ARIES

Accelerator Research and Innovation for European Science and Society

Horizon 2020 Research Infrastructures GA n° 730871

DELIVERABLE REPORT

Applications of electron beams in the environmental area

DELIVERABLE : D.3.1

Document identifier:	ARIES-D.3.1.
Due date of deliverable:	End of Month 24 (April 2019)
Report release date:	02/04/2019
Work package:	WP3: Industrial and Social Applications (ISA)-NA
Lead beneficiary:	INCT
Document status:	Final

ABSTRACT

This report presents recent industrial pilot and full scale applications of electron accelerators for flue gas treatment. The engineering solutions regarding accelerators and process equipment developments are discussed. New possible applications of accelerator technology for other environment applications, like marine diesel off-gases purification, ship ballast water treatment and municipal wastewater treatment plants sludge hygenization are reviewed. The conclusions of the report support a broad possibility of technology applications, however their acceptance by industry depends on the availability of reliable accelerators at competitive prices.

For more information on ARIES, its partners and contributors please see http://aries.web.cern.ch

This project has received funding from the European Union's Horizon 2020 Research and Innovation programme under Grant Agreement No 730871. ARIES began in May 2017 and will run for 4 years.

Delivery Slip

	Name	Partner	Date
Authored by	A. G. Chmielewski	INCT	13/02/2019
Reviewed by	R. Edgecock [WP coordinator]	[HUD	18/02/2019
Approved by	Steering Committee		02/04/2019

TABLE OF CONTENTS

Executive summary

The powerful tools of ionizing radiation, electron accelerators, have been used for radiation processing of materials for more than half a century. However, the possibility of radiation applications for environmental pollution control was realized in the 1970s, when environmental protection agencies were established and standards for pollutant emission limits were set. The special input for the application of the technology was the development of new high power electron accelerators which can be used for on-line processing of huge flow streams of liquid or gaseous pollutants. This report presents recent industrial pilot and full scale applications of electron accelerators for flue gas treatment. Two pilot plants were built to purify flue gases from power station boilers, one using coal as a fuel and the second heavy oil fired. Finally the big industrial installation for the coal fired boiler using four accelerators of total power bigger than 1 MW is described. In all cases transformer accelerators were applied due to the high plug-to-beam energy efficiency. The positive results of these industrial projects, which were managed by one of ARIES consortium member – INCT, were the basis for further research on the other environmental applications of electron accelerators. The R&D works related to the ARIES activities, are: marine diesel off-gases purification, ship ballast water treatment and municipal wastewater treatment plants sludge hygenization. The conclusions of the report support the broad possibility of these technology applications, however their acceptance by industry depends on availability of reliable accelerators at competitive prices. All of these applications are creating a new challenge for accelerator manufacturers and the cooperation of ARIES teams with industry may lead to these new successful applications which are very important for the environment and human health and safety.

1. Introduction

The powerful tools of ionizing radiation, electron accelerators, have been used for radiation processing of materials for more than half a century. However, the possibility of radiation applications for environmental pollution control was realized in the 1970s, when environmental protection agencies were established and standards for pollutant emission limits were set. The special input for applications of the technology was the development of new high power electron accelerators which can be used for on-line processing of huge flow streams of liquid or gaseous pollutants. The accelerators were employed for off-gas and wastewater treatment and disinfection testing of biological sludge from a wastewater treatment plant. A review of the R & D work and its implementation are covered in papers [1,2]. A variety of industrial electron accelerators can now provide electron energies from 0.3 MeV to more than 10 MeV, with average beam power capabilities of over 300kW[3]. However further development in accelerator construction is needed, as most of environmental applications require continuous machine operation in harsh conditions like power plants, wastewater treatment plants, municipal waste incinerators, ship diesel compartments, etc. In some cases, the required operation time exceeds 8000 hours annually. Therefore further developments in accelerator engineering are needed, in particular the application of new materials for electron exit windows, cathode and other components, higher plug-to-beam energy efficiency, etc. These developments can be achieved by synergy and diffusion of new developments and solutions from other ARIES work packages. The basis for planning of these requirements are experiences of the electron accelerator applications in industrial conditions in the projects developed by INCT. The current applications of electron beam accelerators up to 10 MeV in R&D study and industrial implementation were reviewed by Zimek in the report prepared under ARIES MS-13 [4]. Moreover, electron accelerator environmental applications are driven by new environment protection standards, like the International Maritime Organization (IMO) regulations regarding SO_x and NO_x control in Emission Control Areas; IMO regulations regarding ballast water microbiological control, an EU directive imposing a ban on landfill storage of municipal wastewater plant sludge, etc. These are the new fields of possible electron accelerator application, however further research on these technologies is needed. All of these applications are creating a new challenge for accelerator manufacturers and the cooperation of ARIES teams with industry may lead to new methods for successful applications which are very important for the environment and human health and safety.

2. History of Electron Accelerator Environmental Applications Developed and Implemented by INCT

2.1. ELECTRON BEAM FLUE GAS TREATMENT (EBGFT)

Air pollution is an important issue among present day society, with people living in big cities at the greatest risk of harm. Despite the fact that air quality has risen significantly in comparison to the last century, there is still a lot of room for improvement. According to WHO (World Health Organization), more than 80% of people living in cities and towns are affected by the air pollution which exceeds safe norms set by WHO with countries of low economic status suffering the most from toxic pollutants. The observed emission of pollutants and environmental degradation are reasons why the most developed countries have introduced emission limits; mostly such action started at the end of the twentieth century. Fossil fuel combustion leads to acidic pollutants such as SO_2 , NO_x , HCl emission. Different control technologies are proposed; however, the most popular method is a combination of wet FGD (flue gas desulfurization) and SCR (selective catalytic reduction). The first, using lime or limestone slurry leads to SO_2 capture and gypsum as a product. In the second process, ammonia is used as a reagent, and nitrogen oxides are reduced over a catalyst surface to gaseous nitrogen, which removes NOx. A new advanced method uses EB for simultaneous SO_2 and NO_x removal. Early possibilities for EB applications in pollution control have been reported. The pioneering works in these applications were from Takasaki, Japan. The special input for the technology application was the development of the new high power electron accelerators, which can be used for the processing on line of the huge flow streams of liquid or gaseous pollutants.

2.1.1. Pilot plant for EBFGT at coal fired power station

The pilot plant with a capacity of 25,000 Nm^3/h [5] was constructed at the Power Station Kawęczyn (Fig.1), which provides heat for Warsaw's central heating system. It uses coal as a fuel. Three boilers were operated at the time of pilot plant testing.

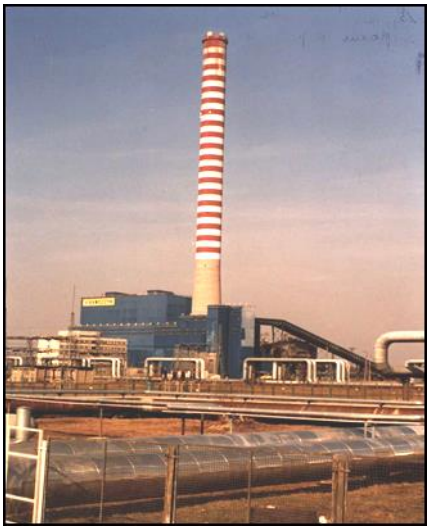

Fig.1 Power Station Kawęczyn.

It was installed on a bypass of the main flue gas stream from the boiler WP - 120. The flue gases are cooled in a spray cooler working under "dry-bottom" conditions and then irradiated in two stages in the reaction vessel, which is 7 m long cylinder and 1.6 mm diameter. A double titanium window system was employed. An "air curtain" was used to separate the secondary window from the corrosive flue gas. Gaseous ammonia is injected by nozzles upstream of flue gas irradiation. The aerosol formed in the process (ammonium sulfate and nitrate) consists of small solid particles with a diameter of less than 1 μm. Three types of filters were tested - bag filter, gravel bed filter and electrostatic precipitator. Finally, the electrostatic precipitator constructed by ELWO SA, Pszczyna, was applied as a byproduct collector. The scheme of the installation is presented in Fig.2.

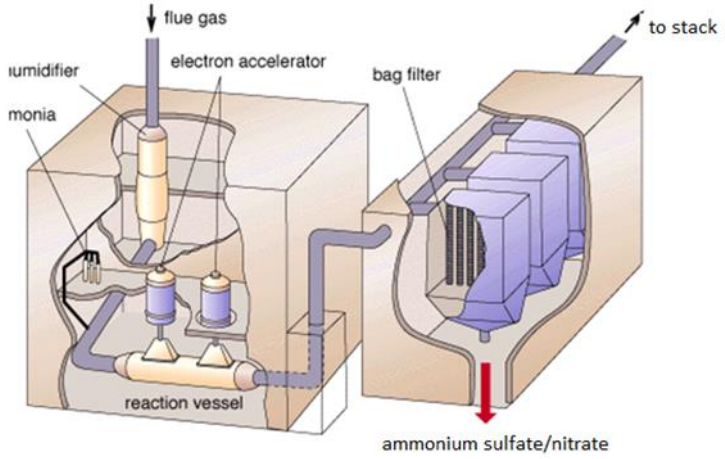

Fig.2 Scheme of EBFGT pilot plant.

Two accelerators ELV-3a (50 kW, 700 keV) were installed in series on a reaction vessel. For the first time in the case of industrial pilot installation a two-stage gas irradiation cascade was applied. The view of accelerator is presented in Fig.3.

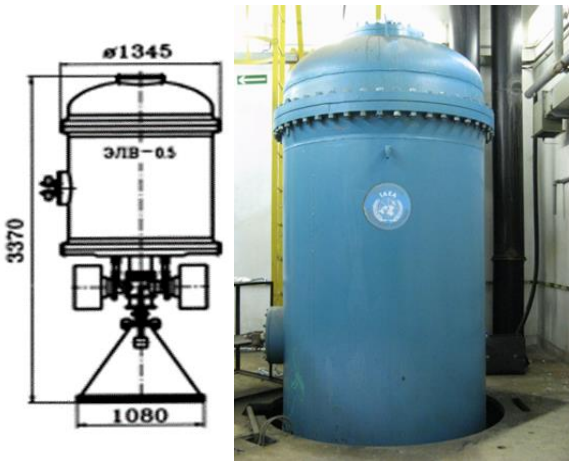

Fig.3 The view of accelerator ELV-3a applied at the pilot plant (two units installed).

The longitudinal gas irradiation was applied and a double stage irradiation was introduced in this case (Fig. 4). This solution leads to the energy efficiency increase by at least 10%. The other solution applied was an air curtain to prevent corrosion of the secondary window [6]. A titanium foil 50 μm thick was used as the material for both widows..

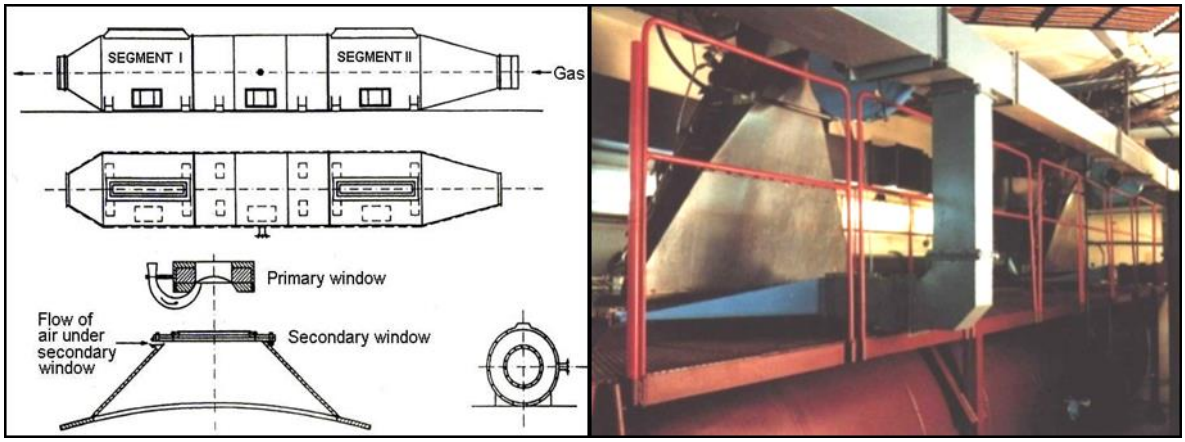

Fig. 4 Cross section of process vessel (left) and view of two scanning accelerator horns mounted on the top of it (right).

The energy of electrons has to be well selected taking into account the irradiation vessel diameter and the foil thickness, and is presented in Fig. 5. The curves present energy losses vs. electron beam energy.

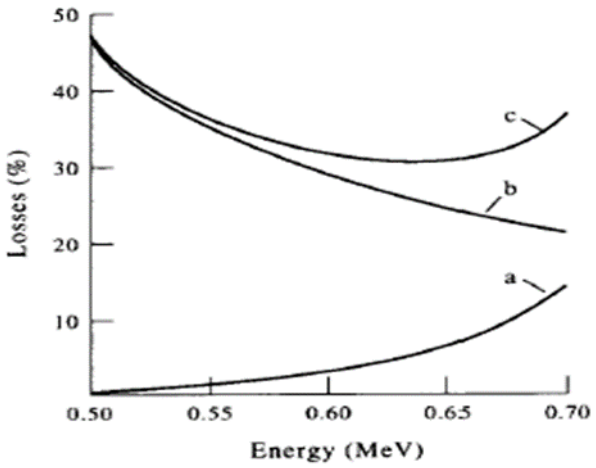

Fig. 5 Energy losses vs. electron beam energy (a-bottom wall, b-windows foil, c-total).

The minimum losses in window and bottom wall are in the region 0.60 – 0.65 MeV and most of energy is deposited in the flue gas.

2.1.2. Industrial plant for EBFGT at coal fired plant

The first industrial installation for simultaneous removal of SO_2 and NO_x was located in Electropower Station ‘‘Pomorzany’’ in Szczecin (Fig.6), in the north of Poland [7]. The installation purified flue gases from two Benson boilers of $65MW_e$ and $100MW_{th}$ each, the total maximum flow rate is 270,000 Nm^3/h.

Fig.6.View of EPS Pomorzany, Szczecin. Flue gas humidifier tower of EBFGT plant – front left.

With its 1.05 MW total beam power installed it was the biggest accelerator processing facility in the world ever constructed. The installation consists of four main, separated systems: flue gas conditioning unit, ammonia storage and injection unit, process vessels, by-product collecting and storage unit. Before entering the installation, the flue gases from boilers were de-dusted in electrostatic precipitators and divided into two streams. About half of the total flue gas amount was directed to the installation, while the rest is bypassed to the mixer before the stack. The purified part of the gases entered the dry bottom spray cooler, where the water evaporation process took place. As a result of this process the temperature of the gases drops to 65 – 80ºC and the humidity rises up to 10 –14% vol. In this way, the temperature and the humidity of the gases are correlated with each other to a high degree. If the inlet flue gas temperature is low, the humidity may be too low for the proper course of the process. In this case there is a possibility of increasing this parameter by adding steam over the gas outlet from the cooling tower. Ammonia, the main process reagent, is stored as an ammonia water. It may be dosed to the installation in two ways, gaseous ammonia after the evaporation may be injected upstream the irradiation chamber or ammonia water may be sprayed straight to the spray. The chemical reagent may be also dosed both in the form of ammonia water to spray cooler and gaseous ammonia before the irradiation chamber (mixed variant). The tests carried on the industrial installation showed that the way of ammonia adding affects the pollutant (especially, SO_2) removal efficiency. Depending on the process conditions, the ammonia water consumption was in the range of 150 – 600 kg/h. After the ammonia injection the flue gases were guided to reaction unit, where the irradiation and main reactions took part. The doses in the range of 7–12 kGy were applied during tests. The energy of electrons induces a sequence of reactions that results in oxidation of SO_2 and NO and the creation of ammonium sulfate and ammonium nitrate aerosol. Other acidic pollutants such as HCl were removed by straight reaction with ammonia. The by-product aerosol is collected by the electrostatic precipitator and after granulation and storage is shipped to the NPK fertilizers production plant. The by-product consists mainly of ammonium sulfate and ammonium

nitrate. Apart of these, there is also ammonium chloride (from the carbon contained chloride) and other impurities such as ammonium fluoride, insoluble parts (residual fly ash and rust), etc. The impurity content (especially heavy metals) is much lower than the fertilizer standards require, so the by-product has a very good quality for the agricultural uses. The by-product yield is up to 300 kg/h. The flue gases after purification are mixed with the un-purified part of gases and led to the stack. Gas temperature after mixing exceeds 110 ^{o} C, what avoids wet stack problems. The general layout of installation is presented in Fig.7.

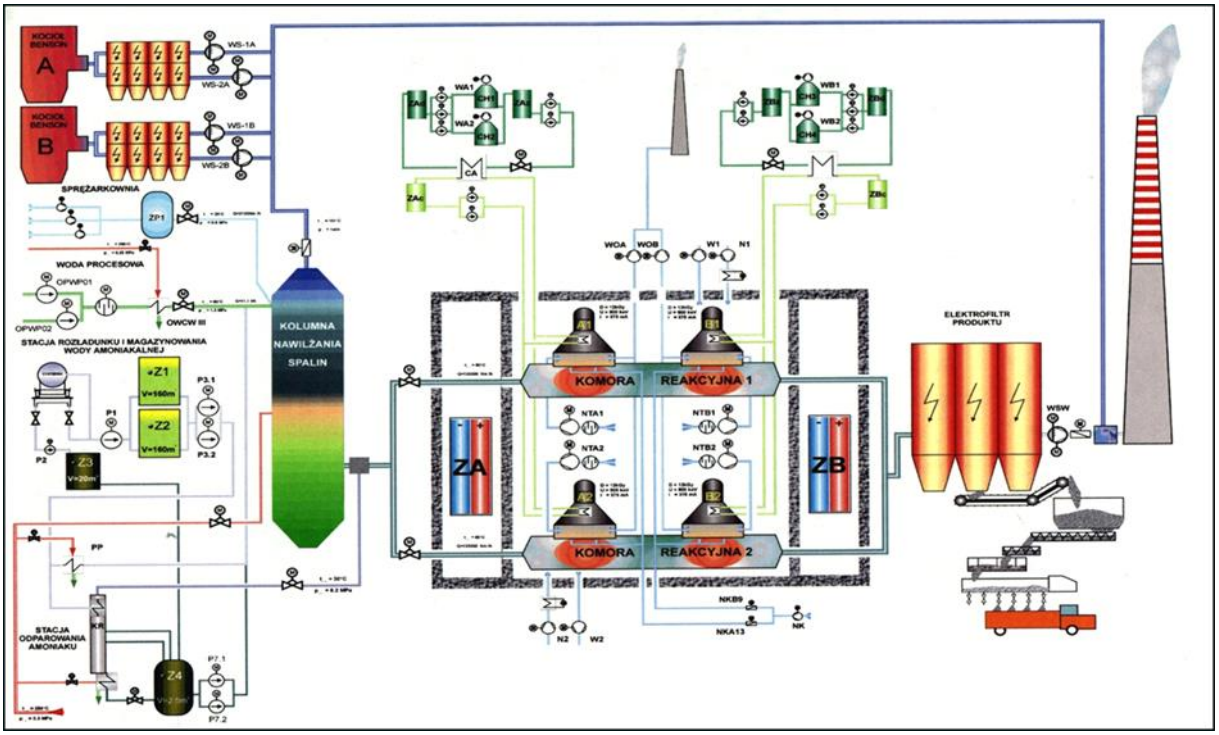

Fig. 7 General layout of the installation.

The reaction unit consisted of two parallel irradiation process vessels equipped with two accelerators (260 kW, 700 keV) each installed in series (Fig.8 and Fig.9).

Fig.8. View of process vessel with installed scanning horn (left) and view of titanium window from inside of the flow system (right).

Fig.9. View of the high power supply (total number two) - left and accelerator head (total number four) – right.

The scheme of process vessels is given in Fig.10 . Double gas irradiation leads to lower energy use. The air curtain applied under the second window protected the titanium foil against corrosion. Longitudinal gas irradiation was applied and the scheme is presented in this figure where the beam scanning horn is located over the secondary window.

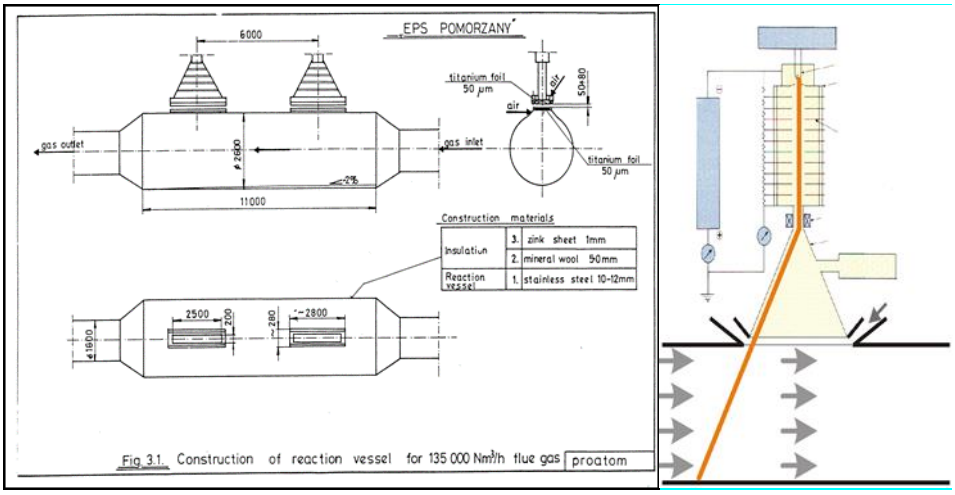

Fig.10. Process vessel cross section (left) and scheme of beam scanning along the gas flow.

2.1.3. Pilot plant for EBFGT at oil fired plant

The pilot scale EBFGT plant was constructed in the boiler area of the Jiddah Refinery [7]. The simplified lay out chart of the plant is shown in Fig.11.

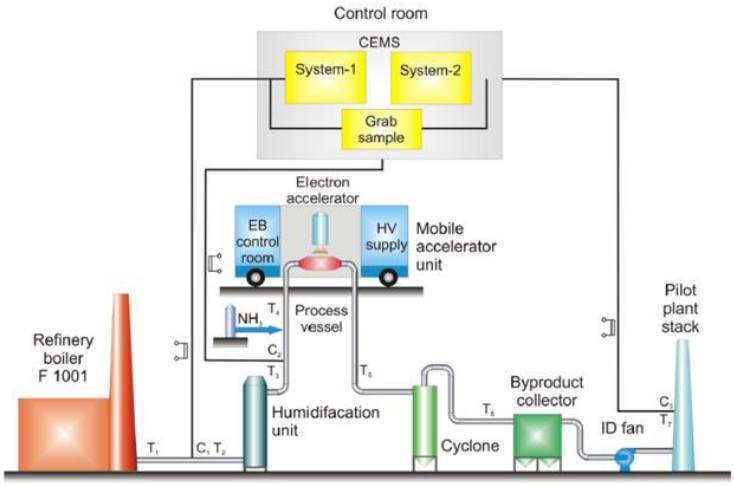

Fig.11a. Layout of pilot plant at the Jiddah Refinery for the electron beam treatment of heavy fuel oil burned flue gas. Not to scale.

The flue gas from the boiler was directed to the cooling and humidification unit and then was irradiated in the reaction chamber. A near stoichiometric amount of ammonia was added to the treated gas up- stream reaction chamber. After irradiation, the gas was directed to the byproduct separation unit consisting of a cyclone and cartridge bag filter or a cyclone and electrostatic precipitator in the second part of the research. Purified flue gas was released to the atmosphere by a separate stack. The gas flow rate was controlled by an ID fan rotation speed regulation. The pilot plant was supplied by a part of exhaust gas from the boiler manufactured by Mitsubishi (Japan). The boiler may be fired by fuel heavy oil or fuel gas. During the research heavy fuel oil was combusted. The pilot plant inlet was

attached to the boiler outlet upstream of the power plant stack. A flap type valve was installed at the gas inlet to the plant. Flue gas temperature at the pilot facility inlet was about 310 °C, therefore, the gas conditioning unit was applied for gas cooling down. Flue gas from the installation inlet was directed to the cooling device by uninsulated 315 mm diameter steel ducts. These ducts served as a pipe heat exchanger lowering the gas temperature before reaching the main cooling device. A counter-current water spray scrubber was applied as a main cooling and humidification device. This device was also designed for dust removal as no other dust collection system was applied in the installation inlet. The water was circulating in a closed loop. Water spraying nozzles were installed under the demister located in the upper part of the column, beneath the gas outlet. Water coming out from the cooling device was filtered to prevent nozzle plugging. In order to stabilize water temperature, a water cooler in the cooling loop was applied. The ducts after the conditioning unit were heat insulated to avoid further gas cooling and water condensation in the ducts. Ammonia was delivered and stored in liquid form in steel cylinders and evaporated during the experiments. A battery of cylinders was used to ensure the proper amount of this reagent. Ammonia was injected into the duct via two nozzles upstream of the reaction vessel. In order to prevent particulate deposition that might lead to nozzle plugging, compressed air was used for ammonia spraying. The amount of injected ammonia was manually controlled via a rotameter with a needle valve. The accelerator ELV with radiation shielding, cooling, ventilation made by EB TECH was applied for flue gas irradiation [2] it was mounted on the trailer (fig.11). The scanner window length was 640 mm. The main parameters of this accelerator are: beam energy 400 to 700 keV, maximum beam current 33 mA. Other auxiliary systems were assembled on a truck trailer, thereby producing a unique mobile system. The shielded irradiation room was of 1554 mm in length, 1380 mm in width and 1410 mm in height, while the free space under the accelerator's scanner was of 530 mm in height. Due to space limitations, the process vessel (PV) was of 1390 mm length including the inlet and outlet part of the device. The cross section of the PV had a quasi-hexagonal shape with a width of 434 mm and a height of 482 mm. Electrons entered the PV via a 640 × 70 mm window. Both the accelerator scanner and the PV windows were made of 50 μm thick titanium foil.

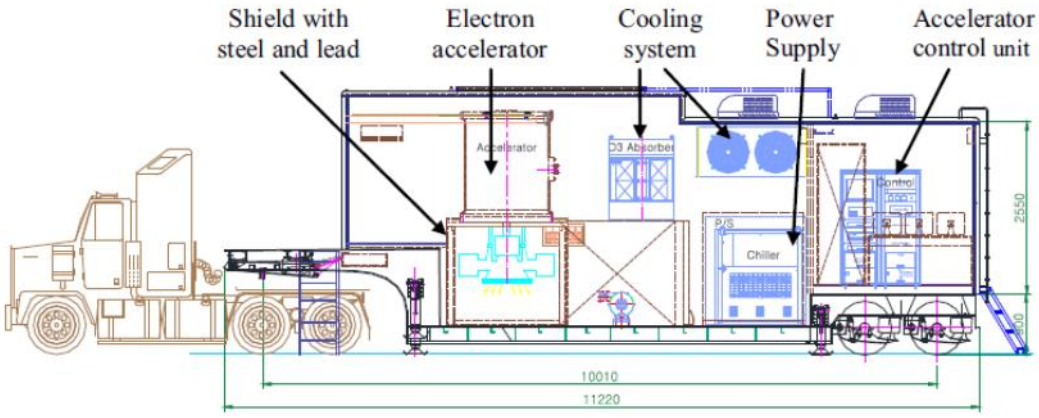

Fig.11b.Mobile EB plant (0.7 MeV, 20 kW), mounted on a trailer.

The byproduct collection unit was composed of two elements: cyclone and bag filter. During further works the bag filter was replaced by an electrostatic precipitator (ESP). The filtration equipment was supplied by EB TECH. The cyclone was installed prior to the bag filter, downstream of the reaction chamber. A typical device of nominal flow rate 60 m3/min manufactured by Clean Air Tech Co., Ltd., Korea, was selected. There were two goals of cyclone application — to collect the initial byproducts and to prolong the reaction time. The byproduct aerosol particulates being formed as a result of EBFGT process were very fine (about 1 μm diameter) and light, therefore cyclone particulate removal efficiency was very low. On the other hand, the PV volume was very small and the residence time was also very short; therefore, the chemical reactions continued even after the gas left this device. Subsequently the cyclone acted as a retention chamber allowing the process reactions to complete. The cartridge bag filter was selected as the main byproduct collecting device. A standard apparatus model CAPS-750HR of 60 m3/ min nominal flow rate, manufactured by Clean Air Tech Co., Ltd., Korea was selected. The byproduct from flue gas was filtered on 18 cartridges, then removed to the hopper by compressed air. Two ESPs manufactured by KC Cottrell, Korea were applied in the second stage of research. The devices were installed in parallel and the gas was directed to each of them by automatic valves. The gas exhaust unit was composed of an ID fan and a stack. The fan (MFsB-013-3-1-H3 type, Nederman, Poland) was an ID fan for the whole pilot plant system. The flow rate of treated flue gas was adjusted by fan rotation speed control. A stack of 315 mm diameter and 5 m height was constructed for gas exhaust to the atmosphere after treatment. The photograph of the whole installation is presented in Fig.11c.

Fig.11c General view of the pilot plant at the Jiddah Refinery. (1) stack of boiler, (2) boiler, (3) flue gas duct, (4) pilot plant control room, (5) gas conditioning column, (6) pilot plant stack, (7) cartridge bag filter, (8) thermal insulated duct, (9) cyclone, (10) ammonia dosing unit, (11) mobile accelerator unit.

Advanced analytical methods were developed at the Kawęczyn pilot plant, were the bases for the Pomorzany industrial plant monitoring and control systems. Similar analytical methods were applied at the Jiddah pilot plant. Two types of monitoring systems were used for reliable and accurate flue gas composition measurements: continuous emission monitoring system (CEMS) for continuous measurements of SO_2 and NO/NO_x concentrations by gas analyzers and grab sample system for occasional determination of various flue gas parameters (e.g. humidity). Grab samples were analyzed using manual analytical methods. Two independent extractive multi-gas monitoring systems were installed for continuous measurement of SO_2 and NO_x concentration in the flue gas: one at the plant inlet (upstream of the humidification unit) labeled System-1 and the second at the plant outlet (downstream of the ID fan) labeled System-2. The UV pulsed fluorescent SO_2 analyzer, Model 40,

and a chemiluminescent NO/NO_x analyzer, Model 10 A/R, manufactured by Environmental Instrument Co. (EIC), USA, were applied in each system. Both systems operated by utilizing the heated sample gas dilution system Model 900 (EIC, USA) with a dilution ratio of 20:1. The flue gas leaving the byproduct collector (cartridge bag filter or ESP) may contain unreacted ammonia which complicates the gas concentration measurement. The outlet gas analyzer system (System-2) was equipped with the heated ammonia scrubber, manufactured by Shimadzu Co., Japan, for selective absorption of ammonia from the extracted sample gas without changing the concentration of other components. Each gas sampling system utilized a stainless steel probe for exhaust gas extraction from duct. The probe tip was equipped with coaxial ceramic coarse and fine gas filters for particulate removal. The probe and gas filters were heated. The representative sample gas was continuously extracted from the duct using a heated sample probe, was filtered at temperatures above the acid dew point temperature, and transported by a heating sampling line to a gas analyzers system installed in the control room. The heated sampling line was kept at the same temperature as the sample probe and the gas filters. Gas sampling points were located before the humidification unit (plant inlet) and at the stack (plant outlet). An additional sampling point for flue gas humidity control was located after the humidification unit. The calibration of each continuous monitoring system was performed using standard gas mixtures. The flue gas temperature was measured at seven essential points of the Jiddah Refinery pilot plant: plant inlet, upstream and downstream of the humidification unit, upstream and downstream of PV, inlet of bag filter or ESP and plant outlet. K-type thermocouples were used for gas temperature measurement. The humidity of the flue gas was determined by a manual analytical method based on the EPA method 4 with the use of granular silica gel filled U-tubes. The portable flue gas analyzer type Lancom Series II manufactured by Land Combustion, UK was applied for auxiliary measurements of CO, CO_2, O_2, SO_2, NO, NO_2, NO_x and hydrocarbons (C_xH_y) concentrations in the flue gas as well as the gas temperature.

The all tests reported above and performed at industrial conditions have proven that the technology can be applied for flue gas treatment for coal (hard and lignite) and oil fired boilers and the by product is a high class fertilizer. The removal of SO_2 approaches 90 % in this dose range 8-10 kGy and that of NO_x is 60 – 70 %. The parameters influencing removal efficiencies are dose, gas temperature and humidity (SO_2), and ammonia stoichiometry. A very important engineering solution developed was the air curtain applied to protect the window of the accelerator from corrosive flue gas atmosphere, and an air curtain protects a secondary window from such effects as well Double irradiation (two accelerators in series) leads to 10% reduction of energy consumption. All results are discussed in [1,2]. The accelerators for these applications already exist [3], however further developments regarding their reliability and plug-to-beam electrical efficiency increase are needed.

3. New environmental accelerator technologies under development

Electron accelerators environmental applications are driven by new environment protection standards, like International Maritime Organization (IMO) regulations regarding SOx and NOx control at Emission Control Areas ; IMO regulations regarding ballast water microbiological control, EU directives imposing a ban on landfill storage of municipal wastewater plant sludge, etc. These are the new fields of possible electron accelerator application, however further research on these technologies are needed. All of these applications are creating a new challenge for accelerator manufacturers and the cooperation of ARIES team with industry may lead to new methods and successful applications which are very important for the environment and human health and safety.

3.1. MARINE OFF GASES TREATMENT

Recently, there has been significant concern about the air pollution from marine sources which currently utilize low quality diesel fuels. As a result, research and development projects have focused heavily on creating cost effective technology that can clean off gases with a high level of efficiency.
Exhausts from marine engines may contain nitrogen, oxygen, carbon dioxide and water vapour as well as nitrogen oxides, Sulfur oxides, carbon monoxide, various hydrocarbons and complex particulate matter. The maritime transport usually uses heavy fuel oil (HFO) with a high content of sulfur, which naturally leads to the three main pollutants derived from shipping: nitrogen oxides (NO_X), sulfur oxides (SO_X) and particulate matter (PM). Around 15% of global NO_X and 5-8% of SO_X emissions are attributable to ocean-going ships. SO_2 emission as a smog component is a precursor to acid rain and it can have a negative influence on plant life as well as on wider ecosystems. Therefore, it is necessary to use a gas purifying method before releasing them into the atmosphere. To address the adverse impacts of sulfur and nitrogen oxides from shipping emission, the maritime sector is required to find highly efficient and low cost methods of gaseous pollutants removal. According to International Maritime Organization regulations (MARPOL Annex VI), there are two sets of emission and fuel quality requirements: global (progressive reduction in global emissions of SOx, NOx and particulate matter) and more restrictive requirements dedicated to ships in deliberately established zones – Emission Control Areas (ECA). Outgoing methods are applied to remove NO_X or SO_2 separately. These technologies are divided into NO_X-reducing devices and SO_X scrubbers and their development is focused on process engineering aspects of such systems, including design of apparatus, main dimensions, advantages/disadvantages as well as processes economy and cost analysis. The removal of nitrogen oxides is a difficult process, requiring the use of expensive catalysts. However, as international emissions regulations on nitrogen and sulfur oxides tighten, current removal methods are becoming increasingly insufficient. First of all, marine's scrubbing and denitration systems are not compatible. NO_X reducing systems usually require a high temperature of

activation, close to 300° C. Simultaneously, SO_2 solubility decreases at higher seawater temperatures. For this reason, equipment manufacturers are expected to provide guidance on the maximum sulfur content of fuel that can be consumed by an engine or boiler with a scrubbed exhaust, so that emissions remain within applicable limits, together with any seawater temperature limitations that may apply and, if applicable, the engine's NO_X certification limits. The main challenges for marine SCR applications are sulfur resistance and low temperature activation.

Currently, the SCR catalyst mainly relies on V_2O_5–WO_3–TiO_2, but V_2O_5 is a highly poisonous material and the active temperature is above 300° C. The mechanism for deposit formation involves an undesirable parallel reaction (to the NO_X conversion) at the catalyst whereby sulfur dioxide in the exhaust is oxidized to sulfur trioxide (SO_3), which can then react with ammonia (used as an reagent in pure or urea solution form) to form ammonium sulphate and bisulphate. Such a process reduces the effective area and shorten the lifespan of the catalyst, with fuel-related hydrocarbon and particulate matter adding to the fouling. As conditions deteriorate, NO_X reduction is impaired and more un-reacted ammonia will slip past the catalyst. This system may reduce the emissions of NO_X by more than 90%, (obligatorily requires comparatively low-sulfur fuel), with cost effectiveness of 873.5 $/ton and SOx emissions by 98% with 3115 $/ton in case of using seawater scrubbing. Researchers have indicated that the urea consumption of SCR system is 8.5% of the consumption of diesel oil, which will surely have a significant influence on size and weight of installation. Therefore, it is necessary to look for new cost effective solutions to remove both nitrogen and sulfur oxides with high efficiency simultaneously.

A new, hybrid technology is based on the concept of combining two methods used to clean up the exhaust gases: Electron Beam (EB) and Wet Scrubbing [8].

The Electron Beam Flue Gas Treatment (EBFGT**)** is one of the most popular non-thermal plasma techniques used due to its high efficiency and has attracted a lot of scientific interest in the environmental protection sector. The exhaust gas is irradiated with the Electron Beam from the accelerator, which causes interactions between the fast electrons and the molecules from the gas, which creates new species such as ions, radicals and excited states (see scheme below Fig.12). Examples of this technology application were presented in Chapter 2. All of these installations were dry ammonia processes, using ammonia as a reagent.

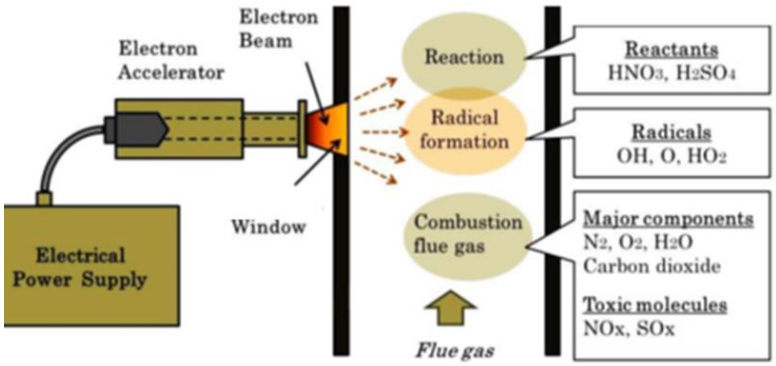

Fig.12. Mechanism of electrons interaction with flue gas molecules.

A new emerging hybrid technology that couples the Electron Beam with the reduced size wet scrubbing methods may provide an answer to the reducing emissions from the marine shipping industry. There are two main stages involved: 1) SO_2 and NO_x oxidation during irradiation by the Electron Beam from the accelerator and 2) the pollution products absorption into aqueous solution. Such a concept aims to enhance the advantages and minimize the limitations of each technology and achieve simultaneous removal of both pollutants e.g. the low removal efficiency when cleaning exhaust gases with high SO_2 and NO_x concentrations with only the EB and the low NO_x removal efficiency with absorption, etc [9]. The organic pollutants (VOC, PAH) may be destroyed in an eb formed plasma as well. As the scrubbing solution used is salty water, easily obtainable by the marine industry, with the addition of the limited concentration liquid oxidant to scrub products of the reactions. Schematic diagram of the hybrid technology principles is presented in Fig.13.

Fig.13. Processes set up of the hybrid technology for marine diesel off-gases treatment.

Technological units of the system are presented in Fig.14, where the photo of an accelerator with a linear cathode, which can be applied in this solution, is presented as well.

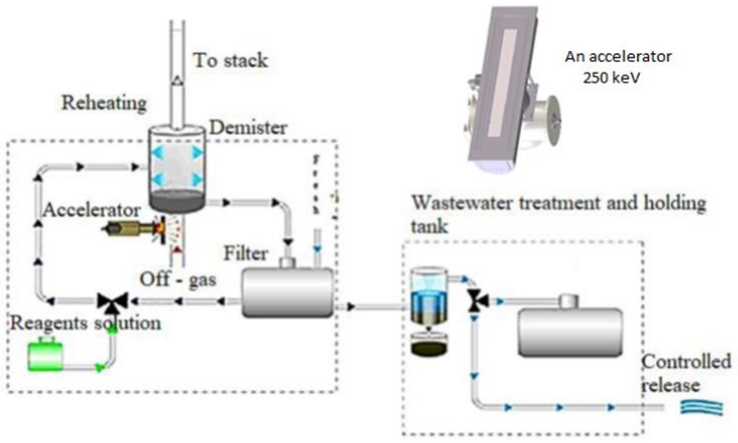

Fig.14 Arrangements of the process units of the hybrid technology for marine diesel of gases treatment.

The NOx removal of hybrid technology is higher than results obtained for SNCR – Selective Non Catalytic Reduction (only low concentration of NO can be treated), ozone injection, bioprocess and other plasmas methods (EB is more energy efficient than e.g. pulsed corona discharge). The SCR catalyst enables a very high removal efficiency for high NO initial concentrations, but the technology is very expensive and requires extensive amount of space. Furthermore, only NO_x can be treated with this technology. The Hybrid eb method by contrast, enables a significant reduction of both pollutants with limited reagent consumption and may assure organic pollutant destruction, which may be required by new standards in the future. The eb process demonstrated the possibility of destroying Polyaromatic Hydrocarbons (PAH) like benzo[a]pyrene. The diagram (fig.15) shows typical pollutant emissions from a marine diesel and methods for their removal – only the hybrid eb process covers all of them.

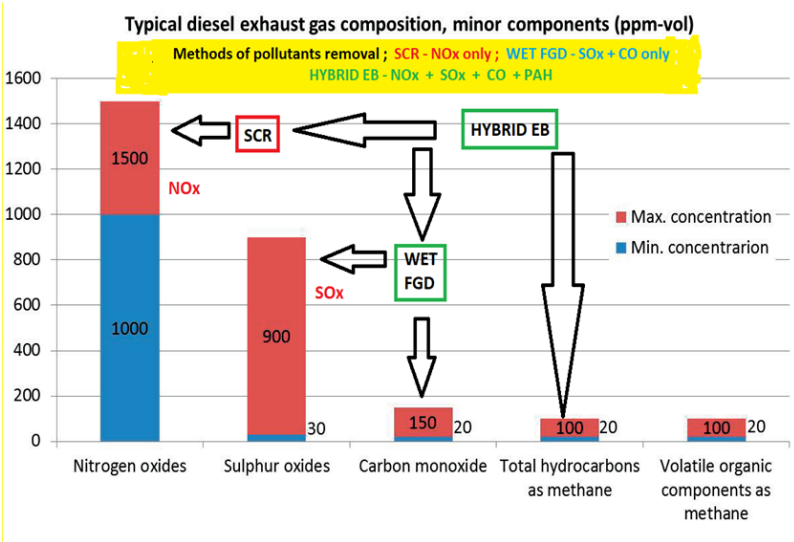

Fig.15. Typical pollutants emission from a marine diesel and methods for their removal.

Taking under consideration all of the advantages of the technology in comparison to other available methods, hybrid technology may become a promising and cost-saving option in the future marine market. The hybrid eb method has a great potential to solve the emerging problem of marine industry and, although it still requires research, its development is now at the level 4 in the Technology Readiness Level. This means that the technology has been optimized at the laboratory level and is in the medium development phase.

3.2. BALLAST WATER TREATMENT

The discharge of sea water used for ballasting ships poses a threat to coastal ecosystems. The introduction of alien species as a result of ballast water exchange may lead to excessive development of these organisms in the new environment and cause a threat to native plant and animal communities. Low salinity is the basic natural factor shaping the biodiversity of the Baltic Sea and results in a small, in comparison with other seas, species diversity. Therefore, brackish seas, such as the Baltic Sea, are particularly sensitive to newly introduced species because they are poor in native species. In 2004, the International Maritime Organization (IMO) developed the Convention on the Control and Management of Ship's Ballast Water (BWM Convention), which provides a uniform legal regulation of the ballast water problem around the world. The implementation of its provisions should contribute to the prevention, minimization and ultimate elimination of the transfer of harmful organisms and pathogens by ballast water. Each vessel covered by the requirements of the Convention is obliged to proceed with ballast water in a manner strictly defined by the Convention and complying with the designated standards, including standard D-2 regarding methods for handling ballast waters. It defines the norms for the amount of organisms and micro-organisms in the ballast water discharged by the ship. In accordance with the legal requirements, ships, including docks, may only discharge ballast water if it contains:

• less than 10 viable organisms per m3 larger than or equal to 50 μm in the smallest dimension,

• less than 10 viable organisms per ml, smaller than 50 μm in the smallest dimension and greater than or equal to 10 μm in the smallest dimension,

and the amount of microorganisms in the discharged water does not exceed:

• for Vibrio cholerae (contagious, O1 and O139) less than 1 colony forming unit (cfu) per 100 milliliters or less than one cfu per 1 gram (wet weight) of zooplankton samples,

• Escherichia coli less than 250 cfu per 100 milliliters,

• Enterococci (intestinal) less than 100 cfu per 100 milliliters.

The ship before entering a shipyard has to replace the ballast water (with its antibiological treatment) in open waters. However some waters still remain, together with solid state sediment containing biological contamination. When the ship is placed on the dry dock for maintenance, repair, painting, etc this ballast water has to be discharged (Fig.16) and units for water sanitization based on UV or chemical method applications are not effective.

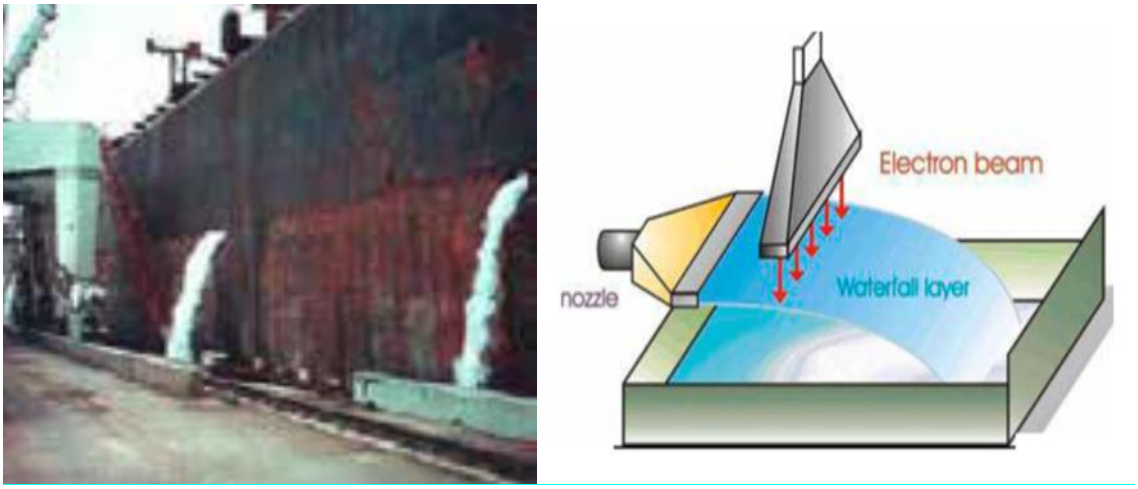

Fig.16 Discharge of ballast water from a ship at dry dock (left) and concept of wastewater treatment (right).

Therefore, the best solution is to use ionizing radiation. For the controlled pathogens, the D_{10} dose [kGy] resulting in a tenfold reduction in the population is:

Vibrio cholerae, V. parahaemolyticus, V. vulnificus, D_{10} = 0.1 kGy,

E.Coli D_{10} = 0.5 kGy,

Enterococci D_{10} = 0.6 kGy.

The most feasible option for this application is a self-shielded electron accelerator. An important additional effect of the irradiation process is the degradation of a number of harmful compounds, like organic compounds. Additionally the use of radiation treatment allows for the complete elimination of nematodes and parasitic eggs (*Ascaris sp., Trichuris sp., Toxocara sp., ATT*) and the practical elimination of pathogens, such as contagious bacterial contamination and *Coliform* titer (decreased by three orders of magnitude for dose 1 kGy), *Clostridium Perfrigenes* titer (decreased by five orders of magnitude for a dose of 1 kGy).

The selection of an accelerator for a radiation installation requires taking into account a number of technical and economic factors and is made after a detailed analysis of a number of factors. The most important are: appropriate range of energy and power of the average beam of accelerated electrons, knowledge of the technology used by the manufacturer and positive feedback from users of accelerators. These parameters should be verified in detail based on the existing data and the implementation of specific construction and installation concepts. Estimated contributions to the capital costs related to the purchase price of the electron accelerator are:

- shielding and ventilation 15%,

- building with fittings 30%,

- technological equipment 20%,

- process control system 5%,

- technical design and permits 10%,

- installation and validation 10-20%,

- depreciation (10 years) 10%,

- cost of service work (fixed / variable) 3-5% .

3.3. "ZERO ENERGY" TECHNOLOGY FOR SLUDGE HYGENIZATION

Nowadays municipal sewage is being cleaned mostly with the use of the method of activated sludge. Excess of activated sludge constitutes biomass which can be utilized to produce energy and at the same time has a value as a fertilizer. However, the problem is that the sludge is microbiologically contaminated by human and animal parasites, their eggs, and also pathogenic bacteria. One of the methods for sludge treatment consists in drying and burning, which is not an environmentally friendly method due to greenhouse gas and dioxins emissions. The energy yield of this method which uses a burning process is reduced due to high levels of hydration of the biomass, which requires the moisture to be evaporated unproductively. Thus the preferred method is methane fermentation whereby biogas is produced. Excess sludges from municipal sewage treatment plants contain organic and inorganic components valuable as soil fertilizer, so if disinfected they can be beneficial and can be recycled in agriculture instead of being a burdensome waste. Experiments have been performed at INCT to test the influence of 10 MeV EB on bacteria, parasites and parasite eggs in municipal sewage sludges from different locations in Poland. Double-bagged samples of sludges (I kg weight and 2 5-3 cm thick) were irradiated with the doses of 5-7 kGy in a Russian electron accelerator of LAE 13/9 type. The sewage sludge produced by the municipal waste treatment plants contained bacteria and viable eggs of intestinal parasites of the genera *Ascaris*, *Toxocara* and *Trichuris* (ATT).The total bacteria content, spore-forming bacteria content, *Coliform* counts and *Clostridium* perfringens counts, as well as the number of parasites and their eggs were determined. The dose of 6 kGy kills all parasite eggs and decreases total bacteria content by 3 logs (Table 1) , spore-forming bacteria and *Coliform* counts by 2 logs and *Clostridium perfringens* counts by 1 log. The units given in the first line of this table are in cfu (a colony-forming unit), while other data refer to the volume of water, expressed in mL in which there is one colony of *Escherichia coli* or *Clostridium Perfringens*. The *Coli* titer is used as an indicator of water purity. Bacterial titer is the maximum dilution of an aqueous suspension of bacteria in which the microorganisms can grow. To determine the bacterial titer, a certain amount of the material being examined, such as soil, water, or food, is placed in a test tube with sterile water and thoroughly mixed. Then 1 milliliter (mL) of the solution in the test tube is diluted tenfold in another test tube. Further dilutions are obtained by repeating the operation many times. By culturing samples of different dilutions in selective or differential diagnostic nutrient media intended for the growth of a given physiological group of bacteria, information may be obtained on the quantity of putrefactive, nitrifying, denitrifying, cellulose, and anaerobic bacteria in the material under study. In the testing of water and food for purposes of hygiene and sanitation, the coli index, or titer of colibacillus (*Escherichia coli*), is of great importance. It is the inverse of the *Coli* index, which determines the number of coli bacteria in one L , based on the culture of the agar. The presence of coliforms in water can be determined in two ways. The fermentation-test method and the membrane filter method are used for this measurement.

Table1. Bacteria and their spore radiation sensitivity.

Bacteria content				
	0	**5,0**	**7,5**	**10,0**
Spore forming bacteria in 1 ml	$8,4\ 10^{4}$	$2,5\ 10^{3}$	$2,1\ 10^{3}$	$2,0\ 10^{2}$
***Coliform* counts**	10^{-7}	10^{-5}	10^{-4}	10^{-4}
Clostridium Perfringens	10^{-6}	10^{-5}	10^{-4}	10^{-1}

Table 2 is giving results obtained for parasites and their eggs, all adult parasites are killed, too, as they are much more radiosensitive than their eggs (Table 2).

Table 2. Adult parasites and their eggs radiation sensitivity.

Dose [kGy]	**Intestinal parasites**			
	Adults	***Eggs [pcs/kg s.m.]***		
		Ascaris sp.	***Trichuris sp.***	***Toxocara sp.***
0	Many live parasites	480	320	320
5.0	0	0	0	0
7.5	0	0	0	0
10.0	0	0	0	0

On the basis of these experiments the concept of installation has been designed for the disinfection of dewatered sewage sludges (Fig.17).

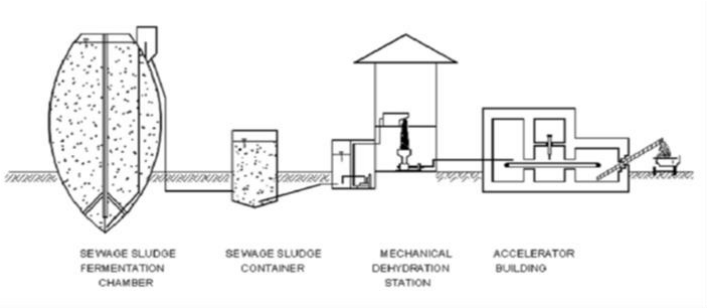

Fig.17 Concept of sludge hygenisation plant with 10 MeV, 10 kW accelerator.

A typical EB sludge treatment plant consists of sludge feeding system and an electron accelerator with shield structure. Dewatered sludge is spread through a flat wide nozzle onto a stainless steel conveyor belt and fed past the EB in an 8–40 mm thick layer at a rate that provides an absorbed dose of 5–10 kGy; the maximum feed rate is 3 ton/h. The thickness of sludge depends on the energy of EB. After irradiation, the sludge is moved to a conveyor belt where it is composted under conditions of controlled aeration and frequent mixing. The irradiated sludge, being pathogen free, can be beneficially used as manure in agricultural fields, as it is rich in required soil nutrients.. Recently INCT has developed a new technology regarding biogas two stages plant engineering and two 1.2 MW units have been constructed.

On the basis of this developments a new concept of "zero energy" sludge hygenization technology was elaborated. According to the invention, biomass originating from waste prior to its fermentation or digestate derived in the process of methane fermentation is irradiated with electron beams that use energies from 1 MeV to 10 MeV, preferably 1-3 MeV. For a digestate derived in the process of fermenting biomass originating from waste and having a liquid form with the content of dry matter less than 5%, the radiation dose is from 1 kGy to 5 kGy, whereas for a digestate from which the aqueous phase has been filtered out and which has a dry matter content up to 30%, the radiation dose is from 5 to 20 kGy.

An electron accelerator is favorably powered with energy provided by a cogenerator fueled by biogas produced in the process of methane fermentation (Fig.18).

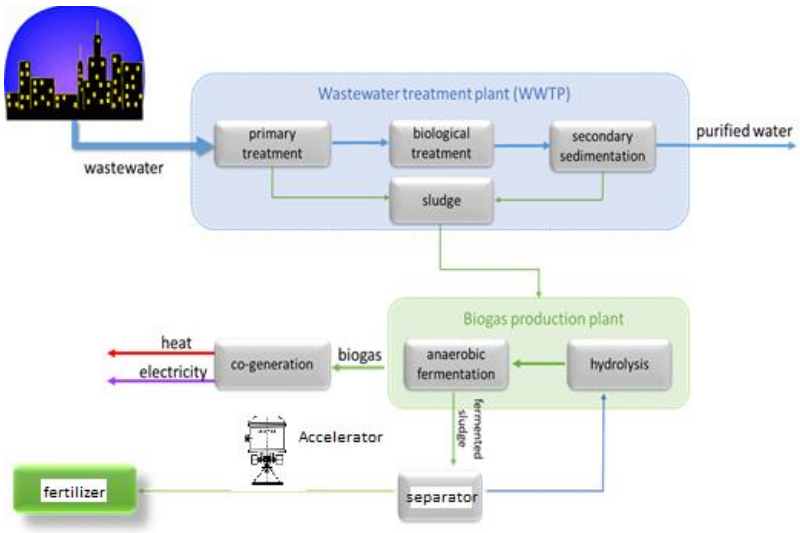

Fig.18. "Zero energy" sludge hygenization technology principle.

The advantage of the method according to the invention consists in the fact that the energy is generated from renewable waste material which is widely available. The method according to the invention does not require energy from external sources and, thanks to the fact that irradiated digestate is utilized as a fertilizer, does not generate waste. The method allows pathogens to be eliminated from sludge and does not have a negative impact on the environment. The plant due to own electricity source may be installed in a remote site, providing electricity for accelerator, wastewater treatment plant and village. The heat from cogenerator may be used for fertilizer drying. The process layout for a biofertilizer preparation line is presented in Fig.19.

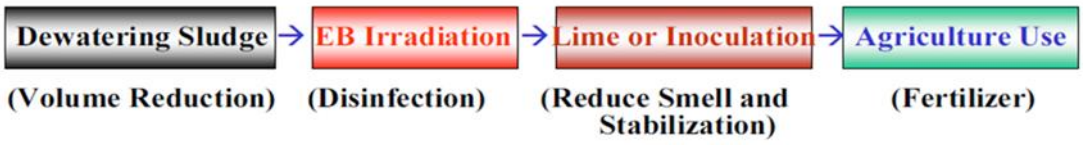

Fig.19 Bio- fertilizer preparation line based on electron beam sludge hygenization.

The advantages of proposed solution are: it is an environmental friendly technology, biogas production is used instead of the disposal of problematic wastes and assures the production of renewable energy through combined heat and power cogeneration and finally it assures the manufacturing of microbiologically safe organic fertilizer due to electron beam hygenization. The technology can be applied in any site with sufficient biomass and municipal sludge resources while there is no need for an external electric energy supply

4. Conclusions

Experience gathered at industrial pilot and full scale plants using electron accelerators for flue gas treatment reported in this report demonstrated the feasibility of this technology application for environment pollution control. However acceptance of these applications by industry depends on availability of reliable accelerators at competitive prices. The engineering solutions regarding accelerators and process equipment developments tested on the industrial scale leads to conclusions that further developments in accelerators' engineering are needed, in particular the application of new materials for electron exit windows, cathode and other components, higher plug-to-beam energy efficiency, etc. These developments can be achieved by synergy and diffusion of new developments and solutions from other ARIES work packages. Moreover, electron accelerator environmental applications are driven by new environment protection standards, like the International Maritime Organization (IMO) regulations regarding SO_x and NO_x control at Emission Control Areas; IMO regulations regarding ballast water microbiological control, EU directive imposing ban on landfill storage of municipal wastewater plant sludge etc. These are the new fields of possible electron accelerators application, however further research on these technologies are needed. All of these applications are creating a new challenge for accelerator manufacturers and the cooperation of ARIES team with industry may lead to these new methods and successful applications which are very important for the environment and human health and safety. These new technologies are being developed in the laboratory scale and new applications are being prepared to get the funds for their demonstration in the pilot scale leading to their final industrial applications. Diesel off gases method development is supported by Proof-of-Concept ARIES' project which should lead to demonstration installation tests in on shore conditions.

5. References

1. Chmielewski A.G., (2011), Electron Accelerators for Environmental Protection, Reviews of Accelerator Science and Technology, 4, 147–159. DOI: 10.1142/S1793626811000501

2. Chmielewski A.G., Bumsoo Han, (2016), Top Curr Chem (Z) 374:68,.DOI 10.1007/s41061-016-0069-4

3. Zimek Z., Chmielewski A.G., (1993), Present Tendencies in Construction of Industrial Electron Accelerators Applied in Radiation Processing, Nukleonika, 38 (2) 3 -20.

4. Zimek Z ., (2018), Current applications of electron beam accelerators up to 10 MeV, ARIES – MS13

5. Chmielewski A.G. at al., (1992), "Pilot plant for electron beam flue gas treatment," Rad. Phys .Chem., 40(4), 321 - 325. https://doi.org/10.1016/1359-0197(92)90088-W

6. Chmielewski A.G. at al.,, (1995), "The double window for electron beam injection into the flue gas process vessel,,, Rad. Phys. Chem., 45(6), 1029.

7. Pawelec A., Chmielewski A.G., Licki J., Bumsoo Han, Jinkyu Kim, Kunnummal N., Fageeha O.I., (2016), Pilot plant for electron beam treatment of flue gases from heavy fuel oil fired boiler, Fuel Proc. Techn., 145, 123–129.

8. Siwek M., Chmielewski A.G.,(2018), Process engineering aspects of diesel engine off gases treatment, INCT Report B, 2/18, Warsaw,http://www.ichtj.waw.pl/ichtj/publ/b_report/b2018_02.htm

9.Chmielewski A.G., Zwolińska E., Licki J., Yongxia Sun, Zimek Z., Bułka S., (2018), A hybrid plasma-chemical system for high-NO_x flue gas treatment, Rad. Phys. Chem., 144, 1-7, DOI: 10.1016/j.radphyschem.2017.11.0010.

10. Chmielewski A.G., Urbaniak A., Wawryniuk K., (2013) Membrane enrichment of biogas from two-stage pilot plant using agricultural waste as a substrate, Biomass Bioenerg, 58, 219-228, DOI: 10.1016/j.biombioe.2013.08.010

11. Chmielewski A.G., Berbeć A., Zalewski M., Dobrowolski A., (2012) Hydraulic mixing modeling in reactor for biogas production, 33(4) 621 – 628, DOI: 10.2478/v10176-012-0052-8

Annex: Glossary

Acronym	Definition
CFU	Colony-Forming Unit
EB	Electron Beam
EBFGT	Electron Beam Flue Gases Treatment
EPS	Electro Power Station
Gy	J/kg
IMO	International Maritime Organization
INCT	Institute of Nuclear Chemistry and Technology
MW	Megawatt