MINING AND METALLURGY INSTITUTE BOR ISSN: 2334-8836 (Štampano izdanje)
UDK: 622 ISSN: 2406-1395 (Online)

UDK: 628.512:662.966:622.33(045)=111 doi:10.5937/mmeb1604011L

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WASTE FLUE GAS DESULPHURIZATION IN COAL COMBUSTION FROM UGLJEVIK BY THE WET PROCESS[***]

Abstract

This paper describes the process of waste flue gas desulphurization (FGD) formed in combustion [1] of brown coal from Ugljevik. For the purposes of development the technology of waste flue gas desulphurization (W) in coal combustion from Ugljevik, the experimental development of technology was approached in the laboratory conditions. For experimental work, an apparatus was designed for combustion the coal samples in a closed system with projected measuring points for measuring the composition of waste flue gases. The wet method was used for desulphurization FGD, i.e. the absorption of sulfur dioxide (SO_2) in the limestone suspension. The advantage of this desulphurization method is as follows:

- *possession a large amount of raw material for S absorption,*
- *relative small investments to prepare the absorption suspension,*
- *very simple method of S absorption of EDC,*
- *verified in operation [2],*
- *high efficiency,*
- *obtaining a potentially useful by-product,*
- *possibility of application in large plants.*

Keywords: *coal, sulfur dioxide, desulphurization, technological method*

INTRODUCTION

Due to the increased pollution of atmosphere with waste gas and various vapors from the industrial plants that are a great threat to the flora and fauna, it is necessary to find a possibility to reduce pollutants. One of the atmospheric pollutants is also SO_2 gas that is one of the constituents of waste gas from coal combustion and whose maximum allowed value in the waste gas is up to 200 mg/m^3 [3].

Description the Technological Process of Waste Flue Gas Desulphurization in Coal Combustion

Waste flue gas desulphurization in the process of coal combustion is a technological method of chemical bonding a free SO_2 gas for components by which a new compound is formed that does not pollute the external environment. Sulfur dioxide is a component of the gas mixture or the coal combustion products that is directly discharged into atmosphere and thus polluting

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[***] *This paper is the result of the Project No. TR 33021 "Research and Monitoring the Changes of the Stress Strain State in the Rock Mass "In-Situ" around the Underground Rooms with Development of Models with Special Reference to the Tunnel of the Krivelj River and Pit Bor", funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia*

the environment. By the presence of SO_2 gas in the exhaust gas and moisture from the air, sulfuric acid is formed which causes some damages to the flora and fauna. Due to this type of pollution the external environment as well as the consequences of pollution that can be produced by SO_2 gas in the external environment, the plants for complete absorption of [3] resulting SO_2 gas are required or to reduce it to the allowed values. The presence of SO_2 gas in the waste exhaust gas is regulated by the EU regulations and maximum allowable amount of SO_2 gas at the outlet of the plant which produces 200 mg/m^3 of gas. To comply with the prescribed amount of SO_2 gas in the outlet gas from plants that rely on fuels containing S, it is necessary to construct a desulphurization plant of waste flue gases.

Desulphurization process can be made in several ways depending on whether [2] desulphurization is done before the fuel combustion containing sulfur or after the combustion of the same.

Methods of desulphurization before fuel combustion:

1. Techniques in the combustion zone
   - Addition of sorbent in a fixed layer
   - Addition of limestone or dolomite into burning layer
   - The simplest method of emission reduction,
   - Low efficiency (15-20%)
   - Efficiency can be increased by water injection into burning layer (0.1 kg water per kg of coal)
2. Combustion in a fluidized bed
3. Additive method

If there is no possibility of desulphurization before fuel combustion, it is necessary to do the FGD desulphurization after combustion in order to reduce the sulfur dioxide emissions to the statutory prescribed value.

Purification methods of waste flue gases after combustion [2]:

- Dry systems: injection of dry sorbent with dry residue.
- Semi-dry systems: sorbent is injected as slime and solid residue is obtained.
- Wet system: both sorbent and residue are wet, non-regenerative and regenerative systems.

EXPERIMENTAL TESTS

Laboratory experimental tests of the flue gas desulphurization process were carried out after the coal combustion process. Due to this reason, the only acceptable method of the proposed 3 is the wet system method where both sorbent and residue are wet [2]. The advantage of using the wet non-regenerative system method is as follows:

- SO_2 is bound into a chemical compound that is used as a by-product or is disposed (waste)
- Sorbent: suspension of limestone or lime
- Sorbent comes into contact with the flue gas, producing a mixture of calcium sulfite and sulfate (gypsum)

For the experimental investigations of waste flue gas desulphurization in coal combustion, a large number of experiments were done at different temperatures of combustion in the range of 500^{o}C to 900^{o}C [1] with introduction of oxygen in the combustion process.

The absorption of flue gas was conducted into 20% suspension of limestone of the known chemical composition, granulation and specific reactivity. The principle of desulphurization FGD is based on the absorption of FGD going through the limestone suspension, whereby a chemical reaction is developed between SO_2 gas and $CaCO_3$ from suspension and $CaSO_4$ and CO_2 are obtained. Reaction between SO_2 and $CaCO_3$ from suspension results to decrease of SO_2 gas [3] in FGD and hence reduce SO_2 gas in the exhaust gases into the atmosphere.

Coal was firstly ground, sampled to determine the physical characteristics and technical analysis of coal, then the experiments were planned, and samples were measured for FGD desulphurization.

For the experiments of waste flue gas desulphurization in coal combustion from Ugljevik, an apparatus was used for combustion the coal samples in a closed system with projected measuring points for measuring the composition of exhaust gases.

Apparatus is shown in Figure 1.

Figure 1 *Apparatus for coal combustion and waste flue gas desulphurization in combustion*

Parts of apparatus for coal combustion and waste flue gas desulphurization (FGD): 1. Mars tubular oven with corresponding tube of Al_2O_3 and associated transformer station for power supply. 2. Connecting gas pipelines with compensators with the measuring point 1 for measuring the composition of gas mixture FGD at the outlet of oven. 3. Two absorption units with 20% suspension of limestone with the known reactivity. 4. Pump for extraction of FDG from oven, which allows the passage of gas mixture through columns with suspension of lime for desulphurization. 5. A part of gas pipeline behind the pumps and absorption units with the measuring point 2 provided for measuring the composition of gas mixture at the outlet of system for gas absorption (desulphurization). 6. Ventilation system for gas extraction from the working space

Coal sample with the known technical analysis and certain physical characteristics is measured in a boat of rotosyl and put in a preheated Mars tubular oven at the pre-set temperature. The tube of oven for combustion of coal samples is made of Al_2O_3. The coal samples are burnt at temperature of 500^oC, 900^oC. The process of coal combustion flows with continuous introduction of oxygen into oven as long as the separation of SO_2 gas. During the combustion process of coal, the composition of waste flue gases is measures at the outlet of oven MM-1, before entering the absorption column and at the outlet of the absorption columns MM-2.

Physical Characteristics and Technical Analysis of Coal from Ugljevik

Physical characteristics of coal were carried out after coal grinding. Determination the physical characteristics of coal were done from two coal samples from Ugljevik 1 and 2.

The results of physical characteristics of coal samples from Ugljevik are given in Table 1.

Table 1 *Results of physical characteristic of coal samples from Ugljevik*

Sample designation	Humidity w(%)	Bulk density [g/cm^3]	Specific weight [g/cm^3]
Sample 1	15.54	1.367	1.611
Sample 2	18.96	1.279	1.579

After determining the physical characteristics of coal, the technical analysis of coal was carried out.

Technical analysis of coal from Ugljevik Bogutovo Selo is given in Table 2.

Table 2 *Technical analysis of coal*

With total moisture			With rough moisture			With hygroscopic moisture		
495 (hg)	**Intervals**		**-495(hg)**	**Intervals**		**-495(hg)**	**Intervals**	
Elements	5.70-10.70	10.70-14.70	Elements	5.70-10.70	10.70-14.70	% ash	5.70-10.70	10.70-14.70
% ash	14.42	16.07	% ash	17.22	18.30	% combustible	21.12	23.11
% combustible	45.91	47.33	% combustible	54.78	53.90	% volatile	67.21	68.09
% volatile	24.19	25.07	% volatile	28.87	28.55	% coke	35.42	36.06
% coke	36.14	38.33	% coke	43.13	43.65	% C-fix	52.91	55.14
% C-fix	21.71	22.27	% C-fix	25.91	25.36	% S-total	31.79	32.03
% S-total	4.71	4.36	% S-total	5.62	4.97	% S-bound	6.90	6.27
% S-bound	1.22	1.08	% S-linked	1.46	1.23	% S-combustible	1.79	1.56
% S-combustible	3.49	3.28	% S-combustible	4.16	3.73	KJ/kgGTM	5.11	4.71
KJ/kgGTM	12794	13364	KJ/kgGTM	15268	15219	KJ/kgDTM	18731	19224
KJ/kgDTM	12385	12934	KJ/kgDTM	14780	14730	% ash	18132	18606

Technical analysis of coal from Ugljevik shows that content of combustible sulphur in it is 3.49%.

Measuring the Composition of Gas Mixture of the Waste Flue Gases from Coal Combustion

Series of samples in each of 5 samples were formed from prepared and analyzed coal for experimental tests of desulphurization FGD at different temperatures of combustion.

In the process of coal combustion at particular temperature, the measurement was firstly performed for composition of the gas mixture of waste gases so that the amount of SO_2 gas was clearly seen in the gas mixture which has to be absorbed in the limestone suspension.

Temperature of Coal Combustion at 800°C

Under the same conditions of coal combustion as it was done at temperatures of 500°C to 700°C, series of combustion the coal samples of 1-5 at temperature of 800°C were also done, and measurements of waste flue gases were done as well as the absorption of waste flue gases during the combustion process. The absorption of the waste flue gases was done in 20% suspension of limestone Spasine Brdjani, granulation 5.6 - 16.0 μm. The oxygen flow in the combustion of coal samples is 2 l/min.

Time of measurement the composition of waste flue gases will flow from the moment when the loaded coal sample in the oven starts to burn. Measurement the composition of gas mixture of waste flue gases is at the measurement point 1 (MM-1) immediately after the outlet of FGD from oven tube in which the coal combustion takes place at particular temperature.

The obtained test results of measurement the waste flue gases on MM-1 from coal combustion at 800°C with the introduction of oxygen are given in Table 3.

Table 3 *Results of measurement the waste flue gases at 800°C on MM-1*

Measurement time (s)	T-gas, °C	CO_2-gas, %	CO-gas, ppm	SO_2-gas, ppm	SO_2-gas, mg/m^3
27	19	0.7	346	2864	8188
44	18.6	1.1	458	3581	10238
255	18.9	0.0	8	1299	3714
263	18.7	0.0	11	1588	4540
275	19.0	0.0	13	1731	4948
613	20.2	0.0	22	415	1187
623	20.2	0.0	22	422	1207
697	20.3	0.0	25	493	1410
782	20.3	0.0	30	516	1474
1073	20.4	0.0	41	597	1706
1085	20.5	0.0	43	603	1723
1375	21.5	0.0	65	635	1814
1380	21.4	0.0	65	657	1877
1476	21.7	0.0	70	746	2133
1537	22.3	0.0	77	819	2343
2144	20.7	0.0	240	1041	2976
2274	20.7	0.0	42	514	1470
2333	20.8	0.0	30	247	707
2491	20.8	0.0	3	73	210
2628	20.6	0.0	2	46	132
3052	20.1	0.0	1	5	14
3121	19.9	0.0	1	1	3
3152	19.8	0.0	1	0	0

It is seen from the measurement results at the combustion temperature of 800°C with the introduction of O_2 that the obtained values for SO_2 gas 8188 and 10238 mg/m^3 are very large in regard to the allowed value of SO_2 gas for discharging intothe atmosphere. For this reason it is necessary FGD desulphurization, thus reducing the SO_2 gas allowed to 200 mg/m^3.

Figure 2 shows the curve of selected CO, SO_2 gases from the composition of the gas mixture FGD during the coal combustion at temperature of 800°C.

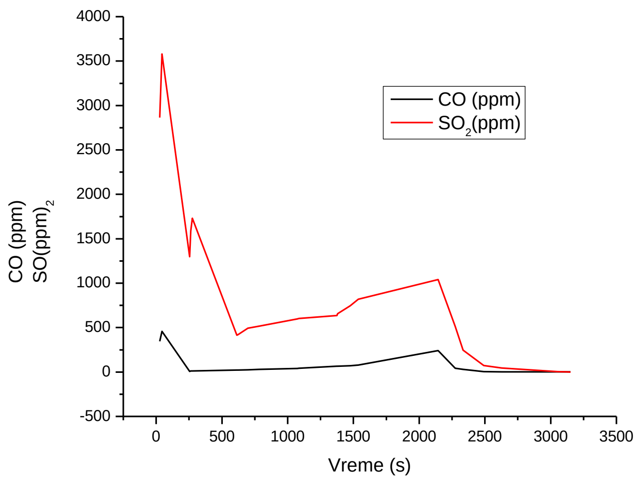

Figure 2 *Diagram of gases on MM-1 at 800°C, (CO, SO_2)*

Diagram in Figure 2 presents the contents of CO and SO_2 in the gas mixture beside the oven for coal combustion on MM-1.

FGD Desulphurization Using 20% Aqueous Suspension of Limestone at the Combustion Temperature of 800°C

The indicated amounts of separated SO_2 gas from combustion of coal at 800°C are very high so it is necessary to reduce them from FDG that would prevent pollution of the environment. Reduction of SO_2 gas from FDG was performed by absorption the same from FDG in the limestone suspension of known granulation, chemical composition and reactivity [4].

For desulphurization the flue gases for samples with combustion at 800°C, the 20% suspension of limestone SP-BRDJANI was used with granulation 5.6 - 16.0 µm and reactivity of 89.89%.

After completion of the FGD desulphurization of a series of 5 samples of coal (100 g), the absorption suspension was filtered, and the content of S in the solid and liquid part of suspension was determined.

The S Absorption in the Solid Part of Suspension (Absorbent)

By analyzing the hard part of adsorbent on the S absorbed from the flue gases in coal combustion at 800°C, the obtained results are shown in Table 4.

Table 4 *Results of the S content in the solid part of absorbent according to the Report on testing No. 195130-688/2016*

Elements	U_{ap}-3	U_{ap}-4	Method	Standard
S (%)	3.98	0.079	ACS	*BMK E.3.1

Based on the obtained results of chemical analysis of sulfur content in the solid absorbent, the balance of S absorption was made from the waste flue gases from coal combustion at 800°C; the obtained results are given in Table 5.

Table 5 *Results of S absorption balance in the solid part of absorbent*

Elements	Amount of solid absorbent U_{ap}-3 (g)	Amount of absorbed S in U_{ap}-3(g)	Amount of solid absorbent U_{ap}-4(g)	Amount of absorbed S in U_{ap}-4(g)	% total of absorbed S
	62.8	2.5	58.1	0.046	73

Based on the balance of S absorption in the solid absorbent, the obtained results show that 73% of S is absorbed from the waste flue gases.

The S Absorption in the Liquid Part of Suspension (Absorbent)

By analyzing the liquid adsorbent on the S content in the form of SO_4^{2-}, the obtained results are shown in Table 6.

Table 6 *Results of the chemical analysis of SO_4^{2-} content in the liquid part of absorbent for combustion of coal from Ugljevik at 800°C*

Sample designation	SO_4^{2-} mg/l	Volume of liquid absorbent (ml)	Amount of absorbed S (g)	% Amount of absorbed S
V-3	1550.0	850	0.43	12.5
V-4	875.0	800	0.233	6.7
			∑0.669	19.2

Based on the obtained results of adsorbed S in combustion of coal of 100g from Ugljevik in solid and liquid absorbents, the amount of 3.22 g S was obtained, what is the total absorbed S of 92.2%.

Such high degree of S absorption in the solid and liquid part of the absorption suspension can be also confirmed by measurement the content of SO_2 gas at the measuring point 2 (MM-2) behind the absorption columns at the same time when it is measured on MM-1. The process of absorption is not interrupted; it is clear from the measurement results that the total amount of separated SO_2 in coal combustion was absorbed in the limestone suspension.

The results of measurement the waste flue gases at the outlet of desulphurization system (MM-2) at 800°C are given in Table 7.

Table 7 *Results of measurement the content of the waste flue gases on MM-2*

Measurement time (s)	T-gas, °C	CO_2-gas, %	CO-gas, ppm	SO_2-gas, ppm
496	20.9	0.0	33	0
504	20.9	0.0	35	0

The obtained results of measuring the composition of waste flue gases on MM-2 show that all released SO_2 gas is absorbed in the absorption suspension of the mounted system for absorption.

Notice

In desulphurization of FGD at the coal combustion temperature of 900^oC, a separation of H_2S gas is developed that is highly toxic and whose separation in chemical processes should be strictly controlled within the allowed limits. The elimination of separated H_2S gas requires a special system for waste gas treatment as well as a gauge for H_2S gas concentration at the outlet of treatment system so that the overdraft of MDK for H_2S would not be developed. The procedure and equipment for waste gas treatment with the present H_2S is very expensive, so whenever it is possible in the chemical process to avoid its formation. Due to the separation of H_2S, it is necessary that the coal combustion process takes place at lower temperature of 900^oC.

CONCLUSION

Based on the experimental testing in the laboratory conditions of coal combustion from Ugljevik and desulphurization of the waste flue gases, formed during combustion, the following could be concluded:

- in coal combustion, it is necessary to introduce oxygen into the process, a flow rate of 2 l/min.
- the highest amount of the obtained SO_2 gas in the waste flue gases is at the combustion temperature of 800^oC.
- the highest degree of SO_2 gas absorption of the waste flue gases (desulfurization) is at the combustion temperature of 800^oC, 92.2%, that is 73% in the solid part of adsorbent, and 19.2% in the liquid part of absorbent,
- for FGD absorption, the suspension of 20% was used, made of composite limestone SP BRDJANI, 5.6-16.0 μm, with reactivity of 89.89%.

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