Chemistry of the electron beam process and its application to emission control

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Abstract

The irradiation of air-like gas mixtures with energetic electrons (300 - 800 keV) generates excited state species, ions and radicals. Only the radicals remain available for reactions with the trace components. Like in atmospheric chemistry, the most reactive radical is OH, hence the pollutants are degraded by oxidation preferentially. Industrial applications of the electron beam process are the removal of NO_x and SO_2 from power plant flue gas and the removal of hydrocarbons from cold off-gas. Further, the process can be used to degrade chlorinated hydrocarbons from contaminated groundwater and to remove VOC and NO_x from automobile tunnel off-gas.

Introduction

Pollutants emitted from industrial processes, such as power plants, production facilities and traffic, are transformed by photo-chemical reactions in the atmosphere yielding oxidized product species which may be gaseous or particulate. By irradiation of the off-gas with accelerated electrons, similar reactions can be initiated directly at the source under controlled conditions and can be used for the reduction of the pollutant emission. The best known application of the electron beam process is the simultaneous removal of NO_x and SO_2 from power plant flue gas, whereby the NO_x and SO_2 are transformed into a mixture of particulate ammonium nitrate and sulfate which may be used as agricultural fertilizer [1]. Recently, it was realized that the electron beam treatment offers further economic alternatives to clean large volume flows which contain low pollutant concentrations. Examples are volatile organic compounds (VOC) in industrial off-gas [2], chlorinated hydrocarbons stripped from groundwater [3] and VOC/NO_x traces in automobile tunnel off-gas [4].

In our laboratory, these different applications have been investigated during the last 10 years using two stationary and one mobile irradiation facility for volume flows from 300 - 1000 Nm^3/h. This has provided a large experimental data base about the dependence of removal efficiencies on different parameters and about the product formation. In addition to the experiments, an extensive theoretical study was performed which has led to the development of the AGATE-code [5]. The code permits to simulate the radiation chemistry of air-like gas mixtures. It includes 730 reactions and 95 species. The results of the calculations have helped to interpret the experimental findings and to realize optimization potentials. This paper gives an overview on the chemical pathways of the electron beam process and its application to emission control.

General Mechanism

The absorption of the electron energy leads to excitation, fragmentation and ionization of the gas molecules. The production rate of the primary active species is proportional to the dose rate and to the mass fraction of the gaseous compound. Hence more than 99 % of the input energy is absorbed by the matrix gas and only a negligible part of the energy is absorbed by the trace components to be removed. The relative importance of the excitation, fragmentation and ionization channels are described by G-values which are available in the literature [6]. Some of the primary species (e.g. the ions) are very reactive, others (e.g. excited state species) are deactivated quickly. Therefore, the direct fingerprints of the absorbed energy are lost readily in dense gas mixtures and hence the G-values need not be known with high accuracy in order to simulate the electron beam induced chemistry [5].
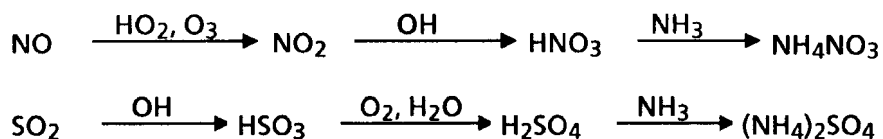
It is more important to understand the difference of reactivity between ionized and non-ionized primary species: Excited state species and radicals are often deactivated or lost after one single collision. In contrast, ion-molecule reactions are usually much faster and proceed without consumption of a charged species. Therefore, the charges may be handed over between many molecules, before they are consumed by neutralization eventually. Moreover, many positive ions react with molecules by dissociative charge transfer, this means under release of a radical. These by-product radicals from positive ion-molecule reactions usually constitute the major radical source in the electron beam process. For instance, under the conditions of combustion flue gas 10 % of the OH radicals result from direct dissociation of water vapour, while 90 % are formed by ion-molecule reactions.

Since the radicals do not react with the matrix gas, only two important reaction possibilities are left for them: reaction with trace components or recombination. The relative importance of these opposing pathways is often a question of dose rate. High dose rate implies a high production rate of radicals and hence a high probability for recombination. At low dose rate, the desired removal reaction with trace components predominates. The practical threshold between these regimes was calculated with the AGATE-code to be approx. 1000 kGy/sec [7].

NO_x and SO_2 removal from combustion flue gas

The simultaneous removal of NO_x and SO_2 from combustion flue gas by electron beam requires three process steps: conditioning of the flue gas, irradiation with electron beam, filtration of the particulate product. In the conditioning step, the flue gas is enriched with water vapour, in order to cool the gas down to the desired temperature (60 - 100 °C) and to increase the relative humidity. Also, ammonia is added to the flue gas in stoichiometric amounts; at stoichiometry = 1, $[NH_3] = [NO_x] + 2 \cdot [SO_2]$.

During the irradiation by electron beam, NO_x and SO_2 are oxidized simultaneously to nitric and sulfuric acid. The acids are neutralized by ammonia and a particulate mixture of ammonium nitrate and sulfate is obtained:

$$NO \xrightarrow{HO_2, O_3} NO_2 \xrightarrow{OH} HNO_3 \xrightarrow{NH_3} NH_4NO_3$$

$$SO_2 \xrightarrow{OH} HSO_3 \xrightarrow{O_2, H_2O} H_2SO_4 \xrightarrow{NH_3} (NH_4)_2SO_4$$

In addition to the radiation induced removal pathways, so-called thermal removal mechanisms occur which take place at surfaces like the particle surface and the filter surface. For SO_2, the thermal removal mechanism is even more important than the radiation induced removal. Figure 1 gives a summary of the SO_2 and NO_x removal pathways and a comparison of their efficiencies. The SO_2 removal is favoured by high relative humidity and by high ammonia stoichiometry for two reasons.

(1)   The radiation induced SO_2 oxidation by OH is accelerated by increasing concentrations of water vapour [8].

(2)   The heterogeneous oxidation of SO_2 takes place in the presence of oxygen, water vapour and ammonia, probably via intermediate ammonium sulfite. Its efficiency is increased by high relative humidity and high ammonia concentration.

Compared to the SO_2 removal mechanism the NO_x removal scheme is more complicated and involves several intermediate species. Besides oxidation to ammonium nitrate, reduction to molecular nitrogen occurs. This has been predicted by the AGATE-code and proved experimentally by Namba et al. [9]. A third product is N_2O, the formation of which can be minimized by proper choice of the ammonia stoichiometry and by reduction of the energy consumption of the process. This has been achieved very recently by a double irradiation technique with aerosol filters after each irradiation step by Paur et al. [10]. The first filter mainly serves to srub intermediate oxidation products from the reacting gas mixture. Thereby, the energy requirement for the second irradiation step is minimized. The second filter is the major product filter. Energy savings up to 50 % can be achieved in this way compared to single irradiation.
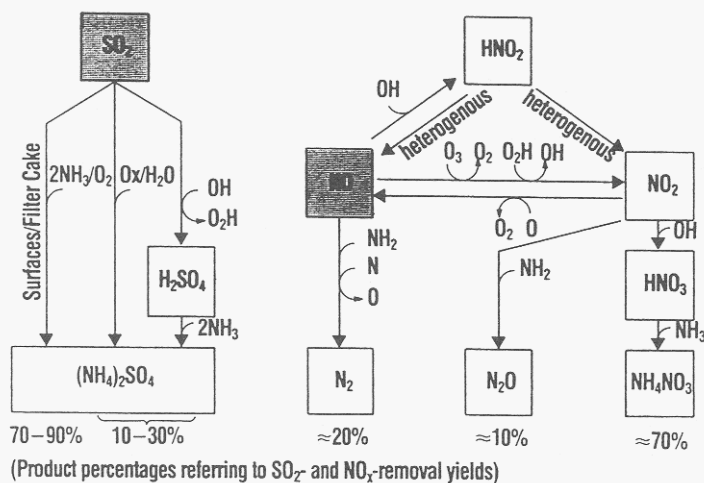
(Product percentages referring to SO_2- and NO_x-removal yields)

Fig. 1: Pathways of SO_2 and NO_x removal by electron beam

VOC removal from industrial off-gas

The removal of volatile organic compounds (VOC) diluted in air has been studied using aliphatic and aromatic compounds and commercial solvent mixtures. The first experimental tests showed high removal efficiencies (up to 40 g C/kWh) and the formation of both gaseous and particulate products [11]. Subsequent product studies showed that aliphatic hydrocarbons like butylacetate can be degraded to merely gaseous products like formic, acetic, propionic, butyric acids and CO and CO_2. Aromatic compounds like xylene are degraded partly to the same gaseous products and partly to a particulate carbonaceous aerosol [2].

The overall C/O ratio of the particulate material is close to 2 : 1, which indicates the presence of highly oxidized compounds. By model calculation, it was shown that the removals of the VOC correlate with the OH concentration and that usually several OH radicals are consumed for the decomposition of one hydrocarbon molecule. A complete reaction mechanism was developed for the degradation of butylacetate by electron beam [4]. The results of the calculation are in good agreement with the experiments. The feasibility of the process has been demonstrated recently at an industrial site with use of the mobile irradiation plant AGATE-M [12].

Cleaning off-gas from automobile tunnels

Besides soot, tunnel off-gas contains approx. 1 - 10 ppm NO_x, 0.1 ppm SO_2 and minor amounts of polycyclic aromatics. According to previous model calculations, these can be removed efficiently by electron beam [11]. The required dose is determined mainly by the initial NO_x concentration. Recent experiments with simulated tunnel off-gas have confirmed the model prediction. Similar to the flue gas application, high relative humidity was found favourable and removal efficiencies around 90 % were achieved at only 1 kGy irradiation dose.

Removal of chlorinated hydrocarbons

Chlorinated hydrocarbons can be stripped from contaminated ground-water by blowing air. The up coming air stream contains comparatively small concentrations of chlorinated methanes, ethanes and ethylenes. According to laboratory studies, these can be decomposed efficiently by electron beam. In particular, trichloroethylene is so reactive that a chain reaction is claimed to explain the high removal rate. The process feasibility was demonstrated recently at a groundwater remediation site using the mobile plant AGATE-M [3]. According to the product analysis, the pollutants can be mineralized almost completely to HCl, CO and CO_2.

Conclusion

By electron beam treatment, gaseous pollutant emissions can be reduced efficiently. The process is applicable to a variety of pollutants particularly in case of low concentrations and high volume flows. A large data base of experimental results exists and additional questions can be answered by model calculation. The mobile irradiation facility AGATE-M is used for process demonstration.

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