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TECHNICAL NOTE

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Plasma technology to remove NO_x from off-gases

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Abstract. Operation of marine diesel engines causes significant emission of sulphur and nitrogen oxides. It was noticed worldwide and the regulations concerning harmful emissions were introduced. There were several solutions elaborated; however, emission control for both SO_x and NO_x requires two distinctive processes realized in separated devices, which is problematic due to limited space on ship board and high overall costs. Therefore, the electron beam flue gas treatment (EBFGT) process was adopted to ensure the abatement of the problem of marine diesel off-gases. This novel solution combines two main processes: first the flue gas is irradiated with electron beam where NO and SO_2 are oxidized; the second stage is wet scrubbing to remove both pollutants with high efficiency. Laboratory tests showed that this process could be effectively applied to remove SO_2 and NO_x from diesel engine off-gases. Different compositions of absorbing solution with three different oxidants (NaClO, $NaClO_2$ and $NaClO_3$) were tested. The highest NO_x removal efficiency (>96%) was obtained when seawater-$NaClO_2$-NaOH was used as scrubber solution at 10.9 kGy dose. The process was further tested in real maritime conditions at Riga shipyard, Latvia. More than 45% NO_x was removed at a 5.5 kGy dose, corresponding to 4800 Nm^3/h off-gases arising from ship emission. The operation of the plant was the first case of examination of the hybrid electron beam technology in real conditions. Taking into account the experiment conditions, good agreement was obtained with laboratory tests. The results obtained in Riga shipyard provided valuable information for the application of this technology for control of large cargo ship emission.

Keywords: Electron beam • Flue gas treatment • Marine diesel engines • NO_x • SO_x • Ship emissions

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Introduction

According to the literature data [1], sea transport is responsible for 15% of global emission of nitrogen oxides and 5–8% of global emission of sulphur oxides. This problem is of great importance because 70% of sea transport emission is generated not longer than 400 km from the land. For better understanding of the magnitude of sulphur and nitrogen oxides emission, it is worthwhile to notice that in 2000 the emission around Europe (area of Baltic Sea, North Sea, north-east part of Atlantic, Mediterranean Sea and Black Sea) of the pollutants was estimated at 2.3 million tons of SO_2, 3.3 million tons of NO_x and 250 thousand tons of particles. It is supposed that in 2020 such numbers would have been 40–50% greater [2].

The problem was noticed worldwide and the regulations concerning SO_2 and NO_x emissions were introduced. The most important are International Maritime Organization (IMO) ship pollution rules, known as MARPOL convention. According to Annex VI of the convention SO_2, emissions shall be reduced to 2 g/kWh that corresponds with

0.5% sulphur content in fuel. In Sulphur Emission Control Areas (SECAs), such emission is limited to 0.4 g/kWh, which corresponds with 0.1% S [3]. For comparison, typical sulphur content in heavy fuel oil used in marine engines is about 3%, which means 12 g/kWh emission level.

In the case of nitrogen oxides, the emissions are also strictly limited. According to MARPOL convention, NO_x emission standard depends on ship production date and rotation speed of engine and for newly constructed ships (after 2016) it varies from 2.0 g/kWh to 3.4 g/kWh, which means the emission reduction at the level of 80% is required [4].

There are several solutions to ensure compliance: application of the low-sulphur fuels (marine diesel), switching to LNG [5] or instalment of the seawater scrubbing systems [6] for SO_2 emission control. In the case of NO_x, fuel combustion process modification (engine modification) [7] or selective catalytic reduction (SCR) process are used [8]. All of these processes have their inherited limitations. Low-sulphur fuel may be harmful for older engines and is much more expensive than regular marine diesel fuel. Similarly, combustion process modification has limited NO_x emission reduction efficiency. Therefore, today the most popular solution in marine industry is combination of seawater scrubbing for SO_2 and SCR for NO_x emission control. However, these are two distinctive processes realized in two separate devices and require application of the specific process parameters (e.g. temperature) as well as costly control and maintenance solutions.

In this case, electron beam flue gas treatment (EBFGT) technology allowing for simultaneous removal of both pollutants in one process may be an alternative. The technology was already applied in the power industry and further research on its development has been carried out in the Institute of Nuclear Chemistry and Technology (INCT). During the research carried out in the Institute, the process was adopted in-lab to the marine diesel flue gases treatment conditions.

In this novel technology, called hybrid EBFGT process, two main processes were combined. In the first step, flue gasses are irradiated for oxidation of NO and SO_2 to higher oxides, while in the second step the pollutants are being absorbed into aqueous solution by wet scrubbing process. It allows simultaneous removal of both SO_x and NO_x with high efficiency. The idea of the process is presented in Fig. 1.

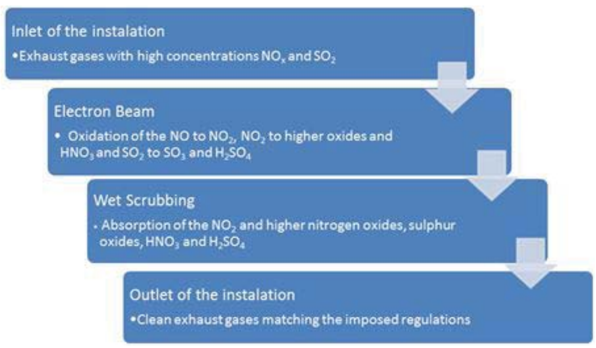

Fig. 1. The concept of hybrid EBFGT process.

Laboratory tests

The first stage of the research on hybrid electron beam technology was conducted in the laboratory of the INCT in batch mode; 5 Nm^3/h of flue gas was irradiated, while 100 l/h was bypassed to the wet scrubber for 15 min. Inlet NO_x concentration was 1500 ppm. During this research, several scrubbing solutions such as 3.5% sodium chloride (simulated seawater), sodium hydroxide solution or simulated seawater with oxidant addition were applied. The highest efficiency of NO_x removal (89.6%) was obtained in combined electron beam – wet scrubbing process where simulated seawater and $NaClO_2$ with phosphate buffer were applied to perform the function of scrubbing solution [9]. A comparison of process efficiencies between method of sole electron beam and a hybrid technology, coupling electron beam with a wet scrubber in two cases – with simulated seawater and with simulated seawater and $NaClO_2$ addition with phosphate buffer – is presented in Fig. 2.

As the application of oxidants results in remarkable increase of NO_x removal efficiency in hybrid EBFGT process, several oxidants (NaClO, $NaClO_2$ and $NaClO_3$) were examined. The most promising results were achieved when sodium chlorite ($NaClO_2$) buffered with phosphate buffer (Na_2HPO_4–KH_2PO_4) was applied [10]. The results of the research are presented in Fig. 3.

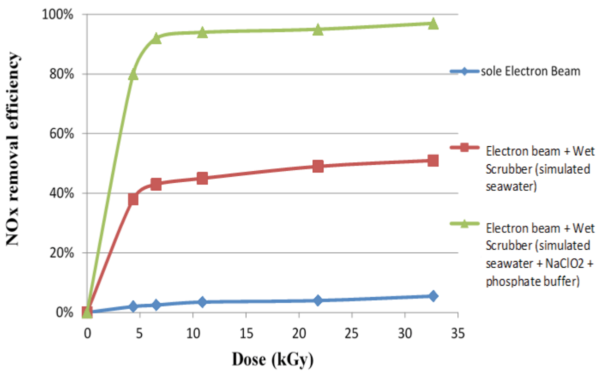

Fig. 2. Comparison of process efficiencies between sole electron beam and hybrid electron beam process with simulated seawater and simulated seawater and $NaClO_2$ addition with phosphate buffer [9].

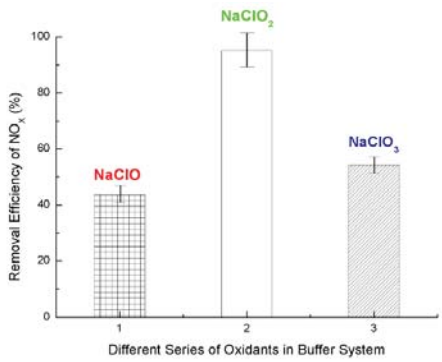

Fig. 3. Comparison of hybrid electron beam wet scrubber process with the addition of different oxidants in the seawater buffered with phosphate buffer solution [10].

Fig. 4. Photo of EBFGT pilot laboratory flow system. Wet scrubber (left) and process vessel (right) under ILU 6 electron accelerator scanning horn.

The researches were continued with use of large laboratory scale installation (Fig. 4) operated in continuous mode. In this part of research, NO_x removals of high inlet concentrations (about 3000 ppm) were examined. Flue gas flow rate was 5 Nm^3/h. In these tests, 3.5% sodium chloride solution as simulated seawater with addition of 10 mM sodium chlorite as oxidizing agent was applied; however, instead of phosphate buffer, sodium hydroxide was used. pH of the scrubbing solution was controlled by pH meter and kept over 7.5, which is the natural pH of seawater.

The obtained NO_x removal efficiencies were about 90% for 10.9 kGy dose. During the experiments, it was noticed that spraying some amount of scrubbing solution inside reaction chamber may remarkably increase NO_x removal efficiency. The obtained result for 10.9 kGy dose was as high as 97% (Fig. 5).

Proof-of-concept tests in real marine environment

Field scale tests (on shore) were realized in the frame of the project "PoC Development of Hybrid Electron Accelerator System for the Treatment of Marine Diesel Exhaust Gases" (ARIES) [11]. The main goal of this project was to demonstrate hybrid EBFGT technology for efficient removal of SO_2 and NO_x from marine diesel engine flue gases. The project was realized in Riga Shipyard (Latvia) in international cooperation between Riga Technical University, Center of High Energy Physics and Accelerator Technologies – RTU (Riga, Latvia), Institute of Nuclear Chemistry and Technology – INCT (Warsaw, Poland), The European Organization for Nuclear Research – CERN (Geneva, Switzerland), Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology – FEP (Dresden, Germany), Remontowa Marine Design – Remontowa (Gdansk, Poland), Milgravja Tehnoloģiskais Parks – Riga Shipyard – RKB (Riga, Latvia) and BIOPOLINEX Sp. z o.o. (Lublin, Poland).

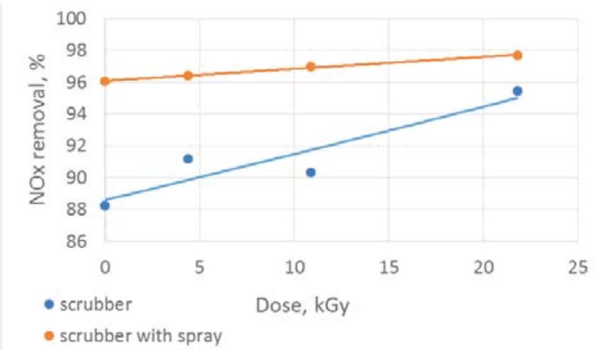

Fig. 5. NO_x removal efficiency in hybrid electron beam wet scrubbing system with and without scrubbing solution spraying inside reaction chamber (3.5% NaCl-NaOH-10 mM $NaClO_2$ as scrubbing solution SO_2: 716 ppm; NO_x: 2263 ppm).

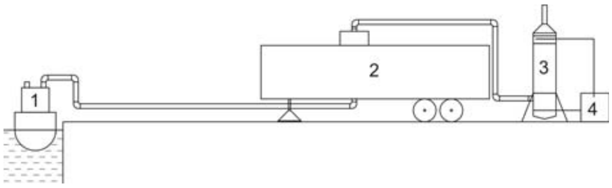

Fig. 6. General scheme of pilot hybrid EBFGT plant. 1 – flue gas source, 2 – mobile accelerator, 3 – scrubber, 4 – seawater tank.

Fig. 7. Photo of EBFGT installation at Riga Shipyard. Mobile accelerator unit (right) and wet scrubber (left).

Pilot hybrid electron beam marine flue gas treatment facility located in Riga Shipyard consisted of the following units:

– flue gas ship diesel engine,
– mobile electron beam unit,
– seawater scrubbing unit,
– scrubbing solution closed loop system, and
– measurement and monitoring system.

The general scheme of the pilot plant is presented in Fig. 6 and the photo of the system in Fig. 7.

A tugboat "Orkāns" of Riga Shipyard, equipped with double two-stroke 450 kW diesel engines, berthed at the pier, was used as the source of flue gas. Outlet of gas pipe of one of the engines was flexibly connected to irradiation device by 320 mm steel pipe.

A mobile accelerator manufactured by Fraunhofer FEP, Germany, was used as an irradiation device. This device was originally designed for seed irradiation and was adopted to flue gas processing for the purposes of this project. Irradiation chamber of rectangular cross section (120 mm × 1560 mm) and 1180 mm height was applied. Gas flowed vertically from bottom to top direction and was irradiated from both sides by two 125 kV accelerators of 100 mA beam current.

Seawater scrubbing was realized in counter-current, packed scrubber. The device diameter was

1.2 m and its height was 5.5 m. Scrubber was filled with Bialecki rings, and filling height was 2.6 m. A closed loop system was applied for seawater circulation in the scrubber. Two tanks filled with 3 m^3 of seawater were used as a scrubbing solution storage in the closed loop system. The water from the tanks was filtered and pumped to a system of nozzles located at the top of the scrubber and sprayed at the top of the filling, and then flowed to the bottom of the device and back to the tanks by gravity. The gas from the irradiation unit was directed to the lower part of the scrubber and was released to the atmosphere by a stack located at the top of the device.

The whole amount of flue gas generated by marine diesel engine (4500–4900 Nm^3/h) of 230–700 ppm NO_x concentration was treated in the system. After engine ignition, the scrubber pump was switched on and required water flow rate was set. Water flow rate was measured by a rotameter. At the same time, the accelerator was started, and after stabilizing of gas flow rate, the gas parameters were recorded.

Water tanks were filled up with Baltic Sea water before the series of experiments. As the salinity of the Baltic Sea is very low (0.7%), 90 kg of NaCl was added to the tanks to increase the salt content to mean salinity of seawater (about 3.5%). The solution was not changed during the whole cycle of experiments. To keep the ability of seawater for acidic gases absorption, pH of the solution was kept over 7.5 by addition of sodium hydroxide. The pH of the scrubber solution was controlled by 3210 Set2 pH meter manufactured by WTW (Germany). To enhance the oxidation potential of the solution and improve the NO_x removal efficiency, $NaClO_2$ as an oxidant was added to the circulating water. A total amount of 10 kg of oxidant was added, leading to 3.3 g/l concentration of this agent.

The measured NO_x removal efficiencies were in good correlation with previously obtained results; however, maximal NO_x removal rates did not exceed 45% (Fig. 8). Observed low NO_x removal rates may be explained by the low doses applied, and they are caused by disrupted functionality of the accelerator system mounted on the both opposite sides of process vessel. One accelerator operation resulted in the fact that only half of the possible dose was available and dose distribution was not uniform due to low penetration range electrons (electron energy was 125 keV). Part of the gas stream flowing opposite to the operated accelerator window received a low absorbed dose. As NO oxidation and further absorption strongly depends on the absorbed dose, such a situation leads to decrease of overall NO_x removal rates.

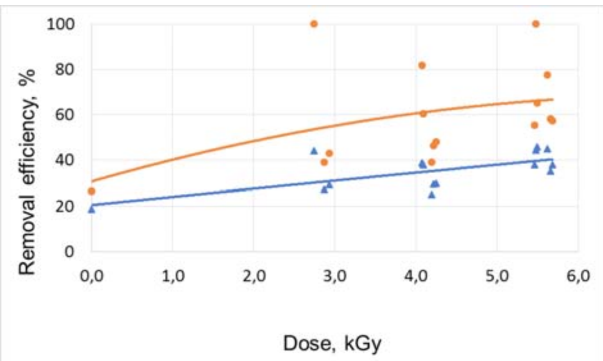

Fig. 8. NO and NO_x removal rates obtained during pilot plant tests.

It is important to note that the pilot plant tests performed in Riga Shipyard was the first attempt to demonstrate hybrid electron beam technology in real conditions. Therefore, one of the primary objectives of this experiment was testing integration of diesel engine with accelerator and scrubber as such. This resulted in a successful conclusion and this novel technology was demonstrated, confirming that the system and its arrangements are fully implementable in real field conditions. It is a significant milestone for the proliferation of the accelerator technology to the marine environment.

Conclusions

Both laboratory and field scale tests showed that hybrid EBFGT method is very promising technology to remove SO_2 and NO_x from diesel engine flue gases.

Application of $NaClO_2$ as oxidation agent in the wet scrubbing solution highly increases NO_x removal efficiency in hybrid EBFGT process.

The highest NO_x removal efficiency (>96%) was obtained when seawater-$NaClO_2$-NaOH was used as scrubber solution with additional injection of scrubber solution inside the reaction vessel.

The operation of the pilot plant was the first case of examination of the hybrid electron beam technology in the real field conditions, where it showed ability of the technology to be used in marine conditions. Taking into account the experiment conditions, good agreement was obtained with laboratory tests in the maximum available at-field test dose range.

The combination of accelerator technology with wet scrubbing process is an innovative solution for simultaneous treatment of SO_x, NO_x and PM from marine diesel engine flue gases. Successful ARIES proof-of-concept tests in Riga Shipyard have demonstrated results that are opening opportunities for further on board tests and application of the on board technology of the sea-going ships on regular routes.

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