

## USE OF MARBLE WASTES AGAINST POLLUTION

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### ABSTRACT

Marble wastes are produced in two different forms in size. One type of the marble wastes is in lump size and easily be evaluated in civil industry and other construction works. The other type of the wastes is in fine particle size and may even deteriorate environment, in particular, agricultural fields near cities. Both types of marble wastes are mainly the by-products of marble processing plants in the country. Beneficiation from these wastes is significantly important for the economy of country. Fine marble wastes may be considered as lime raw materials without calcining by the local lime consumers and may be used as lime in various industrial sectors such as rubber, paper, animal food productions. Another use of marble wastes can be air pollution control and holding up toxic gases in chemical plants.

### 1. INTRODUCTION

Desulfurization of coal has firstly applied for the flue gas in coke production and in fluidized bed combustion systems after coal burning. In recent, the desulfurization methods have significantly been progressed by founded the desulfurization plants in thermal power stations. However, small scale operation of desulfurization plants can not be practical. Solid basic filters, especially using marble waste developed for sulfur dioxide holdup, may be economical in small scale burning systems. In this study, few types of solid basic filters were used in cold medium following the combustion of coal samples and at different burning temperatures in the combustion chamber. Finally, the effects of variables on emission as the percentages of sulfur dioxide holdup were determined.

Burning of high sulfur coals in our country has recently created great sensational contemplation in the society due to environmental concern. In particular, for the recent example of Istanbul, sulfur dioxide amount locally reaching over 400 mg has reflected the importance of this issue for environment.

In the world, the coals containing a total sulfur over 3% are characterised as high sulfur coals, those with a total sulfur content between 1% and 3% are named medium sulfur coals and the coals comprised the sulfur below 1% are called as low sulfur coals. In our country, most of the coals used are high and medium sulfur coals. These types of coals should either be burned in succession to washing, or the sulfur contents of coals should be hold as sulfur dioxide in the burning system.

Holdup of sulfur dioxide gas in the burning systems after coal burning is certainly necessary for the systems using high or medium sulfur coals[1]. On this purpose, several chemical absorbents for sulfur dioxide gas can be used in liquid form or solid form. The absorbents such as ammonia, caustic liquids and solid basic filters such as salt and lime may be used in the desulfurization after coal burning.

Sulfur dioxide hold-up can be easily managed by fine marble wastes without any process requirements and even the used marble waste in the sulfur dioxide hold-up may be a good cement raw material and has thereby been used secondly in another sector.

In this study, the chemical compositions of some marble wastes were researched for suitability on sulfur dioxide hold-up and percentages of sulfur dioxide emission reductions were determined and commented. The economical considerations were also defined. The optimum desulfurization method using marble wastes were introduced. The desulfurization of a type of high sulfur Turkish coal, Sivas-Gemerek coal after coal burning was investigated by means of the varied solid basic filters in terms of reduction of sulfur dioxide emission.

## 2. GENERAL DATA

Coal with a sophisticated chemical structure comprised basically two different types of sulfur[2]. One is inorganic sulfur in the forms of pyritic sulfur, sulfate sulfur and elemental sulfur. The other is organic sulfur. In coal burning, these sulfur components of coal are oxidised and burned together with the coal. A certain part of sulfur content of coal remains in the ash in the forms of sulphate and sulfide. The other part of sulfur content evolved as sulfur dioxide into the atmosphere. The environmental issues such as acidic rains and pollution raise up due to the high amount of sulfur dioxide emissions in extensively industrialised regions. The reduction of sulfur content of coal may eliminate the vital issue in the beginning.

The methods used in coal desulfurization are given in Table 1. The washing methods such as gravity separation, flotation and column flotation of coal can not be effective in total sulfur reduction[3,4]. Even the chemical and biological methods such as caustic, acid leaching and bioleaching of coal may not be economical in coal processing.

During the combustion of coal or following the combustion great amount of sulfur content of coal may be absorbed by liquid or solid reagents. The desulfurization systems previously founded in coking plants have been operated with ammonia or soda and  $H_2S$  scrubbed in the columns[5]. However, ammonia and caustic soda may also be used for absorption of  $SO_2$  instead of  $H_2S$ . Some regenerable basic materials such as soda, lime slurries and lime in solid filter form may be used as absorbents[6]. However, sodium content of soda has caused important fouling problems in the boilers and burning systems. Hence use of soda in combustion desulfurization is limited.

Pulverised lime injection in combustion chamber has significantly reduced sulfur dioxide emission during coal burning. Solid basic filters have recently been developed for desulfurization of coal during coal burning or after coal burning in combustion chamber. In this process, certain filter forms of solid basic reagents such as lime and magnesite can absorb sulfur dioxide during combustion. In fuel bed combustion, suspension firing and cyclone firing systems except fluidized bed combustion systems, solid basic filters may be easily operated. However, the filters should be changed in certain cycles of coal burning.

Table 1. Various methods used in desulfurization.

Type of Methods	Methods
Physical	Gravity Separation
	Magnetic Separation
	Electrostatic Separation
	Flotation
	Column Flotation
Chemical	Chemical communiton
	Acid leaching
	Caustic leaching
	Oxygen leaching
Biological	Biobleaching
	Bio-surface oxidation
	Bio-flotation
	Bio-column flotation
Stack Gas Desulfurization	Fluidized Bed Combustion
	Pulverized Lime Injection
	Ammonia, Caustic Soda
	Lime Slurries

Table 2. Proximate analysis of the coal.

Ash, % (dry)	19.5
Moisture, % (hygroscopic)	17.4
Flue matter, %	49.5
Carbon matter, %	50.5
Total Sulfur, %	5.5
Pyritic Sulfur, %	3.7
Sulfur in Ash, %	2.1
Calorific Value, kcal/kg	4140

### 3. MATERIALS AND METHOD

In this research, a high sulfur type of Turkish coal, Sivas-Gemerek coal represently taken from highly pyritic coal seams in the deposits, was used. The proximate analysis of the coal used in the experiments are given in Table 2. The coal samples were ground to a suitable size, minus 0.600 mm, for easily combustion of coal in the laboratory scale muffle furnace.

Firstly, calcium hydroxide pellets were produced in different particle size fractions and put into a filter form. The effect of amount of calcium hydroxide pellets in the filter on sulfur dioxide holdup was investigated. For this aim, 0.6 g, 0.8 g, 1.0 g, 1.5 g and 2 g calcium hydroxide pellets were subsequently put on the sieve located on the ceramic crucible in the muffle furnace as shown in Figure 1. In each experiment 3 gr coal sample burned. Temperature of furnace was kept at 800°C. The results are shown in Figure 2.

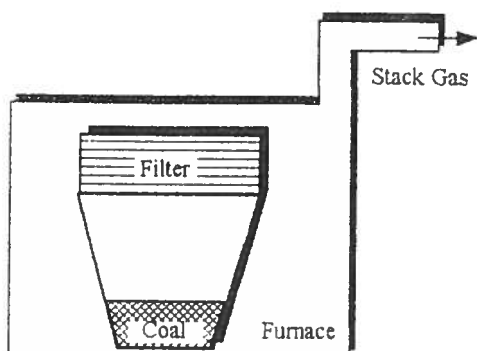


Figure 1 Experimental apparatus for coal.

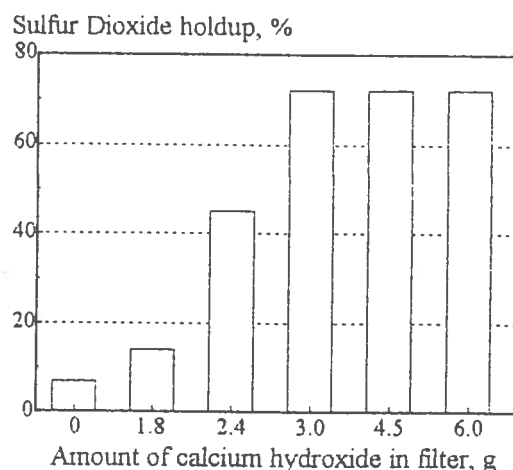


Figure 2. Effect of weight ratio of  $\text{Ca}(\text{OH})_2$  filter to coal on  $\text{SO}_2$  holdup.

Secondly, the effect of particle size fractions of calcium hydroxide pellets in the filter on reduction of sulfur dioxide emission was determined. In these tests,  $-4.25+2.80\text{mm}$ ,  $-2.80+1.70\text{mm}$ ,  $-1.70+0.85\text{mm}$ ,  $-0.85+0.60\text{mm}$ ,  $-0.60\text{mm}$  size fractions of pellets were subsequently experimented with a certain amount of pellet, 3 g. The experiments were carried out at  $800^\circ\text{C}$  and with 3 g coal sample. The results are illustrated in Figure 3.

Further, the effect of burning temperature on the sulfur dioxide holdup of filter was ascertained. The burning temperatures of  $500^\circ\text{C}$ ,  $600^\circ\text{C}$ ,  $700^\circ\text{C}$ ,  $800^\circ\text{C}$  and  $900^\circ\text{C}$  were subsequently tested on 3 g calcium hydroxide pellets in a size fraction of  $-0.600\text{mm}$  with burning 3 g coal samples. The results are shown in Figure 4.

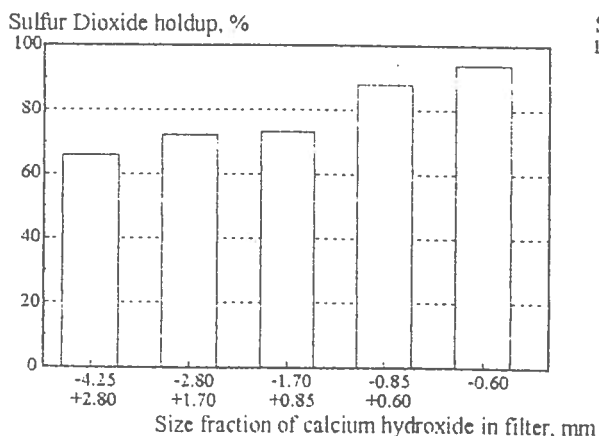


Figure 3 Effect of particle size fractions of  $\text{Ca}(\text{OH})_2$  pellets in the filter on holdup.

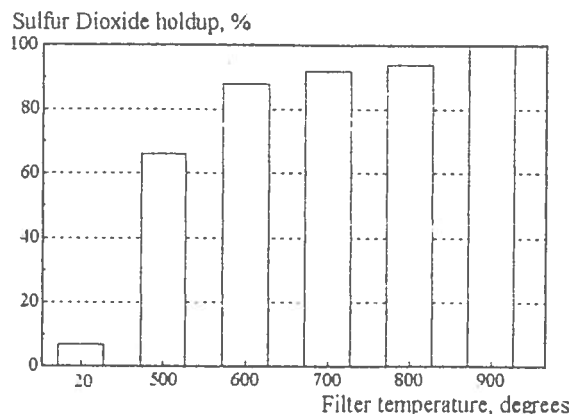


Figure 4. Effects of burning temperature on  $\text{SO}_2$  holdup.

Finally, the effect of the type of solid basic materials on the reduction of sulfur dioxide emission was investigated. Marble waste -0.600mm, Eshka mixture (1 part of  $\text{Na}_2\text{CO}_3$  + 2 part of  $\text{MgO}$ ), magnesia and soda were subsequently used as basic filter. In the experiments, burning temperature was  $900^\circ\text{C}$  and the weight ratio of filter to coal was 1/1. The results are illustrated in Figure 5.

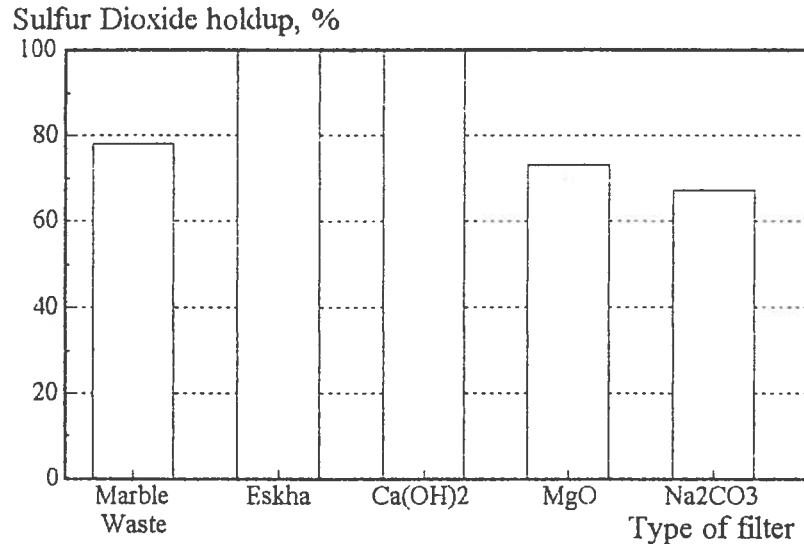


Figure 5. Effect of types of basic filter materials on sulphur dioxide holdup.

#### 4. RESULTS

For the test of cold medium desulfurization by using the stack part of muffle furnace and a ratio of basic filter weight to coal weight of 1/1, 20 g coal samples were combusted in the muffle furnace. In these test, just only 5% of sulfur dioxide emission was kept in calcium hydroxide pellets. This showed that, in cold media, solid basic filters could not keep sulfur dioxide.

As seen from Figure 2, the weight ratio of basic filter to coal of 1/1 is sufficient for holding 72% of sulfur dioxide emission at the pellet size fraction of  $-1.70+0.85\text{mm}$ . Over this weight ratio, the same amount of sulfur dioxide absorption is provided. Under the weight ratio of 1/1, there is a sharp fall in sulfur holdup.

As shown in Figure 3, decreasing  $\text{Ca}(\text{OH})_2$  particle size in the filter is increasing the sulfur dioxide absorption. However,  $-4.25+2.80\text{mm}$  particle size fraction provided a porosity of 67% in the filter. At this porosity,  $\text{Ca}(\text{OH})_2$  filter absorbed 67% sulfur dioxide emission.  $-0.60\text{mm}$   $\text{Ca}(\text{OH})_2$  pellets provided a porosity of 50% in the filter and at this low porosity the filter can keep almost total sulfur dioxide, 94%.

As seen from Figure 4, the highest burning temperature of  $900^\circ\text{C}$  in the study provided the complete desulfurization of coal by holding total sulfur dioxide content of flue gas in the filter. In all temperatures over  $500^\circ\text{C}$ , the sulfur may highly be kept in the filter. For instance, at  $500^\circ\text{C}$  the filter can eliminate 67% of sulfur dioxide emission. At

600°C the sulfur dioxide holdup in the filter is 88%. This high trend of sulfur dioxide holdup in the filter may be very useful for different burners and varied operational conditions of huge combustion chambers.

As shown in Figure 5, the marble filter holds 75% of total sulfur dioxide emission. Magnesia and soda filters hold 67% of total sulfur dioxide emission. The filter of Eshka mixture hold 99% of total sulfur dioxide emission.  $\text{Ca}(\text{OH})_2$  filter provides a complete sulfur dioxide absorption at 900°C.

As a conclusion, total sulfur dioxide content of flue gas after coal burning can be hold by calcium hydroxide or marble waste filters with a porosity of 50% at a weight ratio of filter/coal of 1/1 and at an filter temperature of 900°C.

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