# Application of ionizing radiation to environment protection

Andrzej G. Chmielewski

**Abstract** Radiation technology may contribute to the environmental protection to a great extent. Electron beam industrial installations for flue gases containing  $SO_x$  and  $NO_x$  treatment have been already built in China and Poland. The same technology for high sulphur and high humidity off-gases (low quality lignite) has been successfully tested in an industrial pilot plant in Bulgaria. Pilot plant tests performed in Japan have illustrated that by applying electron beam for municipal waste incinerator off-gases treatment the concentration of dioxins can be reduced by 80%, other persistent organic pollutants can be depredated as well. The positive results of electron beam wastewater treatment are the basis for a full-scale industrial plant being built in the South Korea. A pilot gamma plant for sludge irradiation producing a high grade organic fertilizer is in operation in India. All these achievements are reported in this paper.

Key words electron accelerator • gamma rays • flue gas • wastewater • sludge

A. G. Chmielewski
Faculty of Process and Chemical Engineering,
Warsaw University of Technology,
1 L. Waryńskiego Str., 00-645 Warsaw, Poland
and Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., Warsaw, Poland,
Tel.: +48 22-504 1058, Fax: +48 22-8111532,
E-mail: a.chmielewski@ichtj.waw.pl

Received: 16 June 2005 Accepted: 11 July 2005

# Introduction

Municipal and industrial activities of man lead to environment degradation. The pollutants are emitted to the atmosphere with off-gases from industry, power stations, residential heating systems and vehicles. Fossil fuels, which include coal, natural gas, petroleum, shale oil and bitumen, are the main source of heat and electrical energy. Ironically, coals, which are the dirtiest fuels among hydrocarbons, will be the main fossil fuel for the next two centuries [33].

All these fuels contain major constituents (carbon, hydrogen, oxygen) as well as other materials, such as metals, sulphur and nitrogen compounds. During the combustion process different pollutants as fly ash, sulphur oxides (SO<sub>2</sub> and SO<sub>3</sub>), nitrogen oxides (NO<sub>x</sub> = NO<sub>2</sub> + NO) and volatile organic compounds are emitted. Fly ash contains different trace elements (heavy metals). Gross emission of pollutants is tremendous worldwide. These pollutants are present in the atmosphere in such conditions that they can affect man and his environment.

Air pollution, caused by a particulate matter and other pollutants, not only affects directly on the environment, but also contaminates water and soil and leads to their degradation. Wet and dry deposition of inorganic pollutants leads to the acidification of environment. These phenomena affect human health, increase corrosion, and destroy plants and forests. Widespread forest damages have been reported in Europe and North America. Many cultivated plants are not resistant to these pollutants either, especially in the early period of vegetation. Mechanisms of pollutant transformation in the atmosphere are described by environmental chemistry. Photochemistry plays an important role in these transformations.  $SO_2$  and  $NO_x$  are oxidized, sulphuric and nitric acids, which are formed in the presence of water vapour, fog and droplets.

Another problem caused by human activities is the emission of volatile organic compounds to the atmosphere. These emissions cause stratospheric ozone layer depletion, ground level photochemical ozone formation, and toxic or carcinogenic human health effects, which contribute to the global greenhouse effect, accumulate and persist in the environment [4].

Waters in the open and underground reservoirs are being polluted, cultivated soil and forests degraded. Most of the plants, especially coniferous trees, are not resistant to sulphur oxides discharged from municipal and industrial facilities. Water pollution used to be primarily a local problem, with identifiable sources of pollution by liquid waste. Up to a few decades ago most of the wastes discharged to waters came from animal and human excreta and other organic components from industry.

In areas with low population density and without sewerage systems such problems are alleviated to a great extent by the natural self-purification capacity of the receiving water. However, with increasing urbanization of the last two centuries and a subsequent expansion of sewerage systems without any or adequate treatment, liquid waste loads have become so large that the selfpurification capacity of receiving water downstream of large human settlements can no longer prevent adverse effects on water resources.

An other problem concerns industrial effluents, which carry out chemical contaminations, heavy metals, organic pollutants, most often petrochemicals, pesticides, dyes, etc. Some pollutants are synthesized in situ, as, for example, chloroorganic compounds originating from chlorine application for water/wastewater disinfections. The results of discharges of such materials include dyeing living water reservoirs, inhabitants, risk of infection, health effects caused by contaminated drinking water and offensive smells. Over the years, the pollution load of most receiving waters has further increased. In addition to impacts from point sources, pollution from non-point (diffuse) sources, for example, leaching and runoff from agricultural areas and longrange transported air pollutants, have become increasingly important [13].

Consequently, the associated problems are no longer just local or regional, but have become continental in scope. The situation regarding environment contamination is becoming critical. Therefore, economically and technically feasible technologies for pollution control, gaseous and liquid effluents streams are searched for. Radiation offers advanced solutions to the selected problems as well [10, 31].

### Radiation processing of gaseous systems

Wet flue gas desulphurisation (FGD) and selective catalytic reduction (SCR) can be applied for flue gas

treatment and  $SO_2$  and  $NO_x$  emission control. Volative organic compounds (VOC) are usually adsorbed on carbon, but this process is rarely used for lean hydrocarbon concentrations up to now. All these technologies are complex chemical processes, and wastes, like wastewater, gypsum and used catalyst, are generated [35].

Electron beam technology is among the most promising advanced technologies of new generation. This is a dry-scrubbing process of simultaneous  $SO_2$  and  $NO_x$  removal, where no waste except the by-product is generated. Researches show that irradiation of flue gases with an electron beam can bring about chemical changes that make removal of sulphur and nitrogen oxides easier. The main components of flue gases are  $N_2$ ,  $O_2$ ,  $H_2O$ , and  $CO_2$ , with much lower concentration of  $SO_x$  and  $NO_x$ .  $NH_3$  may be present as an additive to aid removal of the sulphur and nitrogen oxides. Radiation energy is absorbed by gas components in proportion to their mass fraction in the mixture. The fast electrons slow down, and secondary electrons are formed which play an important role in the overall energy transfer.

After irradiation, fast electrons interact with gas generating various ions and radicals. Primary species formed include  $e^-$ ,  $N^{2+}$ ,  $N^+$ ,  $O^{2+}$ ,  $O^+$ ,  $H_2O^+$ ,  $OH^+$ ,  $H^+$ ,  $CO_2^+$ ,  $CO^+$ ,  $N_2^*$ ,  $O_2^*$ , N, O, H, OH, and CO. In the case of high water vapour concentration, the oxidizing radicals OH<sup>•</sup> and HO<sub>2</sub><sup>•</sup> and excited ions as O(3P) are the most important products. These species take part in a variety of ion-molecule reactions, neutralization reactions, and dimerization [29].

The SO<sub>2</sub>, NO, NO<sub>2</sub>, and NH<sub>3</sub> present cannot compete with the reactions because of very low concentrations, but react with N, O, OH, and HO<sub>2</sub> radicals.

After humidification and lowering its temperature, flue gases are guided to a reaction chamber, where irradiation by electron beam takes place. Ammonia is injected upstream the irradiation chamber. There are several known pathways of NO oxidation. In the case of electron beam treatment the most common are [25]:

(1) 
$$\operatorname{NO} + \operatorname{O}({}^{3}\mathrm{P}) + \mathrm{M} \to \operatorname{NO}_{2} + \mathrm{M}$$

(2)  $O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$ 

 $(3) \qquad \text{NO} + \text{O}_3 + \text{M} \rightarrow \text{NO}_2 + \text{O}_2 + \text{M}$ 

(4) NO + HO<sub>2</sub><sup>•</sup> + M  $\rightarrow$  NO<sub>2</sub> + <sup>•</sup>OH + M,

where M is any inert molecule.

After oxidation,  $NO_2$  is converted to nitric acid in the reaction with OH<sup>•</sup> according to the reaction:

(5) 
$$NO_2 + OH + M \rightarrow HNO_3 + M$$

HNO<sub>3</sub> aerosol reacts with NH<sub>3</sub> giving ammonium nitrate according to the reaction:

$$(6) \qquad HNO_3 + NH_3 \rightarrow NH_4NO_3$$

NO partly is reduced to atmospheric nitrogen.

There can be also several pathways of  $SO_2$  oxidation depending on the conditions. In the electron beam treatment, the most important pathways are radio-thermal and thermal reactions [36].

Radio-thermal reactions proceed through radical oxidation of  $SO_2$  in the reaction:

(7) 
$$SO_2 + OH + M \rightarrow HSO_3 + M$$

Then, HSO<sub>3</sub> generates ammonium sulphate in the following steps:

$$\begin{array}{ccc} (8) & HSO_3 + O_2 \rightarrow SO_3 + HO_2 \\ (9) & SO_3 + H_2O \rightarrow H_2SO_4 \\ (10) & H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4 \end{array}$$

The thermal reaction is based on the following process:

(11) 
$$SO_2 + 2NH_3 \rightarrow (NH_3)_2SO_4$$

(12) 
$$(NH_3)_2SO_2 \xrightarrow{(O_2,H_2O)} (NH_4)_2SO_4$$

The total yield of SO<sub>2</sub> removal ( $\eta$ ) consists of the yield of thermal ( $\eta_1$ ) and radio-thermal ( $\eta_2$ ) reactions that can be written [3, 24]:

(13) 
$$\eta SO_2 = \eta_1(\phi, T) + \eta_2(D, \alpha NH_3, T)$$

The yield of the thermal reaction depends on the temperature and humidity. It decreases with increasing temperature. The yield of radio-thermal reaction depends on the dose, temperature and ammonia stoichiometry. The main parameter in  $NO_x$  removal is the dose. The rest of parameters play a minor role in the process. Nevertheless, in real industrial process, dose distribution and gas flow conditions are important from the technological point of view [7]. To achieve reduction of energy consumption, a combined electron beam/ microwave (EB/MW) process has been investigated [32].

# Radiation treatment of SO<sub>2</sub> and NO<sub>x</sub>

Japanese scientists demonstrated in 1970–1971 the removal of SO<sub>2</sub> using an electron beam from a linear accelerator (2–12 MeV, 1.2 kW). A dose of 50 kGy at 100°C led to the conversion of SO<sub>2</sub> to an aerosol of sulphuric acid droplets, which were easily removed [23].

Ebara Co. used an electron accelerator (0.75 MeV, 45 kW) to convert SO<sub>2</sub> and NO<sub>x</sub> into a dry product containing (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·NH<sub>4</sub>NO<sub>3</sub> which could be used as a fertilizer. Using the 'Ebara process', two larger scale pilot plants were constructed in Indianapolis, USA [14] and Karlsruhe, Germany [37]. The Indianapolis plant was equipped with two electron beam accelerators (0.8 MeV, 160 kW) and had a capacity of  $1.6-3.2 \times 10^4$  m<sup>3</sup>/h with gas containing 1000 ppm SO<sub>2</sub> and 400 ppm NO<sub>x</sub>. In Karlsruhe, two electron accelerators (0.3 MeV, total power 180 kW) were used to treat  $1-2 \times 10^4$  m<sup>3</sup>/h flue gas containing 50–500 ppm of SO<sub>2</sub> and 300–500 ppm of NO<sub>x</sub>.

However, the final engineering design technology for industrial applications was achieved at pilot plants operating in Nagoya, Japan [27] and Kawęczyn, Poland [8]. In the case of the latter, new engineering solutions were applied; double-longitudinal gas irradiation, an air curtain separating the secondary window from corrosive flue gases and modifications of humidification/ammonia system (high enthalpy water or steam

η SO<sub>2</sub> (%)  $SO_2$ NOx 100 90 NO. 70 50 SO2 = 280 ppmV 30  $NO_x = 200 \text{ ppmV}$ = 63-65°C t<sub>out</sub> 10 2 6 8 10 12 (kGy)

**Fig. 1.**  $SO_2$  and  $NO_x$  removal efficiency *vs.* dose. The results obtained in the pilot plant experiments.

injection, ammonia water injection) and others. The obtained results (Fig. 1) have confirmed physicochemistry of the process, which was discussed earlier. A high dose is required for  $NO_x$  removal, while  $SO_x$  is removed in proper conditions at low energy consumption.

These new solutions led to the economical and technical feasibility improvement and final industrial scale plant construction. Ebara Corporation has constructed a full scale plant in Chengdu, China, mostly for SO<sub>x</sub> removal, therefore, the power of accelerators applied is 320 kW for treatment of 270,000 cubic meters per hour of the flue gas. Reported efficiency is 80% for SO<sub>x</sub> and 20% for NO<sub>x</sub> [12].

The flue gas treatment industrial installation is located in the EPS Pomorzany in Szczecin in the north of Poland [5]. The installation purifies flue gases from two Benson boilers of 65 MW<sub>e</sub> and 100 MWth each. The maximum flow rate of the gases is 270,000 Nm<sup>3</sup>/h and the total beam power exceeds 1 MW. There are two reaction chambers with nominal flow gas rate of 135,000 Nm<sup>3</sup>/h. Each chamber is irradiated by two accelerators (260 kW, 700 keV), which are installed in series. The applied dose is in the range of 7–12 kGy. The removal of SO<sub>2</sub> approaches 80–90% in this dose range, and that of NO<sub>x</sub> is 50–60%. The by-product is collected by the electrostatic precipitator and is shipped to a fertilizer plant.

The installation consists of four main parts:

- flue gas conditioning unit,
- ammonia storage and dosage unit,
- reaction chambers,
- by-product collecting and storage unit.

A scheme of the installation at EPS Pomorzany is presented in Fig. 2.

As it was previously mentioned, the removal efficiency depends strongly on the process conditions. The highest obtained efficiency for  $SO_2$  reaches 95%, while for  $NO_x$  it reaches 70% (Fig. 3). The obtained results may be compared with those previously reported, based on the pilot plant experiments and theoretical calculations, presented in Fig. 1. Very good agreement between the results obtained may be noticed.

The data obtained during the operation of the installation confirmed the previously assumed theses on the impact of the process parameters on the removal effectiveness. In the case of  $NO_x$  removal the most important parameter is the dose. The inlet concentra-

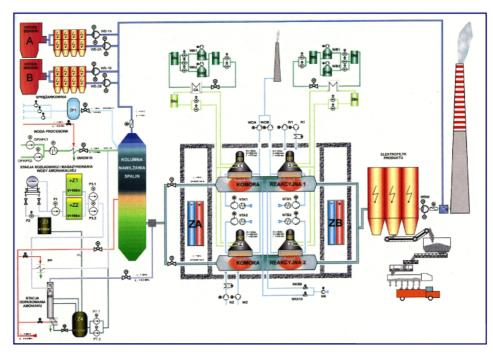
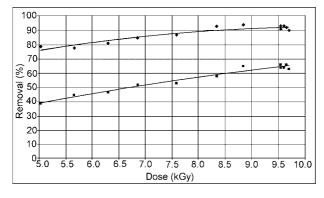


Fig. 2. A scheme of the industrial plan for electron beam flue gas treatment at EPS Pomorzany, Poland.

tion of NO<sub>x</sub> is the second parameter. The impact of these parameters on the pollutant removal was observed. The correlation is linear and the total removal (taken in mg/Nm<sup>3</sup>) increases with inlet concentration of NO<sub>x</sub>, while the relative removal (in %) decreases with increasing this parameter. The ammonia stoichiometry factor has very little impact on the NO<sub>x</sub> removal.

In the case of  $SO_2$  removal there are more parameters, which affect the pollutant removal efficiency. The most important among them is the temperature of the gas down stream humidification tower due to the contribution of thermal reactions. Afterwards, the dose should be mentioned. Although the humidity seems to have the major impact on the process efficiency, it is hard to prove it with no doubt because of the strong correlation between the humidity and the temperature of the process (dew point depends on both parameters: humidity and temperature). During the water evaporation process, the temperature decreased and the humidity increased. A strong influence of ammonia stoichiometry



**Fig. 3.**  $SO_2$  and  $NO_x$  removal efficiency *vs.* dose. The results were obtained in an industrial installation. (SO<sub>2</sub> inlet conc. 1500–1630 mg/Nm<sup>3</sup>, NO<sub>x</sub> inlet conc. 470–540 mg/Nm<sup>3</sup>.)

ratio on the  $SO_2$  removal efficiency has been observed. The other factors as flue gas flow rate and inlet concentration have a much less impact on the removal efficiency. During the experiments, one more parameter having impact on the whole process, has been detected: the ammonia injection mode. It was observed that the injection of the part of ammonia water directly to the humidification tower increased the  $SO_2$  removal efficiency. This phenomenon is under investigation now.

The pilot plant for the treatment of high-sulphur coal lignite fired boiler off-gases has been constructed at the Maritsa 2 East Thermal Power Station in Bulgaria. For high SO<sub>x</sub> and humidity flue gases, high efficiencies of SO<sub>x</sub> and NO<sub>x</sub> removal have been reported.

### Radiation induced VOC removal from off-gases

In the case of VOCs decomposition, the process itself is based on similar principles as primary reactions concerning  $SO_2$  and  $NO_x$  removal, i.e. free radicals attack organic compounds chains or rings causing VOCs decomposition [6].

For chlorinated aliphatic hydrocarbon decomposition (e.g. chloroethylene), Cl-dissociated secondary electronattachment and Cl, OH radicals reaction with VOCs plays a very important role for the decomposition of VOCs.

For aromatic hydrocarbons, the decomposition of VOCs will mainly go through:

#### Positive ion charge transfer reactions

## (14) $M^+ + RH (RH = VOC, e.g. benzene$ $or PAHs) = M + RH^+$

Because RH has lower ionization energy (IE) (benzene: IE = 9.24 eV; PAHs: IE < 10 eV) than most of the

primary positive ions (IE > 11 eV) formed above, part of VOC will be decomposed by rapid charge transfer reactions.

### Radical – neutral particle reactions

The OH radical plays a very important role in the VOC decomposition, especially when water concentration is higher than 10%. 'OH radicals react with VOC in two wys:

•OH radical addition to the aromatic ring (e.g. toluene)

(15) 
$$^{\circ}OH + C_6H_5CH_3 = R1^{\circ}$$

and H atom abstraction (for the alkyl-substituted aromatic compounds) or H atom elimination (for benzene, naphthalene and the higher polycyclic aromatic hydrocarbons)

- (16)  $C_6H_5CH_3 + {}^{\bullet}OH = R2^{\bullet} + H_2O$ (H atom abstraction)
- (17)  $C_6H_6 + {}^{\circ}OH = C_6H_5OH + H$ (H atom elimination)

Radicals (R1<sup>•</sup>, R2<sup>•</sup>) formed above go though very complex reactions:  $O_2$  addition, O atom release, aromatic -CHO (-dehydes), -OH (-ol) compounds formed or ring cleavage products:

- (18)  $R^{\bullet}(R1^{\bullet}, R2^{\bullet}) + O_2 = RO_2^{\bullet}$
- $(19) \qquad 2RO2^{\bullet} = 2RO^{\bullet} + O_2$
- $(20) \qquad \text{RO2}^{\bullet} + \text{NO} = \text{RO}^{\bullet} + \tilde{\text{NO}}_2$
- (21)  $RO^{\bullet} + O_2 = HO_2^{\bullet} + products$ (aromatic-CHO, -O)
- (22)  $RO^{\bullet} \rightarrow aliphatic products$

The possibility of the process application for dioxins removal from off gases has been studied [21, 28] and recent pilot studies demonstrated that the process is technically and economically feasible [20].

## Radiation processing of aqueous system

Irradiation of water with ionizing radiation produces ionized and excited water molecules and free electrons. The excited water molecules quickly return to the ground state. Ionized molecules react in liquid water to form hydroxyl radicals, OH,

$$(23) \qquad H_2O^+ + H_2O \rightarrow H_3O^+ + OH^{\bullet}$$

The free electrons become hydrated

(24) 
$$e^- + nH_2O \rightarrow e_{aq}$$

The radicals react between themselves or with hydrogen ion  $(H_3O^+)$  to form molecules H, HO and H. The yield of radicals and molecular products depends on pH. At low pH, hydrated electrons react with hydrogen ion  $(H_3O^+ \text{ or } H^+)$  to form hydrogen atom

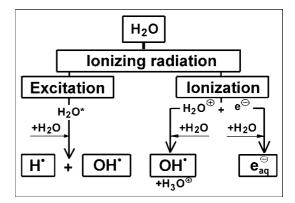
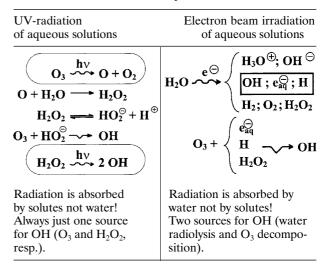


Fig. 4. Water radiolysis: formation of free radical species in water by means of ionizing radiation.

 
 Table 1. Fundamental reactions for OH radicals generation in different advanced oxidation processes



(25) 
$$e_{aq}^{-} + H_3O^+ \rightarrow H_2O + H$$

Radical products are highly reactive and are responsible for most of the chemical reactions when aqueous solutions are irradiated. A scheme of the process is given in Fig. 4 [16].

A comparison of processes induced by UV and electron beam irradiation is presented in Table 1.

# Radiation purification of drinking water and wastewater

Contamination of surface water and groundwater from industrial waste and anthropogenic activities is a serious problem in many countries. The wide application of fertilizers, pesticides, fungicides can lead to ground water pollution and consequent contamination of drinking water. Population growth and declining fresh water supplies make a need for clean water to be one of the critical challenges for the 21st century. Because of the increasing levels and complexity of polluted effluents from municipalities and industry, current wastewater treatment technologies are often not successful for the remediation of polluted waters and disinfection. The development and implementation of alternative technologies for the clean up of industrial wastewater, municipal water, groundwater and drinking water is critical to the sustainability of many countries. Among the possible water treatment alternatives radiation processing, a very effective form of energy use, can degrade toxic organic compounds and biological contaminants. Prof. Pikaev [30] was a pioneer in the development of this technology. Furthermore, important research

has been performed at a Miami pilot facility [22]. Aqueous effluents that have been treated by irradiation include polluted drinking water, liquid industrial and agricultural wastes. However, attention must be paid to the toxicity of the by-products formed in the process which is the main limitation of its implementation. This is the major factor which has to be carefully studied during the implementation of all advanced oxidation technologies (ozone, ozone +  $TiO_2$ , UV) [17]. The differences and similarities of UV and EB water treatment mechanisms are given in Table 1 [15]. The industrial effluents contain a variety of pollutants at high concentrations, and substances that are toxic or difficult to destroy such compounds as salts of mercury and bismuth, cyanides, phenols and dyes. To remove such pollutants by irradiation treatment, high doses are generally required and combined processes, which have been developed in a combination with conventional processes such as chemical, biological, or thermal treatment, floatation, and others, should be applied. Only few full-scale applications are available.

When water containing humic substance is treated with chlorine, carcinogenic chlorinated organic compounds are formed. Studies suggest that a comparatively low dose of 1 kGy will bring about decolourisation, deodorization, and disinfection of natural water and dechlorination of organic chlorocompounds present at low concentrations [1].

An electron accelerator (0.7–1 MeV, 50 keV) was applied at a Voronezh rubber plant in Russia to convert the non-biodegradable emulsifier Nekal in a plant waste into the biodegradable form. The dose required to decompose  $10^{-3}$  mol/dm<sup>3</sup> Nekal in aqueous solution was 300 kGy. The plant had two production lines and could treat up to  $2 \times 10^{3}$  m<sup>3</sup> of effluent per day [2].

The most promising achievements were achieved recently in South Korea, where a pilot plant is in operation [38].

A pilot plant (output 1000 m<sup>3</sup>day<sup>-1</sup>) with an ELV electron accelerator (energy 1 MeV, beam power 40 kW) is in operation since October 1998. Combined electronbeam and biological treatment was used for the purification of dyeing complex wastewater under continuous flow conditions. The main results of pilot-scale experiments consisted, in fact, that a decrease in total content of pollutants after biological treatment was substantially influenced by a preliminary electron-beam treatment (mainly, because of radiolytic conversions of terephthalic acid which is the main pollutant of wastewater). The reduction of non-biodegradable COD (chemical oxygen demand) into biodegradable BOD (biological oxygen demand) compounds was achieved. An equal purification degree corresponded to 17 hours of bio-treatment without preliminary irradiation and

about 8 hours of bio-treatment with preliminary electronbeam treatment at an absorbed dose of 1–2 kGy.

An industrial plant is being constructed. Based on the data obtained in the laboratory and pilot plant experiments, suitable doses are determined as being around 0.2 kGy for a flow rate of 10,000 m<sup>3</sup> effluent per day. Therefore, accelerator with the power of 400 kW is applied for economies and compactness of the plant.

The actual operation cost for 100,000 m<sup>3</sup>/day plants is 430,000 \$US/yr, and, if we consider the interest and depreciation of investment, the cost comes up to around 1 \$USM/yr. It is approximately 0.12 \$US/m<sup>3</sup> for the construction and 0.03 \$US/m<sup>3</sup>/yr for operation, so it is inexpensive as compared to other advanced oxidation techniques such as ozonation, UV techniques etc.

# Radiation induced removal of heavy-metal ions from water

Toxic metals from industrial effluent streams include heavy metals such as lead, mercury, cadmium, nickel, silver, zinc, and chromium. These heavy metals are accumulated in soil and eventually are transferred into human food chain [34]. Ionizing radiation of aqueous solutions generates free radicals, radical ions and stable products:

(26) 
$$H_2O \rightarrow e_{ac}^-, H; OH, H_2O_2, H_2, H_3O^+$$

with yields (G value) of  $0.28(e_{aq}^{-})$ , 0.062(H); 0.28(OH),  $0.072(H_2O_2)$ ,  $0.047(H_2)$  in units of  $\mu$ mol/J.

The hydrated electron  $e_{aq}^{-}$  is the strongest reducing agent.

(27) 
$$e_{aq}^- + H_3O^+ \rightarrow H^\bullet + H_2O$$

Cr(V) is unstable and is further reduced to the stable  $Cr^{3+}$  ions

(28) 
$$\operatorname{Cr}(\operatorname{VI}) + \operatorname{H}^{\bullet} \to \operatorname{Cr}(\operatorname{V})$$

Lead can also be reduced by H<sup>•</sup> atoms

HgCl is not stable and dimerized to  $Hg_2Cl_2$  as a final insoluble products

$$(36) 2HgCl \to Hg_2Cl_2$$

The hydroxyl radical ('OH) is one of the powerful oxidizing species, which lead to the transformation of the metal ions to higher valence states [18]. However, due to the fact that normally the concentrations of heavy metals in wastewater are very low (ppms), the process

does not seem to be technically feasible, since trace quantities of reduced metals have to be separated by a mechanical way from wastewater. For higher concentrations chemical (precipitation, ion exchange) or physical methods (membranes, electrolysis) are more feasible from economical or technical points of view.

### Radiation processing of solid state systems

### Municipal sewage and sludge

Electron beam irradiation is a practical and economic method for disinfecting liquid municipal wastes and sludge. Deer Island Electron Research Facility in Boston found a dose of 0.5 kGy to be sufficient to disinfect municipal wastewater effluent and also to decompose organic pollutants. Takasaki Radiation Chemistry Research Establishment found that a dose of about 0.4 kGy was required in order to disinfect raw wastewater prepared by mixing primary and secondary sewage effluents [26].

Research has shown that sewage sludge can be disinfected successfully by exposure to high-energy radiation. At a plant near Munich, doses of 2–3 kGy destroy more than 99.9% of bacteria present in sewage sludge, and at a plant near Boston a slightly higher dose (4 kGy) was used. Higher doses (up to 10 kGy) are required to inactivate more radiation resistant organisms at plants in Albuquerque, USA and Ukraine. Both gamma sources (Co-60, Cs-137) and electron accelerators can be used for irradiation of sewage sludge. Gamma sources have better penetration allowing thicker layers of sludge to be irradiated [9], although they are less powerful and take longer irradiation time than electron sources [19].

The pilot plant using a gamma source is operating in India. The irradiator system can be easily integrated with a conventional treatment plant with flexibility of operation. Various dose treatment can be imparted to sludge with the addition of sensitising agents such as oxygen, air, ozone, etc. The radioactive source loading, unloading or transport is very easy and very safe. It can be accomplished in a day. After augmentation of source strength in the early 2001, 12 cubic meters of sludge is irradiated in one shift (yielding a 5 ton sludge per month). About 3 kGy of absorbed dose in sewage sludge removes 99.99% of pathogenic bacteria consistently and reliably in a simple fashion.

The process of hygenization of sewage sludge using radiation is very simple. The incoming sludge is taken to an underground reservoir. It is then fed to irradiation vessel of 3 m<sup>3</sup> capacity and circulated continuously in a loop for a pre-determined period. After the radiation exposure, the treated sludge is withdrawn from the irradiation vessel and pumped out to drying sand beds where the water evaporates yielding pathogen free dried sludge. The irradiated sludge being pathogen free can be beneficially used as manure in the agricultural fields as it is rich in nutrients required for the soil. The performed initial field trials in villages of Baroda city on sludge as manure in agriculture fields in winter wheat crops as well as in summer green gram crops have been

very encouraging and have prompted farmers for putting increasing demands. Since the irradiated sludge is free from bacteria, it can also be used as a medium for growing soil useful bacteria like rhizobium and azetobactor to produce bio-fertilizers, which can be used to enhance the crop yields.

#### Soil remediation

The US Environmental Protection Agency (EPA) has found that polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) present serious public health risk and set limits on storage, transport, and disposal of waste materials containing dioxins. A limit of 1 ppb has been established for 2,3,7,8tetrachlorodibenzo-p-dioxin (TCDD), which is the most toxic member of this family of compounds. Studies have demonstrated that TCDD can be converted to products of neglibible toxicity by radiolysis with gamma rays from cobalt-60. Destruction greater than 98% was achieved with a dose of 800 kGy in a soil contaminated with 100 ppb of TCDD. Addition of contaminants such as dichlorobenzene and hexachlorobenzene did not affect the result. The addition of 25% water and 2.5% nonionic surfactant was beneficial with the model soil [19].

### Mail decontamination

Anthrax that was sent in the mail in October 2001 caused several deaths and big economic losses in the USA. Radiation proved to be very effective for mail decontamination. About 4000 tons of letter mail and 200 tons of parcels had been sanitized by the end of 2003 [11].

### Conclusions

- Electron beam flue gas treatment (deSO<sub>x</sub> and deNO<sub>x</sub>) has been implemented on an industrial scale in Poland and China.
- Electron beam flue gas treatment has been proven to be effective for VOC and PAH removal. The discussed technology has been tested in industrial conditions for flue gases from a coal fired boiler and an incinerator plant of municipal solid wastes. Toxicity reduction is the efficiency measure to different by-products formed.
- 3. Regarding the treatment of organic pollutants in the wastewater, similar to other AOT, by-products formed, have to be considered and toxicity tests are the best parameter of the process efficiency. Combined eb/biological process has been studied on a pilot scale in South Korea.
- 4. Biological contamination control of the secondary effluents seems to be the most promising application at the moment and an industrial plant applying the process is constructed in South Korea.
- 5. Pilot plant for gamma ray sludge hygenization has been in operation in India for several years. The

technology proved its effectiveness and the product is a fertilizer of good quality.

6. An new application of the technology based on electron accelerators, namely the mail decontamination against bio-terroristic agents was established.

### References

- Bumsoo H, Jaein K, Jinkuy K et al. (2002) Combined electron-beam and biological treatment of dyeing complex wastewater. Pilot plant experiments. Radiat Phys Chem 64;1:53–59
- Chaychian M, Al-Sheikhly M, Silverman J, McLaughlin WL (1998) The mechanisms of removal of heavy metals from water by ionizing radiation. Radiat Phys Chem 53;2:145–150
- 3. Chmielewski AG (1995) Technological development of eb flue gas treatment based on physics and chemistry of the process. Radiat Phys Chem 46:1057–1062
- Chmielewski AG (2002) Environmental effects of fossil fuel combustion. In: Kubota SH, Magara Y (eds) Encyclopedia of life support systems (EOLSS). EOLSS Publishers, Oxford, UK, www.eolss.net
- Chmielewski AG, Licki J, Pawelec A, Tymiński B, Zimek Z (2004) Operational experience of the industrial plant for electron beam flue gas treatment. Radiat Phys Chem 71;1-2:439–442
- Chmielewski AG, Ostapczuk A, Zimek Z, Licki J, Kubica K (2002) Reduction of VOCs in flue gas from coal combustion by electron beam treatment. Radiat Phys Chem 63;3-6:653–655
- Chmielewski AG, Tymiński B, Dobrowolski A *et al.* (1998) Influence of gas flow patterns on NO<sub>x</sub> removal efficiency. Radiat Phys Chem 52;1-6:339–343
- Chmielewski AG, Tymiński B, Licki J, Iller E, Zimek Z, Radzio B (1995) Pilot plant for flue gas treatmentcontinuous operation tests. Radiat Phys Chem 46:1067–1070
- Chmielewski AG, Zimek Z, Bryl-Sandelewska T, Kosmal W, Kalisz L, Kaźmierczuk M (1995) Disinfection of municipal sewage sludges in installation equipped with electron accelerator. Radiat Phys Chem 46:1071–1074
- Cooper WJ, Curry RD, O'Shea KE (eds) (1998) Environmental applications of ionizing radiation. John Wiley & Sons, Inc., New York
- 11. Desrosiers MF (2004) Irradiation applications for homeland security. Radiat Phys Chem 71;1-2:479–482
- 12. Doi Y, Nakanishi I, Konno Y (2000) Operational experience of a commercial scale plant of electron beam purification of flue gas. Radiat Phys Chem 57;3-6:495-499
- Environmental and health aspects of water treatment and supply (2002) In: Kubota SH, Magara Y (eds) Encyclopedia of life support systems (EOLSS). EOLSS Publishers, Oxford, UK, www.eolss.net
- Frank NW (1995) Introduction and historical review of electron beam processing for environmental pollution control. Radiat Phys Chem 45;6:989–1002
- Gehringer P, Eschweiler H (2004) Radiation processing of secondary effluents from municipal wastewater treatment plants. In: Proc of Int Symp on Advanced Oxidation Technologies, 18 June 2004, Warsaw, Poland, pp 25–28
- Gehringer P, Eschweiler H (2002) The dose rate effect with radiation processing of water – an interpretative approach. Radiat Phys Chem 65:379–386
- Getoff N (1996) Radiation-induced degradation of water pollutants – state of the art. Radiat Phys Chem 47;4:581–593

- Hashimoto S, Nishimura K, Machi S (1988) Economic feasibility of irradiation-composting plant of sewage sludge. Int J Radiat Appl Instrum C: Radiat Phys Chem 31;1-3:109–114
- Hilarides RJ, Gray KA, Hakoda T, Guzzetta J, Cortellucci N, Sommer C(1996) Feasibility, system design, and economic evaluation of radiolytic degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin on soil. Water Environ Res 68;2:178–187
- Hirota K, Hakoda T, Taguchi M, Takigami M, Kim H, Kojima T (2003) Application of electron beam for the reduction of PCDD/F emission from municipal solid waste incinerators. Environ Sci Technol 37;14:3164–3170
- Hirota K, Tokunaga O, Miyata T *et al.* (1995) Pilot-scale test for electron beam purification of flue gas from a municipal waste incinerator with slaked-lime. Radiat Phys Chem 46;4-6:1089–1092
- Kurucz CN, Waite TD, Cooper WJ (1995) The Miami Electron Beam Research Facility: a large scale wastewater treatment application. Radiat Phys Chem 45;2:299–308
- 23. Machi S (1983) Radiation technology for environmental conservation. Radiat Phys Chem 22;1-2:91–97
- Mätzing H, Namba H, Tokunaga O (1993) Kinetics of SO<sub>2</sub> removal from flue gas by electron beam technique. Radiat Phys Chem 42;4-6:673–677
- Mätzing H, Paur HR (1992) Chemical mechanisms and process parameters of flue gas cleaning by electron beam. In: Nriagu JO (ed.) Gaseous pollutants: characterization and cycling. Wiley, New York, pp 307–331
- Miyata T, Kondoh M *et al.* (1990) High energy electron disinfection of sewage wastewater in flow systems. Int J Radiat Appl Instrum C: Radiat Phys Chem 35;1-3:440-444
- 27. Namba H, Tokunaga O, Hashimoto S *et al.* (1995) Pilotscale test for electron beam purification of flue gas from coal-combustion boiler. Radiat Phys Chem 46;4-6:1103–1106
- Paur H-R, Baumann W, Mätzing H, Jay K (1998) Electron beam induced decomposition of chlorinated aromatic compounds in waste incinerator off gas. Radiat Phys Chem 52;1-6:355–359
- 29. Person JC, Ham DO (1988) Removal of  $SO_2$  and  $NO_x$  from stack gases by electron beam irradiation. Radiat Phys Chem 31:1–8
- 30. Pikaev AK (2002) New data on electron-beam purification of wastewater. Radiat Phys Chem 65;4-5:515–526
- Proceedings of 15th Symposium on Environmental Protection and Safety, October 17, 2003, Seoul, South Korea
- 32. Radoiu MT, Martin DI, Calinescu I (2003) Emission control of  $SO_x$  and  $NO_x$  by irradiation methods. J Hazard Mater B 97:145–158
- 33. Rukes B, Taud R (2004) Status and perspectives of fossil power generation. Energy 29;12-15:1853–1874
- Sarma KSS (2004) Prospects and development of radiation technologies in developing countries. In: Emerging applications of radiation processing. IAEA-TECDOC-1386. IAEA, Vienna, pp 14–20
- 35. Srivastava RK, Jozewicz W, Singer Ĉ (2001) SO<sub>2</sub> scrubbing technologies: a review. Environ Prog 20:219–227
- Tokunaga O, Suzuki N (1984) Radiation chemical reactions in NO<sub>x</sub> and SO<sub>2</sub> removals from flue gas. Radiat Phys Chem 24;1:145–165
- Wittig S, Spiegel G, Platzer K-H, Willibald U (1988) Simultane Rauchgasreingung durch Elektronenstrahl. KfK-PEF 45. Kernforschungszentrum, Karlsruhe
- 38. Woods RJ, Pikaev AK (1994) Applied radiation chemistry. John Wiley & Sons, New York