

Flue Gas Cleaning by High Energy Electron Beam – Enhancement Effects Due to Water Droplets Generation

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The electron beam technology has been developed successfully for the removal of sulphur and nitrogen oxides from flue gases and has recently been applied on an industrial scale. The flue gases contain also nitrogen, carbon dioxide, oxygen, water, and ammonia. As the sulphuric acid appears during the chemical processes generated by the beam interactions with the gas phase components, it starts reacting with water, both condensing as fine liquid droplets (nucleation), where other components of the flue gas are absorbed. The chemical processes extend to the liquid phase as reactive extraction of components like SO_2 , HNO_3 , HNO_2 , O_2 , and NH_3 . The rate of the latter is influenced by both the gas to liquid mass transfer and the thermodynamic equilibrium instantaneously established at the gas-liquid interface. To the best of the authors' knowledge, this approach proposes the first complex mathematical model which includes the concomitant chemical processes in the gas and liquid phases, as a way to better understand the electron beam flue gas treatment mechanism. The flue gas was assumed to be irradiated over a period of 12.6 s at 1 atm and 60 °C with a dose of 10 kGray. The kinetics, involving 139 chemical reactions, were assembled from various sources, and integrated into a first principles based mathematical model, consisting of a system of 70 unsteady-state mass balance equations. Dissociation of the absorbed component into ionic species was also modelled, according to the appropriate mass and charge balances. The results are in satisfactory agreement with published data from industrial and laboratory scale experiments.

1. Introduction

Atmospheric pollution and climate change have been topics of interest throughout the last decades. Sulphur and nitrogen oxides emitted from the burning of fossil fuels in industrial facilities, power stations, residential heating systems and engine vehicles have adverse effects on human health, lead to global warming, contaminate soil and water and are the main causes of acidification and eutrophication.

Although there has been registered a steep decrease in the amount of SO_2 and NO_x emitted over the last two decades due to the stringent limitations regarding air quality (in the EU-27 the sulphur dioxide emissions decreased by 80 % between 1990 and 2009, while the nitrogen oxides were reduced by 44 %), current deposition is still well above the levels needed for recovery of ecosystems and further reduction of these pollutants is still required.

Numerous methods for the removal and control of the sulfur and nitrogen oxides have been developed and are currently employed industrially, with proven efficiency. However, their investment and operating costs are quite high and additional treatment of the waste generated in the process is usually required.

Modern technologies have been developed to overcome the limitations of these conventional processes. One of these is the electron beam treatment of flue gases (EBTFG), which has been developed over 30 years ago and proved to be one of the most effective methods for the simultaneous abatement of sulphur and nitrogen oxide. The EBTFG has in time become available for pilot scale applications in USA, Germany and Poland and has made the transition to industrial scale in Japan, China, Poland and Bulgaria.

However, the EBTFG is still in its early phases of market penetration and the development of a mathematical model that can accurately describe it is important for the future acceptance of this

technology on a much larger scale (Chmielewski et al., 2012). This work focuses on attaining this objective by the concomitant modelling of gas- and liquid-phase reactions, providing a novel approach for such a complex system.

2. Theoretical aspects

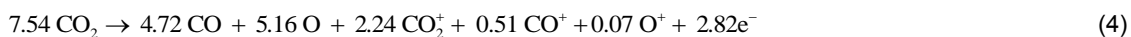
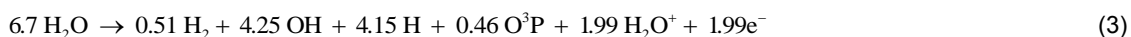
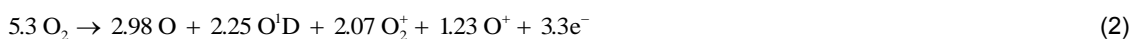
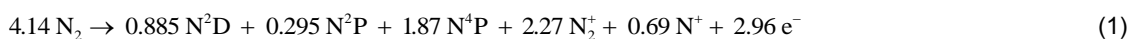
The working principle of the EBTFG is the ionization of flue gases (FGs) due to the interactions of chemical species with fast electrons, followed by chemical and plasma-chemical reactions in the ionized gas, which result in a decrease in the concentration of toxic impurities.

Ionizing radiation reacts with the main components of the FGs (N_2 , H_2O , O_2 , and CO_2) to produce electrons, ions, excited atoms and molecules, and free radicals in the gas phase. These extremely reactive species interact in turn with SO_2 and NO_x and oxidize them in the presence of water to form the corresponding acids: H_2SO_4 , HNO_2 and HNO_3 . Prior to irradiation, a reagent (commonly NH_3) is added to the gas flow to react with the acids and form salts, mainly ammonium sulphate and ammonium nitrate, which can be used pending purification as fertilizers.

The main physico-chemical steps which take place during the EBTFG process include energy absorption of electron beam with active species generation, plasma – chemical reactions in gas phase, aerosol formation and growth, and liquid – phase radiation induced chemical reactions.

2.1. Generation of reactive species

Radiation energy is absorbed by the gas components directly proportional to their molar fraction in the mixture. The primary radiolysis phenomena are described by Eqs.(1 – 4). The radiochemical yield of each species was taken from (Schmitt et al., 2009):



2.2. Gas phase chemical reactions

The most complex kinetic models consulted indicate the occurrence of over 850 chemical reactions in both liquid and gaseous phases. Our model takes into consideration only 122 gas phase reactions (Schmitt et al., 2009) and 17 liquid phase reactions (Li et al., 1998). Other sources were also consulted to ensure the proper kinetic constants are selected for the gas phase and the liquid phase reactions.

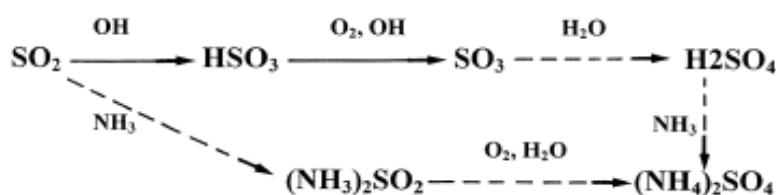


Figure 1: Mechanism of SO_2 removal in gas

The chemical reactions taking place in gas phase have been divided in five categories: generation of secondary ionic and radicalic reactive species, reactions between ions and molecules, reactions with transfer of charge, termination reactions (for the free radicals involved) and molecular reactions.

The SO_2 removal is based on two different pathways (see Figure 1): 1) the thermal and 2) the radiation-induced processes. At zero irradiation, the SO_2 removal is caused only by the thermal reaction with ammonia in the presence of oxygen and moisture.

The nitrogen oxides are removed solely as the result of irradiation either by reducing reactions which generate N_2 or by oxidation reactions, the result of which being the formation of NO_3 , N_2O_5 , HNO_2 and HNO_3 as depicted in Figure 2.

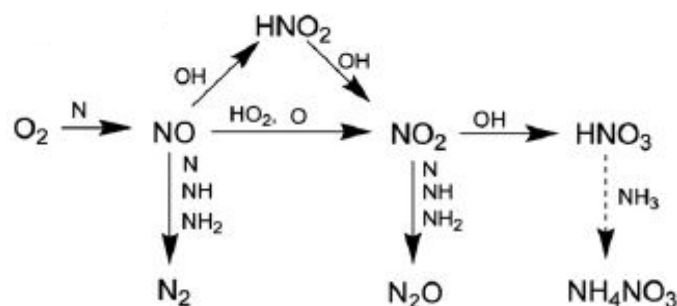


Figure 2: Mechanism of NO_x removal of in gas

2.3. Formation of aerosols and droplets

The H₂SO₄ molecules produced in gas phase will rapidly acquire water vapour and nucleate to form small H₂SO₄/H₂O droplets or condense on existing particles. For the sake of simplicity, we have neglected the condensation process and only took into account the nucleation, since this is the main phenomenon responsible for the formation of the liquid phase (Calinescu et al., 2012).

However, the nucleation process for water – sulfuric acid aerosols in the temperature range of 60 – 90 °C, where the electron beam process takes place, is complex and has not been extensively studied. Empirical formulas have been employed for the computation of the nucleation rate (Seinfeld et al., 1998) and the characteristics (size, composition, density) of the clusters (Vehkamäki, 2002).

2.4. Liquid phase phenomena

The liquid phase kinetics quantifies an important mechanism for the removal of sulfur dioxide, which is absorbed from the gas phase into the condensed droplets along with oxygen, ammonia, nitrous and nitric acids. The species then dissociate into their corresponding ionic states, undergo irradiation (which generates HO• and HOO• radicals) and interact with each other resulting in a heterogeneous chain oxidation mechanism responsible to a large extent for the SO₂ removal from FGs (Potapkin et al., 1995).

3. Mathematical model

The mathematical model proposed in this work aims to investigate the process and to predict accurately the influence that changes in the operational conditions will have on the overall efficiency.

The developed mathematical model is based on the following assumptions: a) the energy absorbed by irradiation is evenly distributed in the gas phase as well as in the droplets and is proportional to the density of the two phases; b) the thermodynamic equilibrium between the liquid and the gas phases is attained instantaneously; c) the condensation of aerosols onto other particles or the reactor walls and the coagulation phenomena were neglected; d) the nucleation process has a much higher rate than the condensation and coagulation processes; e) the FG was taken as ideal gas and the mass transfer effects were neglected. The simulation was conducted for a FG with the composition presented in Table 1 at 1 atm and 60 °C. The mathematical model was coded using the Matlab[®] programming environment and its structure follows the main phenomena involved in the EBTFG process; its solution is based on the Matlab[®] stiff differential equations solver ode15s.

3.1. Gas phase transformations

The gas phase chemical species mass balance was written using the generalized equation (Chmielewski et al., 2012):

$$\frac{dc_i}{dt} = G_i \times D^* \times X_i + \text{rate of formation} - \text{rate of decomposition} \quad (5)$$

where c_i represents the concentration of the reactive species i ; D^* is the irradiation rate; X_i denotes the molar fraction of the species i and G_i is the corresponding radiochemical yield, defined as the number of molecules or ions produced or destroyed per 100 eV of absorbed ionizing energy.

The first term accounts for the generation of reactive species via irradiation while the rates of formation and disappearance are associated to the chemical reactions involving the components of the gas.

Table 1: Chemical composition of the flue gas

Component	Volumetric percent
Sulfur dioxide	0.061
Nitrogen oxide	0.0375
Ammonia	0.1595
Nitrogen	70.25
Oxygen	7.5
Carbon monoxide	8
Water	14

3.2. Nucleation process

For the nucleation phenomena and the composition of critical clusters, we employed empirical models. The domain of validity for the parameterizations used is between 300 – 400 K, concentrations of sulphuric acid ranging from $10^4 - 10^{16}$ molecules/cm³ and a relative humidity larger than 35 %. The empirical equation used to compute the nucleation rate was taken from (Seinfeld et al., 1998):

$$\log J_{nuc} = 7 - 64.24 - 4.7 \cdot RH + (6.13 + 1.95 \cdot RH) \log[H_2SO_4]_g \quad (6)$$

where J_{nuc} is the nucleation rate for sulfuric acid, RH represents the relative humidity and $[H_2SO_4]_g$ is the sulphuric acid concentration in gas phase. The composition of the clusters was determined using the set of parameterized equations presented in (Vehkamäki, 2002).

3.3. Absorption phenomena

The species absorbed in the solution of H₂SO₄ in H₂O are: sulphur dioxide, ammonia, oxygen, nitric and nitrous acid.

Due to the small concentration – in the range of a few ppm, Henry's Law – Eq. (7) applies, for the gas-liquid equilibrium:

$$c_i = p_i \cdot K_H \quad (7)$$

where c_i – the concentration of species i in liquid (mol/L); p_i – the partial pressure of component i in gas phase (atm); and K_H – Henry's constant for species i (mol/L/atm).

The formula used to compute the number of molecules freshly absorbed in the liquid is:

$$\Delta_n^L = \frac{k_H \cdot N_{nG}^t \cdot V_L - K_{gas} \cdot N_{nL}^{t-1}}{K_{gas} + k_H \cdot V_L} \quad (8)$$

where Δ_n^L is the number of freshly absorbed molecules; N_{nG}^t is the number of molecules of the species in the gas phase at time t ; K_{gas} is the total number of molecules in the gas phase; N_{nL}^{t-1} is the number of molecules absorbed in the liquid phase at time $t-1$ and V_L represents volume of the liquid phase (cm³).

The dissociation phenomenon is modelled by writing the mass and charge balance for the liquid phase; this gives a system of 15 non-linear equations, solved using the built in Matlab function *fsolve*.

3.4. Liquid phase phenomena

To determine the rate of formation of the reactive species in the liquid phase, the densities of the two phases are calculated to establish the distribution of the electron beam current between the two.

The radiolysis in the droplets is described by the following equation (Li et al., 1998):



A similar mass balance is written for the liquid using Eq. (5) and it is added to the routine describing the gas phase reactions.

4. Results and discussion

The results of the simulation show that for the experimental conditions, the sulfur dioxide removal is complete after approximately 8 seconds while the removal efficiency for the nitrogen oxides reaches 72 %.

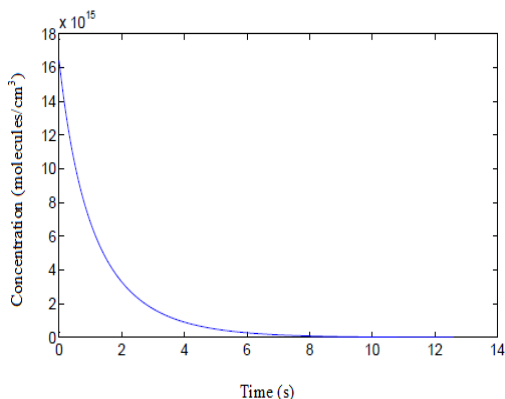


Figure 3: Sulfur dioxide concentration vs. time

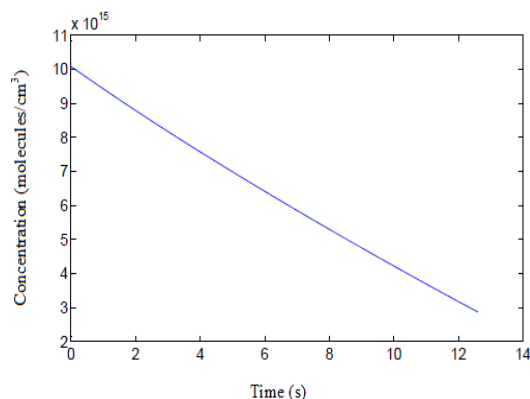


Figure 4: Nitrogen monoxide concentration vs. time

Figure 3 presents the variation of the sulphur dioxide concentration as a function of the irradiation time. The sulphur dioxide's concentration exhibits an exponential decrease and reaches zero after the first 8 s of irradiation. This can be explained by the existence of multiple reaction paths that lead to the removal of SO₂ from flue gases and their over-lapping contributions.

The behaviour of the nitrogen monoxide is presented in Figure 4. Its concentration is shown to linearly decrease during the 12.6 s of irradiation. The nitrogen monoxide is simultaneously reduced to atmospheric nitrogen and oxidized to form nitrogen dioxide, nitrous acid and ammonia nitrite. The simulation results show that the favoured route for nitrogen oxide removal is oxidation. The large rate of ammonium nitrate formation is evidence supporting this statement, while the profile of this species' concentration is presented in Figure 5.

Ammonium nitrate is solely generated from the reaction of nitric acid with ammonia; nitric acid obtained from the reaction of nitrogen oxides with the highly reactive chemical species HO• and HOO•. After the removal of sulfur dioxide from the gas, the increase becomes relatively linear as ammonia is more readily available for reaction with nitric acid. Moreover, as fresh liquid is no longer formed by sulphuric acid nucleation, the rate of absorption and dissociation of both ammonia and ammonium nitrate decreases.

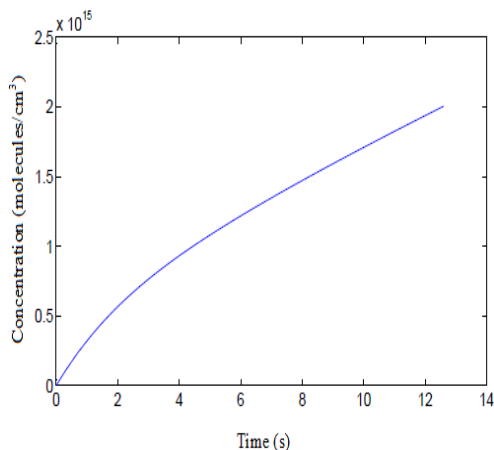


Figure 5: Ammonium nitrate concentration vs. time

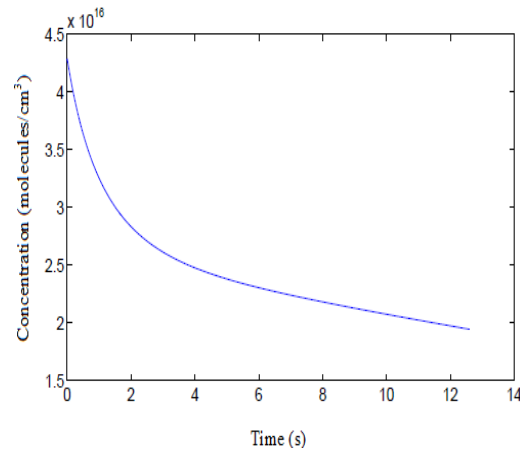


Figure 6: Ammonia concentration vs. time

The ammonia is added stoichiometrically with respect to the amount of sulphur and nitrogen oxides in the flue gas as it was shown experimentally that this ratio leads to the highest overall removal efficiency. For the first 8 seconds of irradiation the concentration of ammonia decreases exponentially as a result of chemical reactions and absorption in liquid. After the sulphur dioxide is almost entirely consumed, the decrease in ammonia concentration becomes linear, as shown in Figure 6.

From the 10 constituents of the liquid phase, we have chosen to depict the concentration variation of the bisulphite anion in Figure 7.

The bisulphate anion is generated as a result of the dissociation in the droplets of the complex formed between SO₂ and water. In the first stages of irradiation the concentration of sulphuric acid is quite low and thus the number concentration of the droplets is relatively small. Thus the yield of irradiation in the liquid is low and HSO₃⁻ ions are accumulated. After the amount of liquid becomes significant, the bisulphate ions

are oxidized by hydrogen peroxide and hydroxyl radicals to form SO_3^{2-} , SO_5^{2-} . The concentration of the bisulphite anion reaches zero after the first 6 s of irradiation. This mirrors the behaviour of sulphur dioxide in the gas phase.

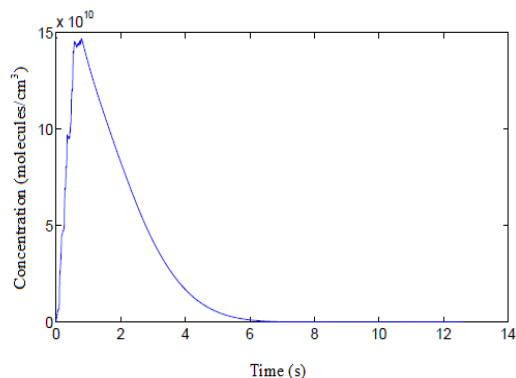


Figure 7: HSO_3^- concentration vs. time

5. Conclusions

The results obtained from this model are in satisfactory agreement with other theoretical and empirical models presented in literature. The nitrogen and sulphur oxides' removal efficiencies (72 and 100 %) are similar to those obtained experimentally for a residence time of 12.6 s and an irradiation dose of 10 kGray. The sulphur dioxide is removed more easily than the nitrogen oxides, mainly due to the reduced temperature of the process, moderate irradiation rate and oxygen content, in approximately 8 s of irradiation treatment. The removal of sulfur dioxide is enhanced by the stoichiometrically added ammonia, as experimental studies have shown that at zero irradiation dose the SO_2 removal efficiency reaches almost 50 – 60 %.

Nitrogen oxides' comparatively poorer removal can be explained by the relatively low temperature of the process (optimal NO_x removal has been observed around 70 – 90 °C). The temperature effect on the nitrogen oxides abatement process is more pronounced than that in the case of SO_2 , for which the increase in temperature has a negative effect above 125 °C.

The model proposed for the characterization of the capture of sulphur and nitrogen oxides can predict in a consistent manner the overall process efficiency of the irradiation beam treatment for flue gases.

The modelling of the formation of liquid droplets and of the physical and chemical phenomena occurring in the liquid phase is a novel approach to describing the electron beam irradiation treatment; this in turn provides a better interpretation of experimental results and helps form a better understanding of the process.

As the liquid phenomena prove to be extremely important in modelling the EBFGT, further work aims at better investigating the droplets' formation by developing a structured model based on the size and age of the liquid droplets.

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