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E-Beam SO_2 and NO_x removal from flue gases in the presence of fine water droplets

Ioan Calinescu [a], Diana Martin [b], Andrzej Chmielewski [c], Daniel Ighigeanu [b,*]

[a] University POLITEHNICA of Bucharest, ♯149 Calea Victoriei St., 010072 Bucharest, Romania
[b] National Institute for Lasers, Plasma and Radiation Physics, Electron Accelerators Laboratory, P.O.Box: MG-36, ♯409 Atomistilor St., 077125 Magurele, Ilfov, Romania
[c] Institute of Nuclear Chemistry and Technology, ♯16 Dorodna St., 03-195 Warsaw, Poland

HIGHLIGHTS

- The medium-energy EB accelerators are proposed for flue gases treatment.
- The energy losses in the windows and in the air gap between them are reduced.
- To increase the density of the reaction medium and to reduce the penetration depth of EB fine water droplets (FWD) are used.
- Determining the energy efficiency the favorable effect of the method was demonstrated.
- The maximum amount of FWD was determined from the total energy balance of the process.

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ABSTRACT

The Electron Beam Flue Gas Treatment (EBFGT) has been proposed as an efficient method for removal of SO_2 and NO_x many years ago. However, the industrial application of this procedure is limited to just a few installations. This article analyses the possibility of using medium-power EB accelerators for off-gases purification. By increasing electron energy from 0.7 MeV to 1–2 MeV it is possible to reduce the energy losses in the windows and in the air gap between them (transformer accelerators can be applied as well in the process). In order to use these mid-energy accelerators it is necessary to reduce their penetration depth through gas and this can be achieved by increasing the density of the reaction medium by means of dispersing a sufficient amount of fine water droplets (FWD). The presence of FWD has a favorable effect on the overall process by increasing the level of liquid phase reactions. A special reactor was designed and built to test the effect of FWD on the treatment of flue gases with a high concentration of SO_2 and NO_x using high-energy EBs (9 MeV). By determining the energy efficiency of the process the favorable effect of using FWD and high-energy EB was demonstrated.

1. Introduction

New technologies and processes have promoted our economic growth and have been remarkably changing our lifestyles. However, technological innovation is not always welcome. It has impact on the environment and may have effects related to the people's health. The emission of inorganic pollutants such as nitrogen oxides (NO_x) and sulfur dioxide (SO_2) has been remarkably reduced by application of state-of-the-art technologies during the past 60 years. However, industrialized countries have been using the big amounts of oil and coal for energy production via combustion of fossil fuels to convert chemical energy of the substrate into electricity, vehicles fuels and process heat to be used in industries.

Although the developing countries also try to increase the consumption of environment-friendly energies instead of fossil fuels, the steep demand for energy due to the recent economic growth makes it difficult or even impossible to reduce the usage of fossil fuels. This causes a large amount of emission of NO_x, SO_2, as well as carbon dioxide to the atmosphere (Gaffney et al., 1987; Kato and Akimoto, 2007; Ramanathan and Feng, 2009; Streets and Waldhoff, 2000).

While the industrial countries have achieved a sufficient reduction of NO_x and SO_2 emissions, it is still an urgent issue for the developing countries to follow this trend. To meet the strict regulations established by local governments, the wet lime scrubber method and the selective catalytic reduction method

* Corresponding author. Tel.: +40 214574346; fax: +40 214574243.
E-mail addresses: calin@tsocm.pub.ro (I. Calinescu), chmielewski@ichtj.waw.pl (A. Chmielewski), daniel.ighigeanu@inflpr.ro (D. Ighigeanu).

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have been applied to treat SO_2 and NO_x. However, the wet lime scrubber method requires wastewater treatment, and the catalysts have to be replaced periodically. New technology is expected for simple and simultaneous treatment processing of the both pollutants. The electron-beam irradiation process for flue gas purification (EBFGT) has been proposed as an efficient method because it has the following advantages (Hatano et al., 2011):

- has simultaneous denitrification and desulfurization possibilities,
- no wastewater treatment is required,
- no expensive catalyst is required,
- provides simple process and its operation,
- produces profitable products.

The application of electron beams to treat flue gases, such as removing sulfur dioxide, was started by Ebara Corporation in Japan and in the US (Chmielewski, 2011).

There are only few pilot and industrial installations for flue gases treatment by electron beam (EB) irradiation (Chmielewski et al., 2004) operated at this moment. Its drawback, like in other conventional technologies, is high energy consumption (the necessary power for the electron beam is around 2–4% from the total electrical energy produced by the plant) (Hackman and Akiyama, 2000; Licki et al., 2003) and the difficulties in operation of very high power accelerators. That is why it is mandatory to find new solutions and to develop strategies for diminishing radiation dose absorbed in the flue gas and to optimize the process for better uses of EB energy.

Subjected to the electron beam irradiation process, the main components of flue gases (N2, O2 and H2O), are transformed into divergent ions and radicals. The primary species include: e^-, N_2^+, N^+, O_2^+, O^+, H_2O^+, OH^+, CO_2^+, CO^+, N_2^*, O_2^*, N, O, H, OH and CO (Mätzing and Paur, 1992; Tokunaga and Suzuki, 1988). In the case of high water concentration, oxidizing radicals HO and HO_2 and excited species such as $O(^3P)$ are the most important product formed (Person and Ham, 1988). In the presence of water droplets, the radiolytically produced hydrated electron reacts very fast with the dissolved oxygen to produce the superoxide (O_2^-) radical. Since the O_2^- has a pK_a value of 4.7, it will be converted to HO_2 in acidic medium. HO_2 is also produced by the reaction of H-atom with oxygen. However the yield from this reaction is only about 0.06 μmol per joule.

$$N_2, O_2, H_2O_{(vapors\_at\_high\_concn)} + e^- \rightarrow HO^\bullet, HO_2^\bullet, O^*, \text{ions}, \text{excited-species} \quad (1)$$

In the presence of these reactive species, NO_x and SO_2 from flue gases are oxidized and produce nitric acid and sulfuric acid, respectively, as intermediate products. These acids are neutralized with ammonia, giving powders of ammonium nitrate and ammonium sulfate, respectively (Namba et al., 1998) (Fig. 1).

The total yield of SO_2 removal consists of the yield of thermal and radiation induced reactions that can be written (Chmielewski et al., 1995a; Mätzing et al., 1993):

$$\eta_{SO_2} = \eta_1(\Phi, T) + \eta_2(D, \alpha_{NH_3}, T) \quad (2)$$

The yield of the thermal reaction depends on the temperature and humidity. The yield of the radiation induced reaction depends on the dose, temperature and ammonia stoichiometry. The main parameter in NO_x removal is the dose.

The presence of water vapors is mandatory for the efficient removal of SO_2 and NO_x from gases. By radiolysis of water the HO radical is obtained and this radical will oxidize both SO_2 and NO_x (Genuario, 2009):

$$NO + HO^\bullet + M \rightarrow HNO_2 + M \quad (3)$$

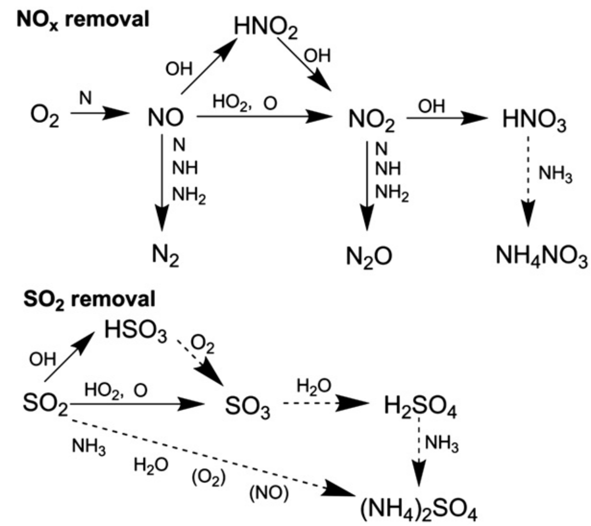

Fig. 1. The main reactions used in EBFGT to convert SO_2 and NO_X (Namba et al., 1998).

$$NO_2 + HO^\bullet + M \rightarrow HNO_3 + M \quad (4)$$

$$SO_2 + HO^\bullet + M \rightarrow HS^\bullet O_3 + M \quad (5)$$

$$HS^\bullet O_3 + O_2 \rightarrow SO_3 + HO_2^\bullet \quad (6)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (7)$$

$$NO + HO_2^\bullet \rightarrow NO_2 + HO^\bullet \quad (8)$$

A gas humidity 8–10 vol% is necessary to obtain the optimal removal-efficiencies of both pollutants (Chmielewski, 2007).

The selection of an adequate accelerator is an important issue in the process engineering. The primary effect of any ionizing radiation is based on its ability to excite and ionize molecules, and this leads to the formation of free radicals, which then initiate chemical reactions.

Accelerated electron beams suitable for flue gas treatment have sufficient energy (up to 5 MeV) to affect the electrons in the atom shell, but not its nucleus, and can therefore only initiate chemical reactions (Zimek, 1995). Typically, the reactions initiated by electron beam are extremely fast and are completed in fractions of a second.

Electrons that are capable of electronically exciting and ionizing molecules, such as N_2, O_2, CO_2, H_2O etc., must have energies in the range from 12 to 16 eV. Such electrons can be produced from fast electrons by the energy degradation process in solids, liquids, and gases. These secondary electrons show energy distribution with the maximum in the range from 50 to 100 eV. In contrast to fast electrons, exhibiting energies in the keV and MeV range, secondary electrons are capable of penetrating solids and liquids only a few nanometers. Consequently, they generate ions, radicals, and excited molecules in "droplets" along the paths of the fast electrons (Drobny, 2010). Fig. 2 illustrates schematically the process of generation of reactive species.

The basic fundamental properties for the EB machine; beam current and beam energy should be derived from the process requirements to ensure satisfactory results with minimum capital and operating costs. The power of EB is determined function of the flow rate of the treated material and the absorbed dose needed for the process:

$$D_{(ave)} = F_{(p)}P/(M/T) \quad (9)$$