 26.70, 33.00 and 33.90 (mg SO_3 /mL slurry). Since, the total sulfation capacity of the slurry having Mg^{+2} ion concentration of 4000 ppm was nearly the same to the slurry that has 5000 ppm Mg^{+2} ion concentration, optimum value for the ion concentration in the slurry was accepted as 4000 ppm.

In order to investigate the effect of different magnesium and calcium salts on sulfation properties of trona slurry, MgO, $Mg(OH)_2$, $MgSO_4 \cdot 7H_2O$, CaO, $CaCO_3$ and $Ca(OH)_2$ were used as additives. The total sulfation capacities of the slurries having these additives with an ion concentration of 4000 ppm were given in Table 4. As can be seen from the results given in Table 4, total sulfation capacity of slurry increased with the addition of MgO and $Mg(OH)_2$ salts, but $MgSO_4 \cdot 7H_2O$ addition caused only a minor increase in the total sulfation capacity of slurry. While total sulfation capacity of slurry reached to the value of 10.85 (mg SO_3 /mL slurry), this value was determined as 33.00, 32.10, 11.45 (mg SO_3 /mL slurry) for the slurries prepared by the addition of MgO, $Mg(OH)_2$, $MgSO_4 \cdot 7H_2O$, respectively. These results clearly show that presence of SO_4^{-4} ion in the slurry resulting by dissolution of $MgSO_4 \cdot 7H_2O$ salt cause a decrease in solubility of SO_3^{-2} ion due to ion pair interaction.

Table 4: The total sulfation capacities of slurries having different additives

	MgO (%)	$Mg(OH)_2$ (%)	$MgSO_4 \cdot 7H_2O$ (%)	CaO (%)	$CaCO_3$ (%)	$Ca(OH)_2$ (%)
Total sulfation capacity (mg SO_3 /mL slurry)	33.00	32.10	11.45	25.30	21.25	25.80

When soluble MgO and $Mg(OH)_2$ salts are added to solution, Mg^{+} ion accumulates in solution reacts with SO_2 and forms high soluble $MgSO_3$. The formation of $MgSO_3$ in solution increases both dissolved alkalinity and total sulfation capacity of solution.

From Table 4, it can be seen that the addition of CaO, $CaCO_3$ and $Ca(OH)_2$ salts to the slurries has caused nearly the same increase in the sulfation capacities. Sulfation capacity values were determined as 25.30, 25.80, 21.25 (mg SO_3 /mL slurry) for the slurries prepared by the addition of CaO, $Ca(OH)_2$, $CaCO_3$, respectively. These results clearly showed that, the increase of Ca^{+2} ion concentration in the slurry resulting from the dissolution of the calcium salts also creates an improvement in the total SO_2 removal efficiency. But, the increments observed in the total sulfation capacity values by the addition of MgO and $Mg(OH)_2$ salts were found to be higher than the values obtained by the addition of CaO, $Ca(OH)_2$ and $CaCO_3$ salts. This result clearly indicates that MgO and $Mg(OH)_2$ are the best additives that can be used to improve the desulfurization efficiency of trona slurries.

4. Conclusions

The total sulfation capacities of trona slurries were changed depending on sulfation conditions. Statistical evaluation of the experimental results clearly showed that the effect of sorbent content on the sulfation capacities of slurries is the strongest. The total sulfation capacity values by the addition of MgO and Mg(OH)₂ salts were found to be higher than the values obtained by the addition of CaO, Ca(OH)₂ and CaCO₃ salts. The results of this study clearly indicated that MgO and Mg(OH)₂ are the best additives that can be used to improve the desulfurization efficiency of trona slurries.

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