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Flue gas cleaning by high energy electron beam – Modeling and sensitivity analysis

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HIGHLIGHTS

- A mathematical model for the electron beam flue gas treatment was developed.
- The main chemical processes in both gas and liquid phases are accounted for.
- The droplet generation and adsorption of gas components are taken in consideration.
- The model is in good agreement with the experimental data in bibliographical sources.
- The sensitivity of the process was tested using a fractional factorial white experiment.

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ABSTRACT

The removal of sulfur and nitrogen oxides from flue gases using high energy electron beams is based on the generation of excited molecules when the flue gas is bombarded by accelerated electrons. The excited molecules undergo ionization, dissociation and electron attachment to yield reactive species (ions, metastables, free radicals and electrons) which interact with the flue gas components. A complex mathematical model was built-up, which includes the main chemical processes in both gas and liquid phases together with the droplets generation and thermodynamic equilibrium between the two phases. The simulation results are in good agreement with the experimental data gathered from literature. Modeling the formation of liquid droplets and the adjacent physico-chemical phenomena provide a better understanding of the process and a more accurate interpretation of the experimental results. The model enables the investigation of the treatment efficiency's sensitivity upon the main operating parameters. A fractional three level factorial white experiment was designed using as parameters the irradiation dose, the water vapor content and the nitrogen oxide initial concentration of the flue gases. The removal yield of SO_2 is rather insensitive to the said parameters, while, on the contrary, the removal yield of NO is very sensitive.

1. Introduction

Growing population and the rise of industrial activities have taken their toll on the quality of the environment. The pollutants emitted from industrial facilities, power stations, residential heating systems and engine vehicles have adverse effects on human health, cause stratospheric ozone depletion, which in turn leads to climate change, and contaminate soil and water, leading to acidification and eutrophication [12].

Conventional methods for the removal of sulfur and nitrogen oxides such as flue gas desulfurization and selective catalytic reduction [14] have long proved their high removal efficiencies [29]. However, this achievement is accompanied by large energy consumption and space requirements resulting in soaring investment and operating costs [28].

Thus, new methods have been devised for the abatement of sulfur and nitrogen oxides from flue gases. The electron beam flue gas treatment (EBFGT) is a relatively new procedure, developed in the late 1970s by the Ebara Corporation, in which the pollutants are subjected to ionizing radiation leading to the formation of a high-quality fertilizer mixture [8]. While achieving high removal efficiencies for both sulfur and nitrogen oxides, the process can be extended to the treatment of other gaseous pollutants and liquid effluents [16,21].

Compared with more traditional methods, EBFGT has the advantage of scalability and simplicity in addition to being an easily

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controllable process [5]. The technology has gradually achieved some level of market penetration, at first with the construction of a series of pilot plant installations in Japan, USA, Germany and Poland, among others, and, more recently, with the development of two industrial facilities in Poland and China [7].

However, the technology suffers, just like the conventional treatment methods, from large energy requirements [2] and from reliability issues associated with the continuous operation of high energy electron accelerators [20]. Consequently, numerous investigations have been made into the possibility of reducing the energy consumption for the process: employing hybrid irradiation methods such as combined microwave and electron beam treatment [18], turning to alternative non thermal plasma generation methods [10], fitting the plasma reactor with a catalytic layer [15], using a variety of additives such as ammonia, hydrogen peroxide [1], natural gas and hydrated lime [25]. The potential use of medium energy accelerators has also been investigated [5], with the provision that a dispersed liquid phase should be introduced in the reactor before the beginning of the irradiation treatment.

Another method to reduce the energy consumption and the operating costs is the investigation of more appropriate reactor configurations [23], either experimentally or through the use of mathematical modeling [8]. The first mathematical models developed started from the simplest reaction systems, formed only of N_2, O_2 and NO, considering as little as 29 chemical reactions [22] and have been gradually improved to include over 850 chemical reactions in the gas phase [26]. However, the size of the kinetic system greatly impacts the computational capacity so, more recent modeling studies have only taken into consideration a fraction of these chemical reactions [6,11] or have resorted to empirical or semi-empirical approaches [9]. Despite early interest in modeling the liquid phase phenomena taking place during irradiation [19], the low liquid to gas ratio experimentally observed [32] has lead researchers to neglect the formation and behavior of this liquid phase in their modeling efforts. However, experimental evidence shows that the introduction of fine water droplets, even in small amounts, in the irradiation chamber can lead to serious energy savings and lowers the operating costs [5].

The aim of the current paper is to advocate a complex mathematical model, considering 90 gas phase and 32 liquid phase chemical reactions that can accurately describe the behavior of the sulfur and nitrogen oxides subjected to electron beam irradiation. The model is, then, used to investigate the treatment efficiency's sensitivity upon the main operating parameters.

2. Theoretical aspects

The treatment of flue gases with electron beams is based on the generation of high energy electrons that ionize the components of the gas carrying the pollutants and give rise to a series of reactive species: ions, radicals, metastables, etc. These in turn react with the main components of the flue gas (N_2, O_2, CO_2, H_2O) and promote the transformation of sulfur and nitrogen oxides into their corresponding acids. Ammonia is added to the gas stream with the aim of neutralizing the acids to ammonia sulfate and nitrate – which are collected in an electrostatic precipitator [6,7].

The mathematical model proposed in this work follows the main physico-chemical phenomena occurring in both gas and liquid phases during the irradiation treatment. The inclusion of the liquid phase phenomena together with the thermodynamic equilibrium between the liquid and the gas phases represents an original approach in modeling the electron beam treatment, one that proves relevant in the light of more recent energy-reducing developments, i.e. introducing fine water droplets in the irradiation chamber [5].

Despite being slighted in the mathematical modeling of the electron beam treatment of exhausts for the last decade, the modeling of liquid phase phenomena proved to be relevant in the economy of the process [5]. Our paper proposes new approaches to the liquid phase modeling as well as a more extended kinetics: 19 chemical species and 32 chemical reactions, listed in the Supplementary material.

2.1. Generation of reactive species

Radiation energy is absorbed by the gas components which undergo ionization, excitation, dissociation and charge transfer reactions. These processes are referred to as primary radiolysis phenomena and have a time scale in the range of 10^{-14}–10^{-7} s. As it has proven quite difficult to accurately determine the rates of these reactions, the notion of electrochemical yield (G – value) has been introduced to account for the number of molecules or ions produced or destroyed per 100 eV of absorbed ionizing energy. The interactions between fast electrons and the gas components are described by Eqs. (1)–(4) [27], which are the most cited in literature.

$$4.14N_2 \rightarrow 0.885N^2D + 0.295N^2P + 1.87N^4P + 2.27N_2^+ + 0.69N^+ + 2.96e^- \quad (1)$$

$$5.3O_2 \rightarrow 2.98O^{\bullet} + 2.25O^1D + 2.07O_2^+ + 1.23O^+ + 3.3e^- \quad (2)$$

$$6.7H_2O \rightarrow 0.51H_2 + 4.25OH^{\bullet} + 4.15H + 0.46O^3P + 1.99H_2O^+ + 1.99e^- \quad (3)$$

$$7.54CO_2 \rightarrow 4.72CO + 5.16O^{\bullet} + 2.24CO_2^+ + 0.51CO^+ + 0.07O^+ + 2.82e^- \quad (4)$$

2.2. Chemical reactions in gas phase

The species produced by the abovementioned primary radiolysis phenomena react further with each other giving rise to a complicated reaction system. During these secondary radiolysis phenomena, the reactants undergo ion–ion recombination, radical–neutral and radical–radical reactions as well as molecular reactions. The most complex models consulted accounted for the occurrence of over 850 chemical reactions in the gas phase involving more than 100 neutral and charged species [27].

We started to model the gas phase processes considering the stoichiometry proposed by Ref. [31]. Afterward, we improved our model using the stoichiometry presented in Ref. [27] and completed with that of [22]. This way, we assembled a model consisting of 370 chemical reactions and 70 chemical species.

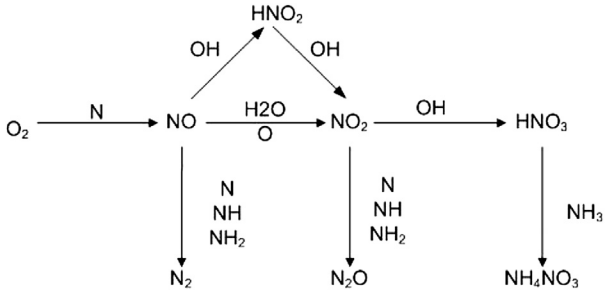

Fig. 1. Mechanism of NO removal during EBFGT treatment.