Flue Gases Treatment by Irradiation with Electron Beam in the Presence of Fine Water Droplets

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This paper presents the experimental results obtained during the irradiation process with electron beam of flue gases generated by burning fuel with a high content in sulphur. The ALIN-10 accelerator was used for generating the electron beam. The necessary water was sprayed into the gaseous mixture as fine droplets by the mist pump. The highest removal efficiencies were obtained in the presence of ammonia, electron beam and fine water droplets: 94% for SO_2 and 98% for NOx, respectively. Moreover, in this case, SO_2 and NOx were transformed into the useful products: ammonia sulphate and nitrate, respectively.

Keywords: electron beam, flue gases, NOx and SO_2, fine water droplets

At this moment, at global level there are few pilot and industrial installations for flue gases treatment by electron beam (EB) irradiation [1]. Their inconvenient is the energy consumption which is rather high (the necessary power for EB is around 2-4% from the total electrical energy produced by the plant) [2,3]. That is why it is mandatory to find new solutions and to develop strategies for diminishing both the energy and the costs.

When they are subject to electron beam irradiation process, the main flue gases components (N_2, O_2 and H_2O) are transformed into reactive species (free radicals, ions, excited atoms) that have a high oxidation potential [4,5]:

$$N_2, O_2, H_2O_{(vapor)} + e^- \rightarrow HO^\bullet, HO_2^\bullet, O^*, ions, excited-species \qquad (1)$$

In the presence of these reactive species, NOx and SO_2 from flue gases are oxidized and produce nitric acid and sulphuric acid, respectively, as intermediate products. These acids are neutralized with ammonia, giving ammonium nitrate and ammonium sulphate, respectively:

$$SO_2 \xrightarrow{HO^\bullet} HSO_3 \xrightarrow{O_2, H_2O} H_2SO_4 \xrightarrow{NH_3} (NH_4)_2SO_4 \qquad (2)$$

$$NO \xrightarrow{O^*, HO_2^\bullet} NO_2 \xrightarrow{HO^\bullet} HNO_3 \xrightarrow{NH_3} NH_4NO_3 \qquad (3)$$

Besides these radiation induced reactions, ammonium sulphite and sulphate are also produced by thermal pathway [6]:

$$2NH_3 + SO_2 + H_2O \rightarrow (NH_4)_2SO_3 \qquad (4)$$

$$2NH_3 + SO_2 + H_2O + 1/2O_2 \rightarrow (NH_4)_2SO_4 \qquad (5)$$

After EB irradiation and in the presence of NH_3, SO_2 and NOx are transformed into products used in agriculture as fertilizers, namely $(NH_4)_2SO_4$ and NH_4NO_3 [1,3,7].

The present research paper highlights the advantages of the EB irradiation treatment in the presence of fine water droplets performed into a laboratory scale installation. The particularities of this experimental stage represent the gas burner that was introduced in the laboratory scale installation in order to burn a liquid mixture, giving gases with a composition similar to that obtained at the industrial scale, and also the device that sprays water into the gas mixture as fine droplets in order to assure the necessary amount of water. Thus, the processes performed at large industrial combustion plants are reproduced with a high accuracy at laboratory scale.

Experimental part

Obtaining the flue gas

The experimental part took place in the irradiation laboratories of the National Institute for Lasers, Plasma and Radiation Physics Bucharest. For the experimental programme accomplishment, the flue gas obtained had a composition similar to gases from power plants that burn coal or oil. The sulphur and nitrogen content from the diesel-fuel used was assured by adding carbon disulfide and aniline, respectively. The added amounts and the sulphur and nitrogen concentrations obtained are given in table 1.

Table 1
CONTENT OF SULPHUR AND NITROGEN OF MIXTURES DIESEL-FUEL:ANILINE:CS_2

	Density, g/L	**Molecular mass, g/mol**	**Volume, L**	**Mass, Kg**	**Sulphur, g**	**Sulphur content, % gram**
CS_2	1.26	76.0	0.12	0.1512	127.3263	3.0307
diesel-fuel	0.9		4.5	4.05		
Total				**4.2012**		
	Density, g/L	**Molecular mass, g/mol**	**Volume, L**	**Mass, Kg**	**Nitrogen, g**	**Nitrogen content, % gram**
Aniline	1.022	93.0	0.03	0.0307	21.0993	0.5171
diesel-fuel	0.9		4.5	4.05		
Total				**4.0807**		

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Table 2

CONTENT OF SULPHUR AND NITROGEN OXIDES FROM GASES OBTAINED AT DIESEL-FUEL BURNING WITH A CONTENT OF 3% SULPHUR AND 0.5 % NITROGEN, FUNCTION OF THE USED AIR EXCESS

Air excess Fed O_2 / Burned O_2	CO_2, % vol.	O_2, % vol.	SO_2			NO			Gas type
			ppmv	ppmg	mg/Nm^3	ppmv	ppmg	mg/Nm^3	
1.0	10.07	0.00	1397.55	3130.55	3993.00	537.67	564.56	720.10	wet
1.0	11.29	0.00	1565.99	3358.11	4474.26	602.47	605.60	806.90	dry
1.5	6.71	7.00	931.78	2257.06	2662.24	358.48	407.04	480.11	wet
1.5	**7.23**	**7.54**	**1003.77**	**2373.00**	**2867.91**	**386.17**	**427.95**	**517.20**	**dry**
2.0	5.04	10.50	698.87	1764.68	1996.77	268.87	318.24	360.10	wet
2.0	5.32	11.10	738.60	1834.77	2110.28	284.16	330.88	380.60	dry

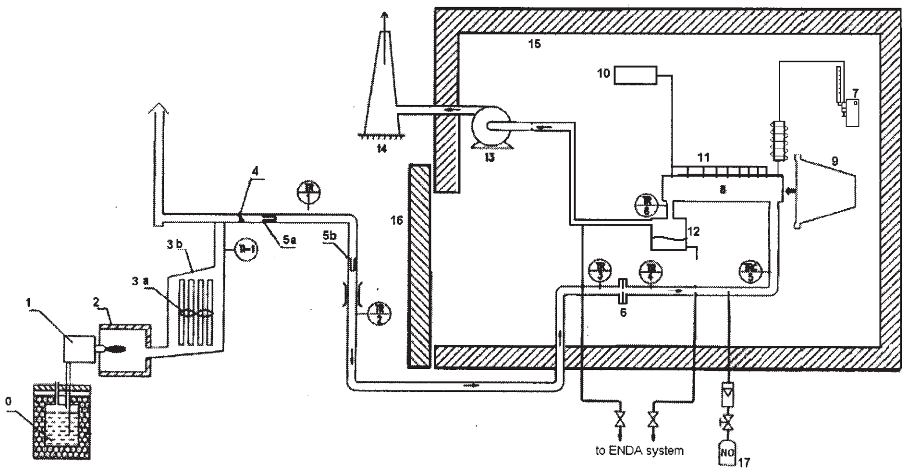

Fig. 1. The laboratory installation scheme for the treatment of flue gases obtained by gas burner and in the presence of ALIN-10 accelerator, by EB irradiation (after [8]) . 0 – liquid fuel tank; 1 – burner; 2 - oven; 3 – heat exchanger; 4 – flow rate adjustment choke; 5 – macroscopic particles and soot filters; 6 – Pitot flow rate device; 7 – ammonia solution dispenser; 8 – reaction chamber with EB irradiation; 9 – EB accelerator; 10 – high pressure water pump; 11 – water sprays; 12 – gas/liquid separator; 13 - fan; 14 – exhausting stack; 15 – concrete wall for screening; 16 – concrete door for screening; 17 – supplementary feeding with NO

Then, in this mixture, a known flow rate of water was introduced as fine droplets.

Function of the air excess and supposing the complete conversions of sulphur and nitrogen into the corresponding oxides, theoretical values obtained are presented in table 2.

From table 2 data, the values obtained for an air excess of 50% are the most similar to the real burning conditions. Even in this case, the content in nitrogen oxides is of approximately 130 ppmv, from which 35 ppmv are obtained by nitrogen from air oxidation in the gas burner conditions. It is stated that only 25% from the nitrogen existent in fuel is transformed into NO.

NH_3 was used as reagent, as an aqueous solution of 25% concentration. The flow rate of ammonia solution was determined to obtain some stoichiometric ratio of ammonia:

$$SR(NH_3) = [NH_3]/(2\times[SO_2]+[NOx])\times 100 \qquad (6)$$

(concentrations of NH_3, SO_2 and NOx were in ppmv).

Laboratory installation

The laboratory installation for flue gases treatment with EB, generated by ALIN-10 accelerator of 6.23 MeV and adjustable output power up to 164 W, is presented in figure 1. The flue gas is emitted by the burner passes through the conditioning system and then it is subject to EB irradiation in the processing vessel. A stoichiometric amount of ammonia is added into the flue gas mixture before entering the processing vessel. Also, water is sprayed as fine droplets. The by-product obtained during the flue gases irradiation is separated as liquid, and the treated flue gas is eliminated into the atmosphere by an exhausting stack from stainless steel.

The flow rate of the flue gas processed through the installation is situated between 1-20 m^3/h and controlled by a valve. Then, the concentrations of SO_2, NOx, CO_2, CO and O_2 were analyzed by Horiba ENDA 600 equipment, which has the possibility of sampling from two measurement distinct points (entrance and exit). The liquid product obtained was analyzed by 792 Basic IC type ion-chromatograph. The analyses were performed by chemical suppression for anions, with the Metrohm Suppressor Module. The used chromatography column was Metrosep A Supp 1 of 4.6 x 250 mm, number 06219820, 10.0 μm particles dimension. The eluent was 3 mmol/L Na_2CO_3 solution.

The laboratory installation consists of the following technological units: i) the fuel burning unit; ii) the flue gas conditioning system, iii) the flue gas irradiation with EB, iv) the liquid product separation unit, v) the continuous gases monitoring system and vi) the treated gas elimination unit.

Results and discussions

In the first stage, the flue gas flow rate was determined by a special device with a Pitot tube (with a diameter of 0.8 cm). Function of the tube diameter, and especially of the gas flowing rate that was varied during the experimental determinations, the gas flow rate was calculated in each case. These values obtained are given in table 3.

When the gas flow rate was of approximately 5200 L/h, only in the presence of ammonia injected into the gaseous mixture, which has already contained water, and in the absence of EB irradiation, SO_2 is removed with a high efficiency. In this case when the irradiation dose is 0 kGy, the NO removal efficiency has very low values. Table 4 presents these values of efficiency. Based on the ion chromatography analyses that were performed after, the obtained product consists mainly of ammonium sulphite and ammonium sulphate, and the ammonium nitrate and nitrite concentrations are insignificant due to the very low transformation of NO into them (table 7).

Table 3
FLUE GAS FLOW RATE FUNCTION OF THE GAS FLOWING RATE

Diameter, cm	Area, cm^2	Flowing rate, cm/s	Gas flow rate,		
			cm^3/s	L/s	L/h
3.0	7.065				
0.8	0.5024				
	6.5626	**220**	1443.77	1.4438	**5198**
2.0	3.14				
0.8	0.5024				
	2.6376	**1500**	3956.40	3.9564	**14243**
2.0	3.14				
0.8	0.5024				
	2.6376	**850**	2241.96	2.2420	**8071**

Table 4
REMOVAL EFFICIENCIES FOR SO_2 AND NO AT A GAS FLOW RATE OF ~5200 L/h AND ONLY IN THE PRESENCE OF AMMONIA

SO_2, ppmv	NOx, ppmv	CO, ppmv	CO_2, %	O_2, %	NH_3 stoich.	SO_2 removal efficiency, %	NO removal efficiency, %
Entrance (at 40 °C)							
812	44	218	9.3	8.4			
Exit (only with NH_3)							
206	39	187	8.7	9	1	**74.6**	**11.4**

Table 5
REMOVAL EFFICIENCIES FOR SO_2 AND NO AT A GAS FLOW RATE OF ~7500 L/h AND IN THE PRESENCE OF AMMONIA AND EB

SO_2, ppmv	NOx, ppmv	CO, ppmv	CO_2, %	O_2, %	NH_3 stoich.	SO_2 removal efficiency, %	NO removal efficiency, %
Entrance (at 39.5 °C)							
1061.5	37	277.5	9.07	8.575			
Exit (with NH_3 and with EA 62W)							
160	8	350	8.6	9.12	1.22	**84.93**	**78.4**

Table 6
REMOVAL EFFICIENCIES FOR SO_2 AND NO AT A GAS FLOW RATE OF ~5200 L/h AND IN THE PRESENCE OF AMMONIA, EB AND FINE WATER DROPLETS

SO_2, ppmv	NOx, ppmv	CO, ppmv	CO_2, %	O_2, %	NH_3 stoich.	SO_2 removal efficiency, %	NO removal efficiency, %
Entrance							
812	44	218	9.27	8.37			
Exit (with NH_3, with EA 62W and with fine water droplets)							
47	1	197	8.54	9.2	~0.8	**94.21**	**97.73**

Table 7
MEAN CONCENTRATIONS OF NITRITE, NITRATE, SULPHITE AND SULPHATE FOR DIFFERENT WORKING CONDITIONS

Experimental conditions	Compound	Mean concentration	
		mg/L	%
with NH_3	nitrite	35.89	0.47
	nitrate	208.29	2.74
	sulphite	3523.40	46.27
	sulphate	3846.69	50.52
with NH_3 and EB	nitrite	34.80	0.29
	nitrate	241.72	1.99
	sulphite	233.96	1.93
	sulphate	11613.85	95.79
with NH_3, EB and fine water droplets	nitrite	99.46	3.60
	nitrate	59.44	2.15
	sulphite	58.85	2.13
	sulphate	2545.01	92.12

The next experimental set took place for a gas flow rate of approximately 7500 L/h. The procedure was performed in the presence of ammonia and under irradiation with EB. It is observed that for this time, the conversion process of the two acidic oxides into products take place in better conditions, SO_2 being removed in proportion of 85%, while the removal efficiency for NO was very high 95% (this value is also due to the initial low NOx concentration). The ion chromatography analyses confirm that in this case SO_2 is mainly converted into ammonium sulphate, while NO into ammonium nitrate, the useful products obtained in the final (table 7). Table 5 presents the values of efficiency obtained in this case.

For a gas flow rate of 5200 L/h, under EB irradiation and in the presence of fine water droplets (33 L/h water as droplets with a diameter of approximately 10 μm), the results obtained are presented in table 6.

In this case, the volumetric density of gases rises and thus the EB irradiation is more efficient. This fact confirms the results obtained: the removal efficiency for SO_2 is 94%, while that for NOx is 98%. The ion chromatography analyses for the final product obtained at the end of this experimental stage also confirm the SO_2 and NO transformation into useful products like: ammonium sulphate and nitrate (table 7).

The mean concentrations of ammonia sulphate, sulphite, nitrate and nitrite in different experimental conditions (only with NH_3, with NH_3 and EB, and with NH_3, EB and fine water droplets) are given in table 7.

From table 8 data, it is observed the high influence of the gaseous medium density upon the penetration depth

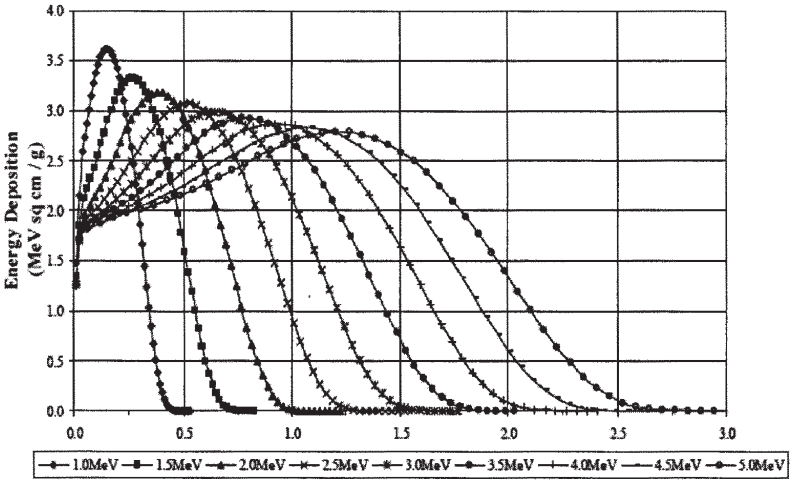

Fig. 2. Energy deposition in cm of water for different values of EB current (MeV) [9]

Table 8
THE GASEOUS MEDIUM DENSITY INFLUENCE UPON THE PENETRATION DEPTH OF EB INTO THE MEDIUM AND UPON THE EFFICIENCY FOR ELECTRONS CAPTURE INTO A REACTION VESSEL

EB energy = 6.23 MeV						
Useful distance, cm	**Density,** g/cm^3	**Material**	**Thickness,** cm	**Losses thickness/useful distance,** %	**Penetration depth,** cm	**EB absorption efficiency,** %
0.854701	2.7	Al	0.01	1.17	1.21	
0.512821	4.5	Ti	0.005	0.98	0.73	
1784.758	0.001293	Air	20	1.12	2528.23	
300.3	0.007685	Wet gases	300		425.4	99.9
1784.758	0.001293	Dry gases	300		2528.2	16.8

Table 9
WATER NECESSARY FUNCTION OF THE GAS FLOW RATE AND THE DISPERSED MEDIUM DENSITY

Droplet radius, µm	**Droplet volume,** cm^3	**Water,** % vol.	**Gas density,** g/L	**Droplets** no./ cm^3	**Water volume/** cm^3	**Reactor volume,** L	**Water flow rate,** L/h	**Gas flow rate,** L/h
10	4.2×10^{-9}	0.64	7.68	1.53×10^{6}	6.4×10^{-3}	90	33	5200

of EB into the medium and upon the efficiency for electrons capture into a reaction vessel of 300 cm, respectively. Penetrating power of the electron beam is related to the accelerating voltage and the density of the processed material. Higher voltage causes deeper penetration, and denser material reduces the depth of penetration. The depth dose curves (fig. 2) are convenient aids for estimating the penetration depth. These curves show the penetration for different accelerating voltage to the depth of penetration in a material with mass density equal to that of water.

In order to increase the gaseous medium density, a device for water spraying into fine droplets was used. This was called mist pump, and the results obtained in this case were given in the above table 8.

The water necessary was determined function of the gas flow rate and the dispersed medium density. table 9 presents this computation.

Conclusions

An experimental set was realized, using the ALIN-10 accelerator for irradiation with electron beam and in the presence of a gas device that burns diesel-fuel with content in sulphur and nitrogen that is assured by adding carbon disulfide and aniline, respectively. The working gas flow rates varied.

In the absence of EB and in the presence of ammonia (only thermal), the removal efficiency for SO_2 is of approximately 75%, but the composition of the product obtained has high concentration of ammonia sulphite. For NO, the efficiency value is very low.

In the presence of ammonia and EB, SO_2 is 85% removed, and NO presents a very high removal efficiency of approximately 95%. The ion chromatography analysis confirms the fact that in this case SO_2 is transformed mainly into ammonia sulphate, while NO into ammonia nitrate.

The mist pump that sprays the necessary water as droplets into the gaseous mixture was used. The volumetric density rises and the EB irradiation efficiency was much better: the removal efficiencies for SO_2 and NOx were of approximately 94 and 98%, respectively. The ion chromatography analyses for the product obtained at the end of the experimental stage confirm that SO_2 and NO were transformed into useful products: ammonia sulphate and nitrate, respectively.

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