

REMOVAL OF SULPHUR DURING COMBUSTION OF COAL BY USING LIME

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ABSTRACT

Environmental pollution has become one of the main problems of the world. Air pollution is considered to be one of the main components of this problem. Sulphur dioxide (SO₂) that usually emits into air out of burning of fossil fuels is the most important air pollutant. Filtering the emission of SO₂ is generally accepted as the most effective method for preventing air pollution.

In this study, an alternative technique was applied to coal with high sulphur content in order to prevent the emission of SO₂. Main principle of the method is based on adding a calcinated limestone (CaO) to the coal during combustion. The experiments were carried out with Çan coal mined from the north-west of Turkey. The coal was broken into small particles of <710 µm in diameter. Two different limestone samples (labeled as LS1 and LS2) with the size of <700 µm in diameter were calcinated at 900-950 °C for 180 min. Then, 0.25, 0.50, 0.75, 1.00 and 1.50 g of calcinated limestone samples were well mixed with 5 g of coal. Combustion processes were performed in a fixed batch oven at 850 and 900 °C for 120 and 180 min.

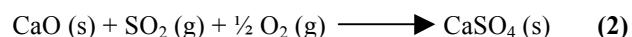
It was found that desulphurization of coal strongly depends on the amount of added limestone and its size, combustion time and temperature.

KEYWORDS: Coal combustion, limestone, desulphurization, calcinated limestone

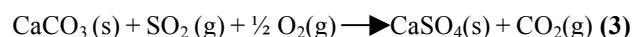
INTRODUCTION

80% of sulphur dioxide emissions into the air comes from fossil fuels [1]. SO₂ is one of the most important air pollutants generated by coal-fired plants, and its emission is commonly accepted as a major contribution to acid rain [2]. Sulphur dioxide released from the stacks as a result of combustion of fossil fuels causes a very serious threat to human and environmental health. Therefore, besides inves-

tigation of clean, renewable energy sources, the studies to develop a low-cost, retrofit technology for control of SO₂ emissions have been going on [3, 4]. An inexpensive way to control SO₂ emission is to use calcium-based agents, such as CaO or limestone, as the adsorbents. Use of natural limestones as sorbents is currently being investigated by a number of researchers with a view of optimizing the conditions of desulphurization. Among various kinds of desulphurization technologies, sulphur removal in furnaces by using limestone is competitive for controlling the SO₂ pollutants derived from coal combustion, due to the low capital and operating costs [5]. Sulphur retention by dry limestone under conditions of combustion has traditionally been described by two consecutive reactions [6]:



Under oxidizing conditions, limestone, at first, calcinates to porous lime, which then quickly captures SO₂ in the flue gas and forms gypsum. Since the gypsum molar volume is greater than that of lime, its existence on the surface of lime blocks the porosity of lime [7]. By increasing the particle size of the sorbent, main resistance to the reaction changes from pore diffusion and surface reaction to diffusion through the CaSO₄ layer formed on the particle surface of the sorbent [8]. From a thermodynamic standpoint, CaO or CaCO₃ can react with sulphur oxides in the temperature range 800-950 °C [2, 9, 10]. It is generally assumed in the literature that the reactions taking place are given with Eqs. 2 and 3 for calcined and uncalcined limestone, respectively.



The reactivity of the sorbent and composition of the final product depend on a large variety of factors, e.g. the combustion temperature, sorbent-gas contact time, limestone type, impurities contained in the coal and sorbent, sorbent pore size, etc [9]. Therefore, it is important to optimize the system to prevent emission of sulphur dioxide more efficiently at lower cost.

Lignites can have varying combustion properties depending on inorganic components and sulphur content. Çan coal, with a high inorganic component and sulphur

content is commonly used in the western of Turkey for space heating and thermal power plants. It is, therefore, important to know the efficiency of using lime in the removal of sulphur during combustion.

There are many studies on desulphurization during coal combustion. Many of them are about desulphurization in the flue gas. It is possible to reach high desulphurization rates by adding limestone to coal during combustion. Calcinations of the limestone before addition to coal produce a higher desulphurization percentage.

In this study, removal of SO₂ in the flue gas formed during the combustion of Çan coal, a Turkish coal with high sulphur content, has been studied as a function of the amount of added limestone, combustion time, combustion temperature and size of the limestone.

MATERIALS AND METHODS

Çan coal (named after the city Çan, located in the northwestern region of Turkey) was used in the experi-

ments. The Çan coal was supplied by Kale Mining Corp. The coal was dried in air, ground and sieved to obtain a fraction size of <710 µm. Moisture of the limestone and coal were removed by heating them in an oven at 110 °C for 180 min prior to the experiments.

Results of the proximate analysis of the coal are given in Table 1. These analyses were performed according to the ASTM Standards (D-5142, D-4239 and D-5865) [11].

Chemical compositions of the limestone samples, which are the adsorbent for SO₂, are given in Table 2

In the combustion experiments, 5 g of coal sample was mixed with lime obtained by calcining the limestone at 900 °C for 3 h at desired ratio. The mixture was combusted at 850 and 900 °C for 120 and 180 min, respectively, in an oven by using a batch combustion system (a Nuve MF-140 furnace). Total residual sulphur analysis was carried out according to Eschka method [12]. Parameter values used in this study are given in Table 3.

TABLE 1 - Proximate analysis of Çan coal used in the study.

Moisture content (%)	Ash content (%)	Sulphur content (%)	Lower Heating Value (kcal/kg)
20.46	33.29	3.74	3636

TABLE 2 - Chemical analysis of limestone samples (%).

Limestone	LOI	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O
LS1	42.62	1.05	0.15	0.01	0.17	54.06	1.96	0.15	0.02
LS2	42.87	0.23	0.11	0.01	0.08	54.04	2.71	0.15	0.01

LOI: Loss of ignition; LS1: Limestone 1, LS2: Limestone 2

TABLE 3 - Parameters and their chosen values in the study.

Limestone samples	1, 2
Ratio of lime amount to 5 g of coal	0.25, 0.50, 0.75, 1.00, 1.50
Time (min)	120, 180
Temperature (°C)	850, 900
Particle size fractions of limestone (µm)	<32; 45-65; 75-106; 150-250; 300-500; 500-700

RESULTS AND DISCUSSION

The effects of amount of lime mixed with 5 g of coal on sulphur removal percentage (SRP) as a function of its type and size along with the combustion time and temperature are shown in Figs. 1-4. As seen in Fig. 1, SRP increased as the lime proportion in coal increased. Although the amount of lime that is stoichiometrically enough to react with the whole amount of sulphur is about 0.21 g in the coal sample, SO₂ could not be absorbed completely, even at the

ratio of 1.5 g lime/5 g coal [13]. The main problem associated with the usage of limestone in a desulphurization process is the low efficiency of reaction [14]. This can be explained in terms of sulphation process by considering pore plugging of the lime by CaSO₃ and/or CaSO₄. Since CaO is converted into CaSO₃ and/or CaSO₄ during this reaction, the molar volume of CaSO₄ happens out to be approximately 3 times greater than that of CaO [3], which turns in a swelling of CaO grains due to sulphation. As a result, pore plugging and loss of porosity at the outer edge

of lime particles occurs. This layer of product acts as a barrier for diffusion of reactant gases (SO_2 and O_2) onto the reactant surface. Covering of the surface of the coal particles with CaSO_4 and plugging the pores renders the reaction of SO_2 and O_2 difficult. In that case, SO_2 leaves the surface without participating to the reaction, and most CaO remains unreacted.

On the other hand, although the sulphur removal percents (SRP) are almost the same at low amount of lime for both types of calcined limestone samples (LS1 and LS2), they happen out to be different when the amount of lime increases as seen in Fig. 1. The lime with different surface area and porosity results in different calcinations. The rate of sulphation reaction could be different, even for limestone samples which have a similar chemical composition. The presence of ions with different oxidation states from Ca^{+2} like Li^+ , Na^+ , Cr^{3+} enhances the sulphation capacity, and hence the rate[15].

The effect of ignition time, representing that time required for the diffusion of O_2 onto the unreacted CaO surface through CaSO_4 film, on the removal percentages of sulphur is shown in Fig. 2 at two different temperatures

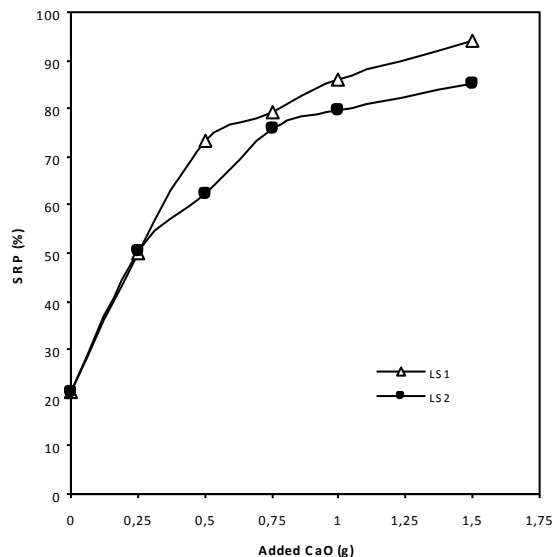
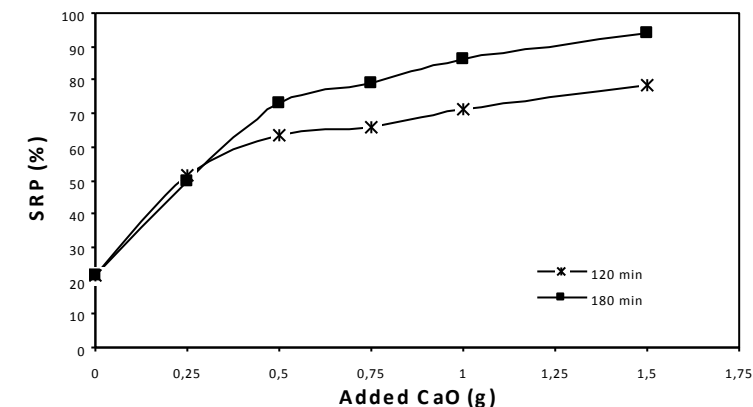
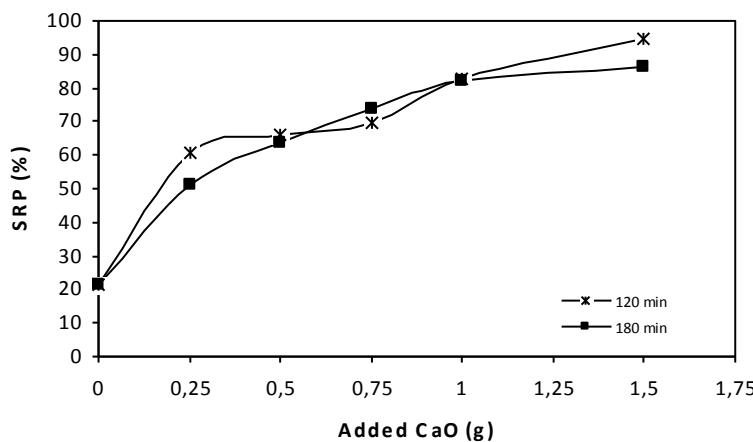


FIGURE 1 - The plots of sulphur removal percentage (SRP) versus CaO amount for 2 limestone samples (850 °C, time: 180 min).



(a)



(b)

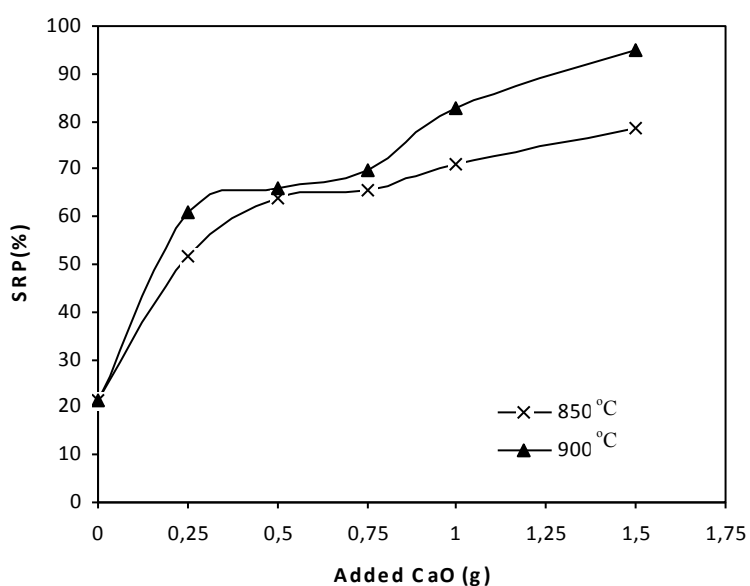
FIGURE 2 - The effect of combustion time on sulphur removal percent (SRP) for limestone 1(850°C (a); 900°C (b)).

(850 and 900 °C). As seen in Fig. 2 (a), removal percentages of sulphur increased as ignition time increased when the experiment was carried out at 850 °C. However, only a slight increase of SRP was observed for the experiments performed at 900 °C.

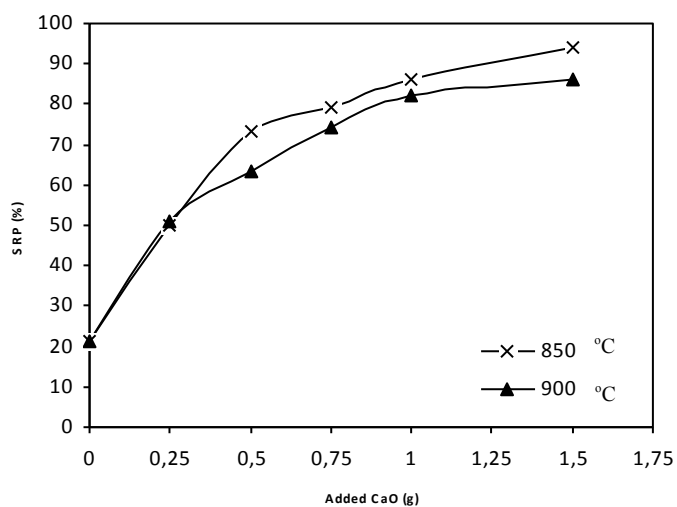
Temperature is one of the most important parameters in the desulphurization process when limestone samples are used. Since the rate of sulphation reaction is controlled by diffusion processes through product layer, the effectiveness of diffusivity enhances as the temperature increases. For this reason, these removal percentages of sulphur were observed to increase with temperature as seen in Fig. 3. The increase in desulphurization rate is a result of the in-

crease in effective diffusivity with temperature because the structure of the product layer becomes more loose and open for entering the reactant gas [16]. It is suggested that, for the direct sulphation of limestone, the temperature effects on the effective diffusivity should be considered to be indicative not for the effect of temperature on the diffusion process, but rather for the effect of temperature on the structure of the product layer [17].

The particular size of the limestone also affected the removal percentage of sulphur [10]. As shown in Fig. 4, the sulphation reaction rate strongly depends on sorbent particle size. By increasing the particle size of the sorbent, main resistance to the reaction changes from pore diffusion and



(a)



(b)

FIGURE 3 - The effect of combustion temperature on sulphur removal percent (SRP) for limestone 1 (time: 120 min (a); time: 180 min (b)).

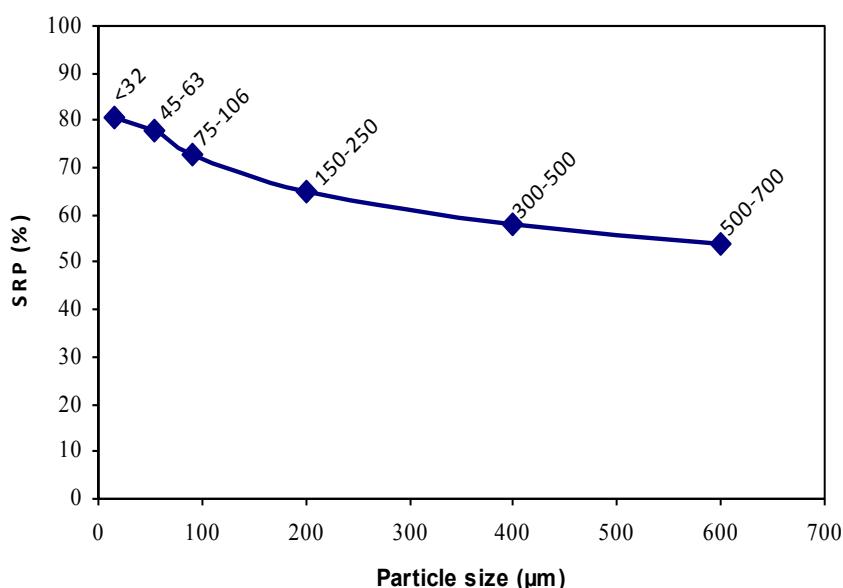


FIGURE 4 - The effect of particle size on sulphur removal percent (SRP) for limestone 1(temp: 900°C; time: 120 min; CaO/Coal: 1g/5g).

surface reaction to diffusion through the CaSO_4 product layer formed on the particle surface. Consequently, the CaSO_4 layer causes pore blockage, which prevents sulphation of the inner parts of the particles, diminishing the maximum conversion of sorbents [16].

Sulphur removal percents increase with the amount of calcinated limestone added to coal. However, addition of this excess CaO results in reducing the amount of heat released during combustion of coal. Therefore, the coal particles cannot react with oxygen sufficiently causing excessive CO emission [18].

Efficiency of the method used for removal of sulphur can vary according to combustion conditions, such as distribution of particle size of coal, combustion temperature and content of limestone etc. In this study, the fixed batch combustion method has been used as model system, and the results obtained will shed a light to the real combustion conditions.

CONCLUSIONS

The results of the study can be summarized as follows:

- Addition of CaO to coal reduces the sulphur release by 96%.
- Different limestone samples have different adsorption amounts of SO_2 .
- Amount of CaO added to coal plays an important role in desulphurization.
- Higher rate of desulphurization of coal by adding CaO can be achieved at a high temperature in a short time.

- Particle size of CaO should also be considered to increase desulphurization percentages - the smaller, the better.
- Inclusion of additional CaO reduces the amount of heat released during combustion of coal.

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