NUKLEONIKA 2015;60(3):689–695
doi: 10.1515/nuka-2015-0098

ORIGINAL PAPER

DE GRUYTER
OPEN

Electron beam treatment of simulated marine diesel exhaust gases

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Abstract. The exhaust gases from marine diesel engines contain high SO_2 and NO_x concentration. The applicability of the electron beam flue gas treatment technology for purification of marine diesel exhaust gases containing high SO_2 and NO_x concentration gases was the main goal of this paper. The study was performed in the laboratory plant with NO_x concentration up to 1700 ppmv and SO_2 concentration up to 1000 ppmv. Such high NO_x and SO_2 concentrations were observed in the exhaust gases from marine high-power diesel engines fuelled with different heavy fuel oils. In the first part of study the simulated exhaust gases were irradiated by the electron beam from accelerator. The simultaneous removal of SO_2 and NO_x were obtained and their removal efficiencies strongly depend on irradiation dose and inlet NO_x concentration. For NO_x concentrations above 800 ppmv low removal efficiencies were obtained even if applied high doses. In the second part of study the irradiated gases were directed to the seawater scrubber for further purification. The scrubbing process enhances removal efficiencies of both pollutants. The SO_2 removal efficiencies above 98.5% were obtained with irradiation dose greater than 5.3 kGy. For inlet NO_x concentrations of 1700 ppmv the NO_x removal efficiency about 51% was obtained with dose greater than 8.8 kGy. Methods for further increase of NO_x removal efficiency are presented in the paper.

Key words: electron accelerator • electron beam treatment • free radicals • marine diesel exhaust gases • NO_x removal • seawater scrubber

Introduction

Around 85% of worldwide trading goods are moved using maritime routes. High-power diesel engines are mainly applied in the marine transport sector as main engines for ships propulsion at sea and as auxiliary engines at a berth. For economic reasons ships generally use low quality fuel oil with high sulfur content. During combustion the fuel sulfur is oxidized mainly to SO_2. NO_x emissions from shipping are relatively high because most marine engines operate with high compression. A typical composition of exhaust gas from large two-stroke diesel engine fuelled with heavy fuel oil (HFO) is presented in Fig. 1 [1].

Emissions from shipping contribute significantly to the concentrations of harmful air pollution in Europe [2]. While pollutant emissions from land-based sources are gradually decreasing, those from shipping show a continuous increase (Figs. 2 and 3) [3]. Under current legislation, it is expected that shipping emission of the SO_2 and NO_x will increase by 40–50% up to 2020, as compared to 2000. In both cases, by 2020 the emissions from international shipping around Europe are expected to equal or even surpass the total from all land-based sources in the 27 EU member states combined. The both gases (NO_x and SO_2) affect adversely on human health and ecosystem [4, 5].

In order to reduce the environmental footprint of ships, the International Maritime Organization

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Received: 24 September 2014
Accepted: 20 May 2015

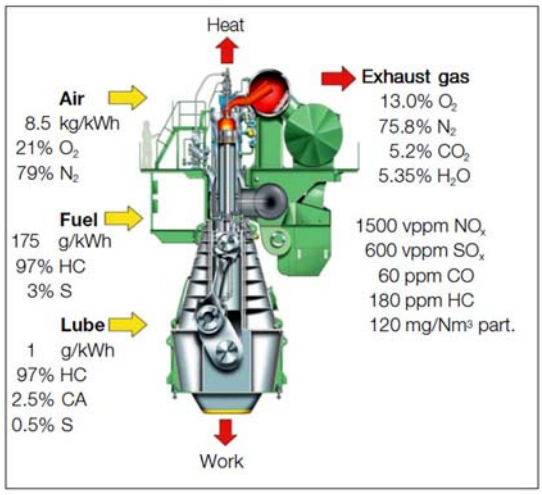

Fig. 1. Flow process and typical exhaust gas composition from two-stroke diesel engine manufactured by MAN B&W Diesel [1].

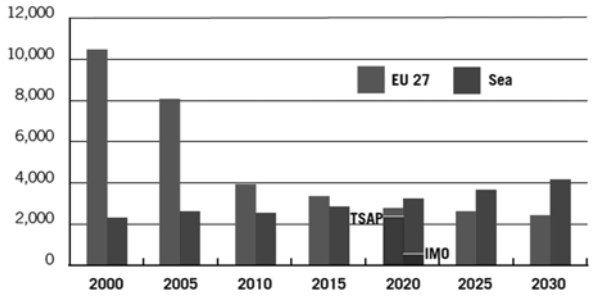

Fig. 2. Emissions of SO_2 in Europe in the period 2000–2030 (in ktonnes) [3]. EU27 – emissions from land-based sources in all 27 EU countries (including domestic shipping) combined. Sea – emissions from international shipping in European sea areas. TSAP – target in line with the EU Thematic Strategy on Air Pollution from September 2005. IMO – expected outcome from implementing the preliminary IMO-agreement from April 2008.

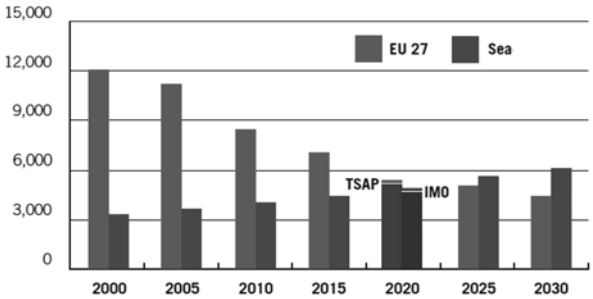

Fig. 3. Emissions of NO_x in Europe in the period 2000–2030 (in ktonnes) [3]. Legend as in Fig. 2.

(IMO) issued the legislation of MARPOL Annex VI guidelines for the Global (all European sea areas) and ECA (emission control area) areas in sulfur content in fuel oil (Fig. 4) and NO_x emissions based on ship engine operating speed (Fig. 5).

Trying to meet these requirements, ship owners have the alternative, either to operate ships with costly low-sulfur fuels, or to keep HFO burning but adopting proper retrofitting devices.

Several commercial technologies have been implemented on board to reduce the level of SO_x and NO_x

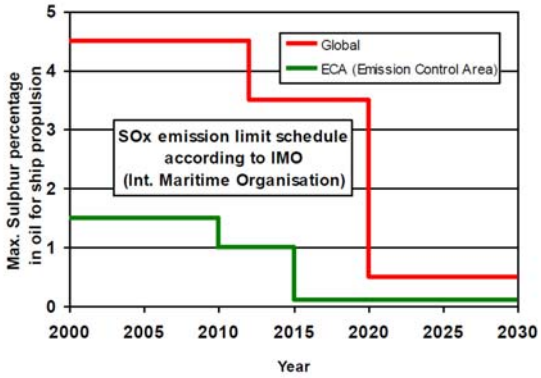

Fig. 4. Maximum allowable sulfur content in fuel oil, according to IMO requirements which are applied to all ships entering a global (all European sea areas) or ECA areas.

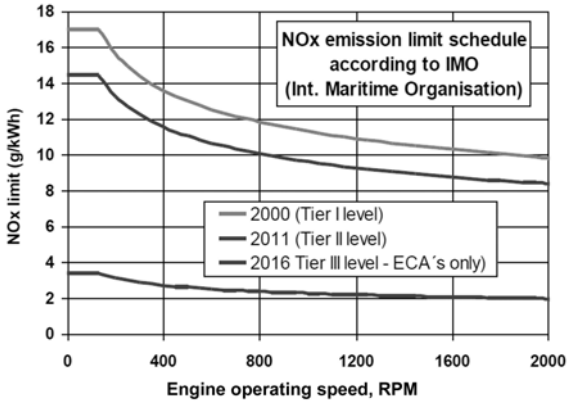

Fig. 5. Maximum allovable fuel specific NO_x emission rate, according to IMO, MARPOL Annex VI. Tier I and Tier II limits are global, while Tier III standards apply only in NO_x emission control areas.

from marine diesel engines [6]. Though those technologies can remove 99% of SO_2 and 90% of NO_x, they posses a number of important drawbacks; two separate technologies for removal of NO_x and SO_x, require high installation cost as well as a lot of space on the ship and requires large storage of ammonia for the removal of NO_x [6]. The applicability of electron beam flue gas treatment technology (in short, e-beam technology) for purification of marine diesel exhaust gas is the main task of this paper. This technology was originally developed for coal-fired power plants. The simultaneous removal of SO_2 and NO_x with the generation of usable byproducts are its main advantages [7]. The e-beam technology has been already implemented on an industrial scale at three coal-fired power plants: Chengdu and Hangzhou in China [8] and Szczecin "Pomorzany" in Poland [9] (Table 1).

In the e-beam technology, electrons are accelerated by a high voltage in a vacuum region before being injected through thin foil windows to the flue gases at the atmospheric-pressure processing chamber (plasma reactor). The energetic electrons collide with exhaust gas molecules and produce reactive free radicals, atoms, ions and secondary electrons that decompose the pollutants molecules in the irradiated flue gases. The present study was performed with high NO_x concentration up to 1700 ppmv. Such high NO_x concentrations were observed in the exhaust gases from marine high-

Table 1. Main parameters of three industrial e-beam plants

Parameters	Unit	Chengdu TPP China	Hangzhou TPP China	Pomorzany EPS Poland
Nominal flue gas flow rate	Nm^3/h	300 000	305 400	270 000
Inlet flue gas temperature	°C	150	145	140
Inlet SO_2 concentration	ppmv	1800	970	700
Inlet NO_x concentration	ppmv	400	200	295
SO_2 removal efficiency	%	80	85	95
NO_x removal efficiency	%	18	55	70
Electron beam parameters	keV	800	800	700
	mA	2 × 400	2 × 400	4 × 375

-power diesel engines fuelled with different heavy fuel oils [10–12].

Experimental

Test facility

The study was performed in the laboratory plant at the Institute of Nuclear Chemistry and Technology (INCT) in Warsaw [7], which was additionally equipped with the dosing systems of gaseous SO_2 and NO from gas cylinders and the seawater scrubber. Figure 6 presents the flow diagram of test facility. The exhaust gas with high NO_x concentration was simulated by the gas mixture containing exhaust gas from burning light fuel oil to which gaseous SO_2 and NO from gas cylinders were dosing. Such gas mixture was irradiated in the process vessel (point 8 in Fig. 6) under which the scanner of electron accelerator ILU-6M (800 keV, max. beam power up to 20 kW) was installed. Two independent extractive monitoring systems were applied for continuous measurement of SO_2 and NO_x concentration in the simulated gas at two crucial points of the plant: at the process inlet (before irradiation, point 6 in Fig. 6) by first system labeled System 1 and at the process outlet (point 12 in Fig. 6) by second system labeled System 2. The flow rate of the model gas mixture was 5 m^3/h. The residence time of gas mixture in the process vessel was equal to 18 s. The natural gas humidity was 8.48 vol.% and was not changed during the all tests.

Results and discussion

The parametric studies were carried out in two steps. In the first step simulated gas mixture was irradiated only by electron beam. In the second step simulated gas mixture undergo the hybrid process of electron beam irradiation plus seawater scrubbing.

First step of parametric studies

The influence of gas absorbed energy dose (in short, dose) and inlet NO_x concentration (NO_x^0) on NO_x removal efficiency is presented in Fig. 7.

The absorbed dose is a primary factor influencing NO_x removal. The process starts at zero efficiency for zero dose and indicates saturation at high dose. Higher NO_x removal was achieved with higher dose and with lower NO_x^0 concentration. The active species (free radicals OH and HO_2, atoms O, N and H, ions and secondary electrons) formed in plasma reactor by electron beam irradiation oxidize SO_2 and NO to SO_3 and NO_2 which in reaction with water vapor (present in exhaust gas) form H_2SO_4 and HNO_3, respectively. NO_x removal is strongly affected by inlet

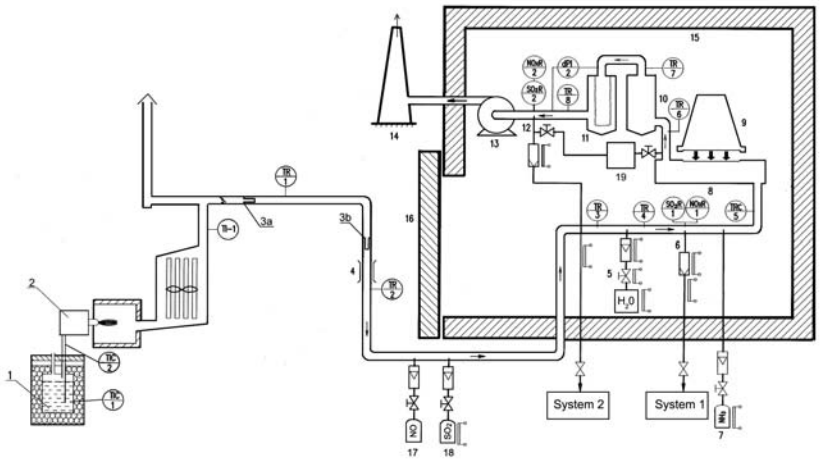

Fig. 6. Flow diagram of the test facility. 1 – termostated fuel oil; 2 – oil burner; 3a – soot filter; 3b – particulate filter; 4 – orifice; 5 – dosage of water vapor; 6 – gas sampling point – process inlet; 7 – ammonia injection; 8 – plasma reactor; 9 – electron beam accelerator; 10 – retention chamber; 11 – bag filter; 12 – gas sampling point-process outlet; 13 – induced-draught fan; 14 – stack; 15 – concrete shielding wall; 16 – concrete shielding door; 17 – NO dosage setup; 18 – SO_2 dosage setup; 19 – seawater scrubber.

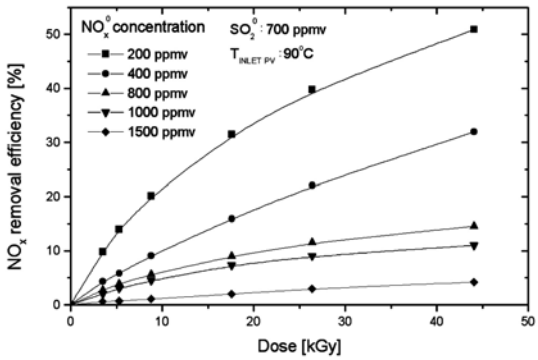

Fig. 7. Effect of absorbed dose on NO_x removal efficiency.

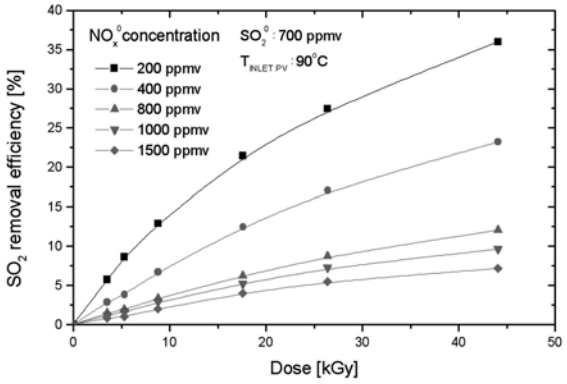

Fig. 8. Effect of absorbed dose on SO_2 removal efficiency.

NO_x concentration. Lower NO_x removal efficiencies were obtained with increasing NO_x^0 concentration even if applied high irradiation doses.

Figure 8 presents the influence of dose and inlet NO_x concentration on SO_2 removal efficiency.

Table 2. SO_2 and NO_x removal efficiencies from gas mixtures irradiated in the process vessel at the following conditions: SO_2^0 – 700 ppmv, gas temperature – 90°C and dose – 17.6 kGy

Inlet NO_x [ppmv]	Removal efficiencies [%]	
	NO_x	SO_2
200	31.41	21.43
400	15.92	12.43
800	9.00	6.20
1000	7.32	5.18
1500	1.97	3.97

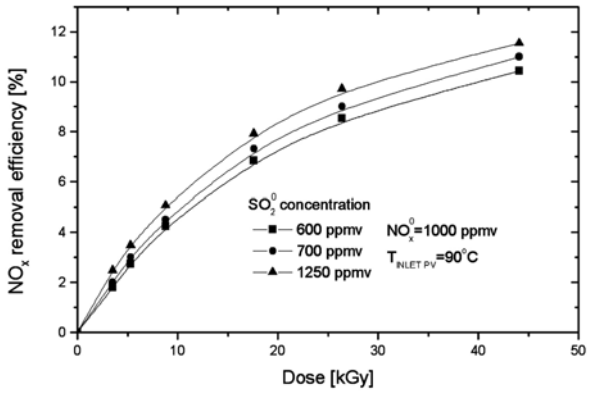

Fig. 9. Effect of inlet SO_2 concentration on NO_x removal efficiency.

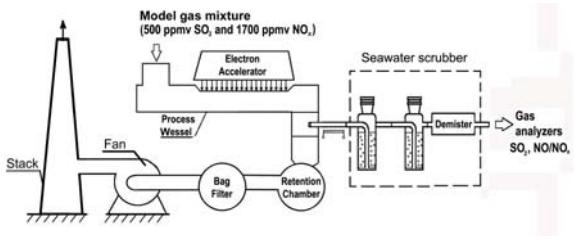

Fig. 10. The schematic diagram of the test facility during the second step of the study.

Electron beam treatment of these gas mixtures with NO_x concentrations above 800 ppmv ensures low NO_x and SO_2 removal efficiencies. Table 2 presents the summary of the removal efficiencies of both pollutants for different inlet NO_x concentrations.

The high inlet SO_2 concentration (SO_2^0) in the exhaust gas enhances NO_x removal (Fig. 9). During e-beam irradiation OH radicals are produced that play the major role in simultaneous oxidation of NO and SO_2 to their respective acids. In the SO_2 oxidation are formed of strongly oxidizing radicals HO_2 which effectively oxidized NO with regeneration the previously depleted OH radicals. This process is explained by the following radiation-induced reactions cycle:

$$SO_2 + {}^{\bullet}OH + M \rightarrow HSO_3 + M$$
$$HSO_3 + O_2 \rightarrow SO_3 + HO_2^{\bullet}$$
$$NO + HO_2^{\bullet} \rightarrow NO_2 + {}^{\bullet}OH$$
$$NO_2 + {}^{\bullet}OH + M \rightarrow HNO_3 + M$$

Second step of parametric study

In this step the combined process of e-beam irradiation plus seawater scrubbing was tested. E-beam irradiation of exhaust gas converts insoluble NO (about 95% of NO_x) to fairly soluble NO_2 which may be easily removed with the wet scrubber. Seawater is around each ship. It is expected that such solution ensures higher removal efficiency of SO_2 and NO_x. Figure 10 presents the schematic diagram of the test facility during the second step of study.

One part of irradiated model gas mixture, leaving process vessel (PV), was directed to the seawater scrubber for further purification. The rest of irradiated model gas mixture passed through the retention chamber, the bag filter and was exhausted through the stack. Figure 11 presents the general view of the test facility.

Figure 12 presents scheme of the seawater arrangement selected for the test facility.

The sample gas passed through two bubbling washers (point 2 in Fig. 12) filled with seawater. Each bottle has a fine fritted dip disc which disperses gas into the millions of small droplets, multiplying the surface area for gas-liquid contacts to ensure high scrubbing efficiency and thereby encouraging transfer species from gas to water. The gas leaving these devices contains droplets of seawater. The demister was installed to precipitate these droplets. Gas leaving the demister was sent to the set of gas analyzers from System 2 to determine the SO_2 and NO/NO_x concentrations in the such treated gas. Additionally, five manually operated shut off valves (V_1,

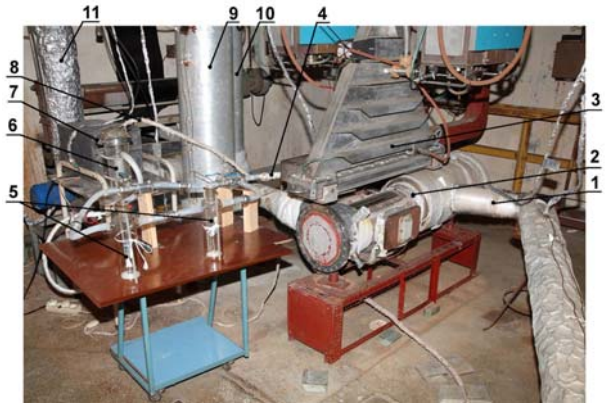

Fig. 11. The general view of the test facility during the second part of the study. 1 – inlet to process vessel; 2 – process vessel with secondary titanium window; 3 – scanner of ILU-6M electron accelerator; 4 – heated sample probe for the seawater scrubber; 5 – two bubbling washers filled with seawater; 6 – demister; 7 – heated sample gas filters; 8 – heated sampling line for set of gas analyzers; 9 – retention chamber; 10 – bag filter; 11 – stack.

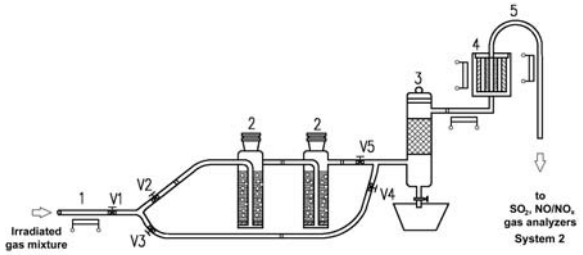

Fig. 12. Scheme of the seawater scrubber arrangement. 1– heated sample probe; 2 – bubbling washer filled with seawater; 3 – demister; 4 – heated ceramic filters; 5 – heated sampling line; V1, V2, V3, V4, V5 – shut off valve manually operated.

V_2, V_3, V_4, V_5 in Fig. 12) were installed to select the way of irradiated gas mixture. When valves V_1, V_2, and V_5 were opened and valves V_3 and V_4 were shut off, it was possible to study the combined process (e-beam process plus seawater scrubber). When valves V_1, V_3 and V_4 were opened and valves V_2 and V_5 were shut off it was possible to determine SO_2 and NO_x removal efficiency only by the e-beam process. The seawater was prepared by addition of suitable amount of pure sodium chloride (NaCl) to the distilled water. Typical seawater contains 3.5 wt% of NaCl.

Figure 13 presents NO_x removal efficiencies obtained in two runs with the purification of model gas mixture containing 400 ppmv of NO_x and 700 ppmv of SO_2 using electron beam irradiation (first run) and combined process (second run). Higher NO_x removal efficiency was obtained in the second run. The scrubbing process enhances removal efficiencies of SO_2 and NO_x. The SO_2 removal efficiencies greater than 98.5% were obtained in the combined process with irradiation dose greater than 5.3 kGy. During the scrubbing process the pH of seawater in the bubbling washers was decreased from initial values about 6.0 to 3.1 in the first bubbler and 4.1 in the second bubbler.

Figure 14 presents the effect of seawater salinity on the NO_x removal efficiency in the combined process. NO_x removal efficiency increases with increase

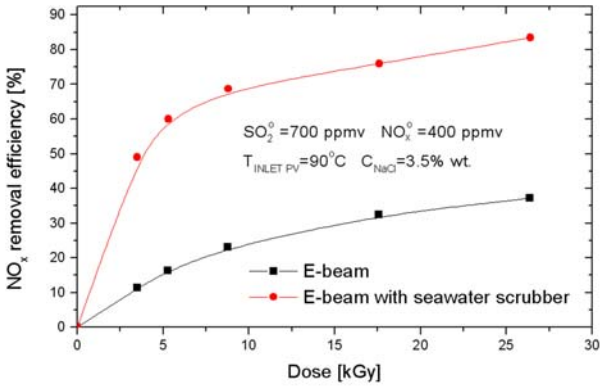

Fig. 13. Comparison of NO_x removal efficiencies obtained only in e-beam process and in e-beam process combined with seawater scrubber.

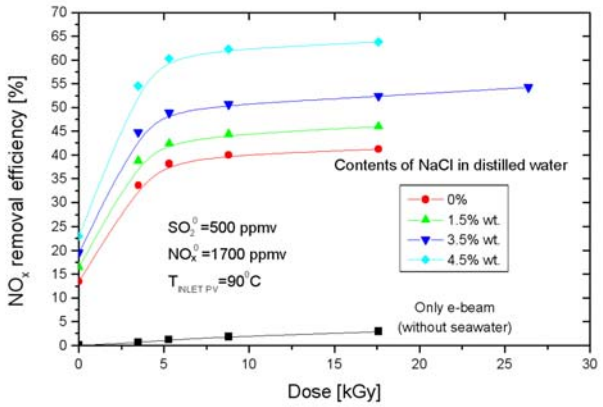

Fig. 14. Effect of seawater salinity on the NO_x removal efficiency obtained in the e-beam process combined with seawater scrubber.

seawater salinity. The scrubbing process is more effective in the more saline waters.

Table 3 presents the effect of gas temperature at the process vessel inlet on the SO_2 and NO_x removal efficiency in the combined process. NO_x removal efficiency increases with increase of irradiated gas temperature.

Table 4 presents the summary of the effect of inlet SO_2 concentration on NO_x removal efficiency obtained in the combined process.

High inlet SO_2 concentration enhances NO_x removal efficiencies. Such improvement was already observed in the e-beam process.

Conclusions

Tests with the purification of simulated exhaust gases from marine diesel engines were performed in the INCT laboratory plant. As first, the electron beam flue gas treatment technology was applied. The simultaneous removal of SO_2 and NO_x was obtained. Their removal efficiency strongly depends on irradiation dose, inlet NO_x concentration, and inlet gas temperature. For NO_x concentration above 800 ppmv, low NO_x and SO_2 removal efficiencies were obtained even if high irradiation doses were applied. In the second part of study, the irradiated gases (after e-beam process) were directed to the seawater scrubber for

Table 3. Effect of gas temperature on NO_x and SO_2 removal efficiencies in the combined process. The experimental conditions: SO_2^0 = 500 ppmv, NO_x^0 = 1700 ppmv, dose = 8.8 kGy, C_{NaCl} = 3.5 wt%

Parameter	Unit	Value		
Gas temperature	°C	70	90	100
NO_x removal efficiency	%	48.02	50.57	51.95
SO_2 removal efficiency	%	98.15	97.06	96.00
Final pH value of seawater in the bubbler:				
– first	–	3.220	3.176	3.067
– second	–	3.824	3.748	3.706

Table 4. Effects of the inlet high SO_2 concentration on NO_x removal efficiency obtained in the combined process. The experimental conditions: NO_x^0 = 1700 ppmv, $T_{INLET\ PV}$ = 90°C, dose = 8.8 kGy, C_{NaCl} = 3.5 wt%

Parameter	Unit	Value		
Inlet SO_2 concentration	ppmv	0	500	1000
NO_x removal efficiency	%	46.01	50.57	51.20
Final seawater pH in the bubbler:				
– first	–	3.606	3.176	2.846
– second	–	3.910	3.748	3.661
Change of seawater temperature in the bubbler:				
– first	°C	0.1	0.3	0.5
– second	°C	0.2	0.3	0.6

further purification. High SO_2 removal up to 99% and NO_x up to 51% were obtained for exhaust gases with 1700 ppmv of NO_x concentration. Scrubbing process ensures high removal efficiencies because:

- electron beam process converts insoluble NO (about 95% of NO_x) to fairly soluble and reactive NO_2 which may be removed with wet scrubber. The SO_2 is also oxidized to SO_3. Such formed NO_2 and SO_3 in reaction with water vapor, presented in exhaust gases, form nitric and sulfuric acids, respectively,
- scrubber consisted of two bubbling washers filled with seawater and demister. Each bubbling washer was equipped with a fine fritted dip disc which disperses gas into the millions of small droplets, multiplying the surface area for gas-liquid contacts to ensure high scrubbing efficiency and thereby encouraging transfer species from gas to water,
- during the scrubbing process the pH value of seawater drops to about 3.0 which makes very good medium for scrubbing of NO_x.

In the combined process, SO_2 and NO_x removal efficiencies were strongly dependent on the irradiation dose and salinity of seawater. Irradiated gas temperature dependence was moderate. The presence of high SO_2 concentration in the exhaust gases enhances NO_x removal efficiency. Thus such solution is preferable for engines fuelled with high sulfur fuel oil.

The Tier II requires 80% reduction of NO_x concentration in the exhaust gases from marine diesel engine. In the performed tests NO_x removal efficiencies up to 51% were obtained. Further increase of NO_x removal may be obtained by addition to the seawater a reducing solution to reduce NO_2 to N_2 with minimum byproducts. Such tests will be performed at INCT laboratory plant. A remarkable reduction of energy consumption in the e-beam process can be achieved with multistage exhaust gas irradiation. Tests performed in Kawęczyn pilot plant have demonstrated about 10–15% reduction by double irradiation [13].

Acknowledgments. This work was supported by the Ministry of Science and Higher Education, project W141/7.PR UE/2014 "The industrial and environmental application of electron beams".

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