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Collection and application of by-product formed in EB flue gas treatment process

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Fine particles of aerosols are formed in reaction of ammonia with acid formed during eb flue gas treatment process. The solid product is a mixture of ammonium sulfate and nitrate. The size distribution of particles at the outlet of irradiation vessel is presented in Fig. 1[1].

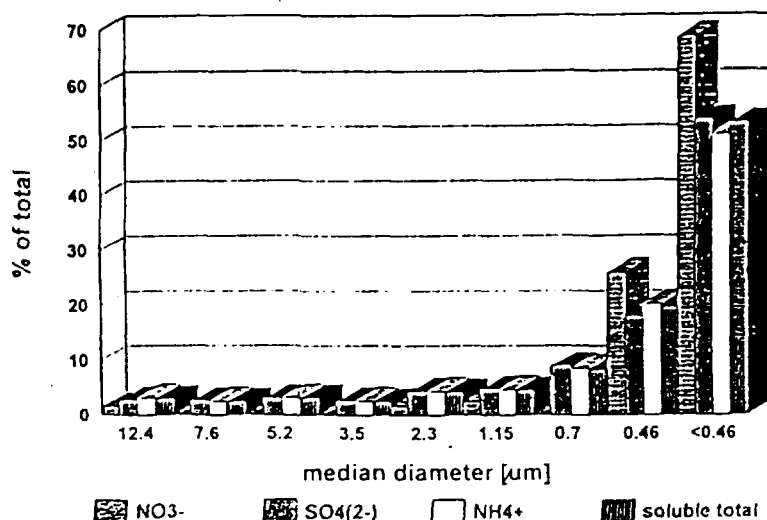


Fig. 1. Size distribution of the components of aerosol collected in flue gas after the reaction chamber Initial SO₂ concentration 250 ppmv, NO_x - 220 ppmv, flow rate 14 000 Nm³/h, dose 5.1 kGy, humidity 7.74% vol., NH₃ stoichiometry - 0.9.

Different methods of filtration were applied to collect the byproduct. These are bag filter [1], wet gravel bed filter. These methods were investigated during joint IAEA-JAERI-INCT research (bag filter and ESP [3] and cooperation project FZ Karlsruhe-INCT (wet gravel bed filter [2]).

Results concerning efficiency and filtration system reability were the basis for system selection to be applied in the industrial scale demonstration plant for flue gas treatment, and ESP was selected. The technical parameters of the ESP are presented.

The agricultural application of the byproduct has been tested by Agricultural Academy, Warsaw and on the basis of the byproduct two types of NPK fertilizers were elaborated by fertilizer company according to existing standards.

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A new flue gas treatment system based on Electron Beam
process

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DOSE RATE EFFECTS ON THE e-SCRUB™ PROCESS -- EXPERIMENTS AND THEORY*

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This paper compares the results of experiments with plasma chemistry calculations to study the effect of dose rate, pulse length and pulse repetition rate on pulsed electron beam processing of nitrogen oxides (NO_x) and sulfur dioxide (SO_2) in gases. The main objectives are to determine if the proposed combination of dose rate, pulse length and pulse repetition rate would have any deleterious effect on the utilization of radicals for pollutant removal.

We find that for a dose rate of 2×10^5 Mrad/s and pulse length of 30 ns, the dose per pulse is sufficiently low to prevent any deleterious effect on process efficiency because of radical-radical recombination reactions. During each post-pulse period, the radicals are utilized in the oxidation of NO_x and SO_2 in a time scale of around 200 μs ; thus, with pulse frequencies of around 5 kHz or less, the radical concentrations remain sufficiently low to prevent any significant competition between radical-pollutant and radical-radical reactions.

The main conclusion is that a pulsed electron beam system, operating with a dose rate of 2×10^5 Mrad/s, pulse length of 30 ns, and pulse repetition rate of up to around 5 kHz, will have at least the same plasma chemistry efficiency as an continuous wave electron beam system.

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Decomposition of Tetrachloroethylene by Ionizing Radiation

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Introduction

Up to the present, we have studied decomposition of several VOC such as benzene, toluene, trichloroethylene and tetrachloroethylene(PCE) by ionizing radiation[1]. It was observed that PCE were more easily decomposed by ionizing radiation than any other VOC and the decomposition efficiency of PCE by electron beam(EB) irradiation was higher than that by gamma ray irradiation. Tetrachloroethylene has been mainly used as the solvent to clean parts of electric equipment and the washing agent of dry cleaning. Tetrachloroethylene is very harmful to a human being because of carcinogenic character and depressing of blood function and causes serious air pollution. So the release of PCE in the atmosphere should be strictly controlled. In this work, the model gases containing vaporized PCE in air from 150 to 1,800 ppm were irradiated with EB and gamma ray in order to study the behavior of PCE decomposition by ionizing radiation.

Experimental

The Pyrex glass reactors were used as irradiation vessels. The reactor have a external dimensions of approximately 50 mm(W) by 200 mm(L) by 50 mm(H) and stop cocks at both sides. Model gas containing vaporized PCE in air was prepared by bubbling the base gas, which contained about 300 ppm water, through liquid PCE. The sample gas was introduced into five reactors connected in series. The PCE concentrations of the last reactor were measured by a gas chromatograph(GC-8A, Shimadzu Seisakusho Ltd.).

For EB irradiation, the reactor containing the model gas was put on a conveyor and irradiated by a 2MV electron accelerator(Cockcroft-Walton type, Nisshin High-Voltage Co. Ltd.). A plate type Co-60 with the capacity of 12,000 Ci was used for gamma ray irradiation. After the irradiation, the PCE concentrations in the model gas were measured by the gas chromatograph.

Result

Figure 1 shows the remaining concentrations of PCE vs. dose by EB and gamma ray irradiations. PCE was more easily decomposed by EB irradiation than gamma ray irradiation at the same initial concentration. For example, the doses necessary to decompose 90 % of PCE by EB and gamma ray irradiation were 2 and 5 kGy at about 300 ppm, 3 and 6 kGy at about 600 ppm and 4 and 6 kGy at about 900 ppm.

G-values of PCE decomposition by both irradiations were calculated using the change of PCE concentration in the low dose range and shown in Figure 2. G-values of decomposition increased with the initial concentration of PCE in both cases. For example, those were 60 and 124 at 700 ppm and 1400 ppm by EB irradiation, 44 and 76 at 900 ppm and 1,800 ppm by gamma ray irradiation, respectively. G-values of decomposition by EB irradiation were about two times higher than those by gamma ray irradiation. G-values of PCE decomposition were much higher than those of active species formation from air component. This suggests that a chain reaction would occur in the decomposition process of PCE[2].

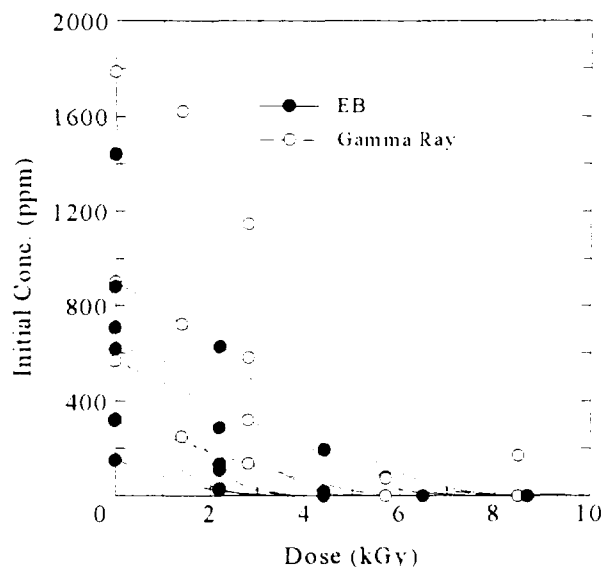


Figure 1. Remaining concentration of PCE vs. dose by EB and gamma ray irradiation.

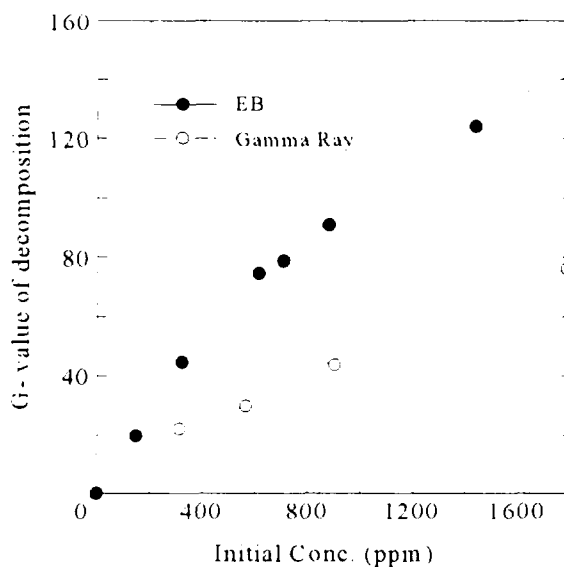


Figure 2. G-values of decomposition vs. the initial concentration of PCE by EB and gamma ray irradiation

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VOC Removal by Simultaneous Electron Beam and Biofilter Application

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During the recent years the stringent legislation and the public environmental knowledge has led to the situation in which many companies have to reduce process and ventilation gas emissions which contain VOCs (Volatile Organic Compound) and are noxious for environment. One new environment and user friendly alternative for VOC control is the biofiltration. There are some different kind of commercial versions (see for example [1,2]). Although different biofilter realizations have great differences the basic idea is same for all of them. Biofiltration is the use of microorganism growing in the media (solid [1,2] or liquid [3]) through which the gas to be treated is forced. While moving through the filter the VOCs in the air transfer from air phase to water phase where the bioorganisms can destroy (metabolize) the contaminants. The products of this VOC destruction process are carbon dioxide, water and different metabolism residues. The microorganisms are maintained by nutrients provided by medium or carried by water and by oxygen and by different components absorbed from the air stream to be treated.

Biofiltration has some notable advantage compared to other VOC control techniques. It has moderate capital costs and low operating costs. The process has no hazardous by-products. Biofilters can be used to control various odors and dilute VOC. The clean-up efficiency is in many cases over 90 %. Biofiltration is a “natural” way to remove VOCs. The water need of biofiltration is small and wastewater flow is fairly clean. Disadvantages of biofiltration are its relatively large

space requirement and that it is not possible to handle effectively sources where the concentration fluctuate severely. The large space requirement is to provide adequate residence time for VOC adsorption and destruction. In some cases VOCs with high concentration are poisonous also for decomposing microorganisms. Therefore the actual filters might be supported by dilution chambers to confirm the filter operation. In addition, biofilter is not an on/off filter, it must have some time to adapt a certain gas stream.

The aim of our study is to solve the biofiltration problems described above by our joint filter. It has been found in the earlier investigations that electron beam can effectively clean different kind of dilute VOC contaminated gases [4,5,6,7]. In electron beam treatment the clean-up efficiency for VOC depends on the organic compound to be treated and its concentration together with the total dose. For example Hirota *et al.* found the removal efficiency at 10 kGy dose to be nearly 90% to xylene but only about 50 % to butylacetate. By joining electron beam treatment and biofiltration we can combine the properties of two good choice. With low emission rate the biofilter can purify the air stream alone and we have the minimum operating costs. With higher emission rates the electron beam treatment is a powerful prefilter which change the VOC concentration to optimal level for biofilter.

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TEST OF REMOVING SO₂/NO_x USING 12MeV ELECTRON LINAC

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Removing efficiency of SO₂/NO_x using 12MeV electron linac was investigated. The accelerator is an electron linear accelerator, the main parameters are as below[1]:

operating frequency:	2856MHz
Electron energy:	12MeV (nominal)
Average beam power:	2kW
Repetition frequency:	250pps
Pulse width:	2.5 μ s
Window width:	600mm
Uniformity of scanned beam	<10%

The flue gas including SO₂/NO_x was gathered from a chimney of the boiler burning coal. The container of SO₂/NO_x flue gas is of glass made and the schematic is shown in Fig.1.

Before test, Valves No.1 and No.2 are closed. Using the mechanical vacuum pump to evacuate the glass container. after closing Valve No.3, open the Valve No.1 to let the flue gas into the container. Then using the 12MeV electron beam to irradiate the flue gas and in the meantime let a flow of NH₃ into the container.

In order to monitor the absorbed dose, radiochromic plastic films developed by Risø National Lab.(Denmark) was used. According to specification of the film, the accuracy is estimated to be $\pm 10\%$, while the precision is $\pm 3\%$. [2].

The electron energy was calibrated using electron penetration in aluminum. According to the empirical formula [3], the probable energy $E_{p,0}$ of the electron beam can be expressed as:

$$E_{p,0} = C_1 \times R_p + C_2 \quad (1)$$

where $C_1 = 5.09 \text{ MeV/cm}$, $C_2 = 0.2 \text{ MeV}$, R_p is the practical range (in cm), and measured $R_p = 2.32 \text{ cm}$. So $E_{p,0} = 5.09 \times 2.32 + 0.2 = 12 \text{ MeV}$.

Measured results are shown in Fig.2. From the Fig, we can see that if the absorbed dose is higher than 1Mrad, more than 95% SO_2 will be removed from the flue gas, but only 80% NO_x is removed at 1Mrad. These results are similar to the results of publications [4]. This means that this method is very usefal and effective. Now we try to increase the beam power and control the reaction temperature, and hope to get better results.

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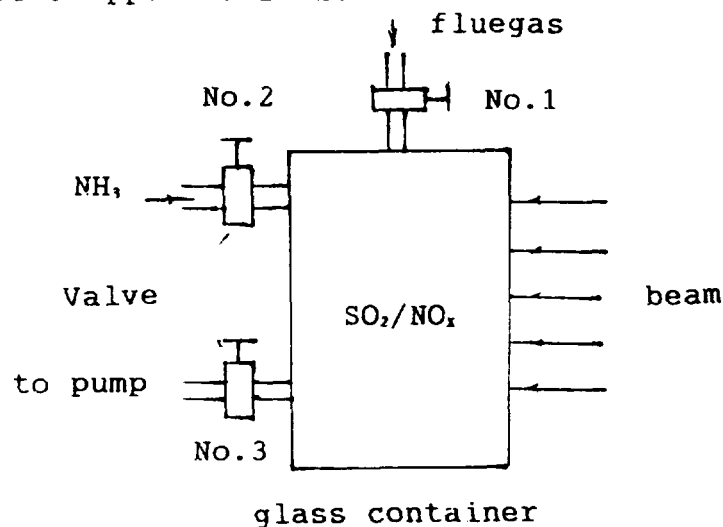


Fig.1 Schematic of the fluegas treatment

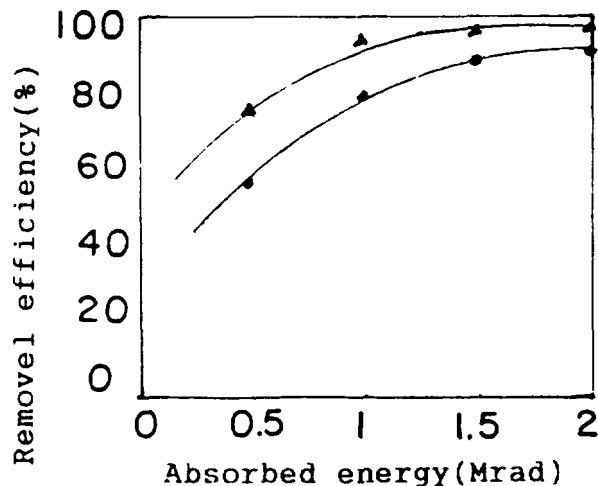


Fig.2 Removal efficiency versus absorbed dose



**PRE-FEASIBILITY STUDY FOR AN ELECTRON BEAM FLUE GAS
TREATMENT DEMONSTRATION PLANT TO ELETROPAULO'S
PIRATININGA POWER PLANT**

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According to Brazil's National Electric Energy Plan (1993-2015) for the next years a minimum thermal program must be implemented to ensure the country's technological development in this area using coal, natural gas, oil products, fuel oil and biomass [1]. Also, the existing thermal power plants have an important status to supply energy during dry seasons, once most of electrical energy in Brazil comes from hydraulic source and also to supply energy in emergency situations such as transmission problems. These plants are usually near great urban centers with all the environmental problems common to these centers: emissions of SO_2 and NO_x into the atmosphere causing air pollution and acid rain.

In Brazil there are laws to control pollutants emission fixed by "CONAMA", the Brazilian National Environmental Council, which establishes maximum values for emissions mainly the SO_2 . This resolution affects new fixed sources of pollution that are coal or oil fuel burning: incinerators, thermal power plants and so on. According to these laws, the development of combustion gases dessulfurization methods is necessary, and in a near future also the denitrification, mainly in attention to the "Agenda 21" adopted in Rio de Janeiro for environmental conservation in 1992.

Eletropaulo - Eleticidade de São Paulo S. A. is the public service electric utility responsible for the supply of energy to more than 5,800,000 customers settled in the city of São Paulo and in other 78 locations, covering an area of 21,168 km^2 where approximately 20,2 million people live.

Eletropaulo's Piratininga Power Plant is located near São Paulo downtown; this big city, in the southeast of Brazil, in São Paulo state, has around 16 million inhabitants. São Paulo city has serious problems concerning air pollution and the Plant is trying to reach the parameters established by the CETESB (Company of Environment Sanitation), a Governmental Institution responsible for the environmental control in São Paulo state. When this plant operates at full load it is the main emission source of SO_2 in the city and it had serious difficulties to operate at full load, when necessary in 1986. This situation is occurring nowadays and the tendency increases for the next years according to the electric system needs.

Piratininga Power Plant is a 470MW - plant, 2 x 100MW, built in 1954 and 2 x 135MW, erected in 1960, which are oil-fueled. The consumption at

full load is 2,800 ton per day (full load). The oil is BTE low sulphur content (< 1%).

Eletropaulo has been worried with air pollution problems since seven years ago, when it started, together with IPEN-CNEN/SP, studies concerning electron beam technology for flue gas treatment, which has the following advantages: efficient simultaneous removal of SO_2 and NO_x ; dry process without waste water treatment, producing a valuable fertilizer by-product; easy to operate with an easy system start-up and shut-down; lower capital investment and competitive operation costs; not so big space required and possibility of using in retrofit installations [2].

In this study it was discussed the mode of operation for the plant and various options that we have for fuel supply, with a sulphur range of 1.0 to 5.0%. It was decided to use a medium point of 2.5% sulphur, since the process is capable of handling swings in the SO_2 content. It was also decided to look at a size of about $150,000\text{Nm}^3/\text{h}$. This is equivalent to about 50MW. Electron beam accelerators and the sizes that would be required were also discussed. Dr. Frank brought information from Nissin High Voltage Co. So, we can use a standard 300kW machine for the proposed study.

For this evaluation, we considered some gas input condition and we obtained an output condition for the process of 80% SO_2 removal for different flue gas flow rates. The estimated implantation cost for flue gas rate of $150,000\text{Nm}^3/\text{h}$ is around 240US\$/kW.

Besides, if Eletropaulo uses this process burning only 4400ton of fuel oil per month, equivalent to operating with 18MW, with high sulphur oil content (2.5%) that is cheaper than BTE low sulphur, it will save US\$ 1590000 per year. So, it pays the project in around eight years.

The Japan Consulting Institute - JCI, has approved the support for a Feasibility Study for a Commercial scale Plant of the electron beam flue gas treatment process in the Piratininga Power Plant. In a further discussion, Eletropaulo has decided to ask this study for a 100MW single unit, with estimated flue gas of $320,000\text{Nm}^3/\text{h}$, considering three alternatives to remove: 70%, 80% and 90% of SO_2 and the correspondent NO_x .

Acknowledgments

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DEVELOPMENT OF A WET VARIANT OF E-BEAM GAS TREATMENT TECHNOLOGY
ADAPTED TO ECONOMICAL AND TECHNOLOGICAL CONDITIONS OF DEVELOPING
COUNTRIES TO REMOVE NO_x , SO_2 AND PARTICULATE FROM FLUE GAS AND
PRODUCE FERTILIZERS

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The Institute Energostal with its co-authors carried out industrial tests of EB flue gas treatment technology [1,2] at a $1000 \text{ m}^3/\text{h}$ pilot facility at Lipetsk Metallurgical Plant (Lipetsk, Russia). On the basis of the results obtained, a wet variant of the EB technology has been developed.

A conceptual and working designs were engineered for a $100000 \text{ m}^3/\text{h}$ EB demonstration unit at Slavyanskaya Power Plant (Donbass, Ukraine). In a wet variant of the technology, the following problems are harmoniously solved: reduction of power consumption for irradiation due to heterogeneous reactions using the droplet mechanism, efficiency and reliability of collecting ammonia salts by wet dust catchers, wet granulation of the by-product using traditional equipment. A wet variant of the EB technology has a low capital cost and requires less floor area. Therefore, despite all its disadvantages typical for any wet method of gas purification, the wet EB technology can find its application in developing countries with low levels of economy. In many countries of this kind, in particular, in the countries of the former Soviet Union, wet methods of gas treatment and fertilizer granulation are still widely used.

A schematic of an industrial EB demonstration unit is shown in Fig.1, its principle of operation being clear from its description. To collect fly ash before irradiation and the

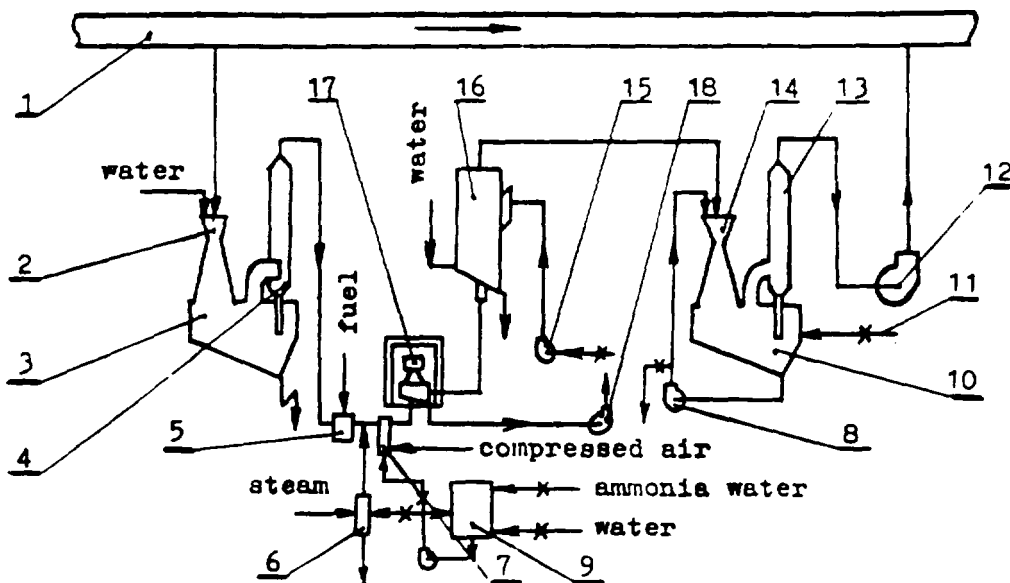


FIG.1. Schematic of E-beam demonstration unit at Slvyanskaya thermal power plant

1. Boiler flue 2. Variable throat Venturi scrubber 3. Separator tank 4. Droplet separator 5. Gas heater 6. Ammonia desorber 7. Ammonia water injector 8. Circulation pump 9. Ammonia water tank 10. Separator tank 11. Water make-up 12. Induced draft fan VVN-20 13. Droplet separator 14. Variable throat Venturi scrubber 15. Fan of type DH/Y 16. "Vikhr" ("Vortex") apparatus 17. Electron beam unit 18. Solution recirculation pump

product after irradiation, similar variable throat Venturi scrubbers 2 and 14 are used. A system to collect ammonia sulphate-nitrate (ASN) salts has a closed loop water supply to enable building up the ASN solution concentration up to 25% after which it is pumped to the granulation unit (not shown). The process chart of the granulation ensures minimum water loss. Prior to irradiation, either ammonia vapour desorbed from ammonia water or finely atomized ammonia water droplets are injected into the gas stream. The electron beam equipment is housed in the foundation of an existing smoke stack to reduce the cost of radiation protection. A modernized ELV-6 electron accelerator (Novosibirsk) with $E = 1 \text{ MeV}$ and beam power 150 kW is used. Within the range of the flue gas flow rate from $30000 \text{ m}^3/\text{h}$ to $100000 \text{ m}^3/\text{h}$, the absorbed dose varies from 1.8 Mrad to 0.54 Mrad, respectively.

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Taking into consideration the eventual reduction of energy consumption for irradiation, the removal efficiency is 75% for NO_x and 80% for SO_2 , the inlet concentration of SO_2 being 5700 mg/m^3 and that of NO_x - up to 1000 mg/m^3 . The specific capital cost is US\$ 43000 per $1000 \text{ m}^3/\text{h}$ of the flue gas being treated. A multi-year research has been carried out to develop a technology to utilize the by-product, ASN salts, as a fertilizer, Ukrainian equipment being used for the granulation. With the ash content in the by-product of 2 - 6%, it is an efficient and safe fertilizer. The demand of Ukraine in the fertilizers of this kind is 3 - 4 mln t/year, they can be used on an area of 500000 ha.

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TECHNICAL AND ECONOMICAL ASPECTS OF EB INSTALLATIONS FOR TREATMENT OF FLUE GAS FROM POWER PLANT

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Environmental impacts associated with the demand and supply of energy become important factors influencing on the development and commercial use of energy and emission-control technologies. Because the production of energy involves long-range transboundary air pollution, coordinated international emission - reduction strategies and policies have been developed to control pollutants of concern such as SO₂ and NO_x.

The emissions of pollutants are determined mainly by energy demand and supply and the presence of emission-control legislation. In particular, the kind of the fuel used in any given region has a great influence on the emissions.

Most of the countries have introduced emission limits depending on their individual situation. Such limits may depend on the kind of plant (new/old), the size of the plant and the fuel used. Emission limits vary by country from, for example, 200 mg/m³ SO₂ in Austria to 2 000 mg/m³ in Australia for the similar plant. This illustrates a trend towards introduction of more strict regulations, especially for new plants.

Fig. 1 presents the comparison of the existing and coming emission limits for SO₂ and NO_x in Poland with obligatory emission limits in EEC countries [1].

In addition to the enforcement of emission standards, further approach such as air-quality standards, fuel-quality standards and taxes on emissions are also used for emission limitation, but a main tools for reduction of pollutants are emission - control.

The market penetration of emission - control technologies depends on such country-specific conditions as energy, economic and environmental situation. Legislation, however, remains the most important factor. In particular, legislation concerning emission standards or the use/disposal of by-products determines the market share, the

velocity of market penetration and the technology used. In the case of SO_2 reduction from combustion installations, wet flue-gas desulphurisation (FGD) is the most wide use method.

The figures shown that the wet scrubbing technology covers about 90 % of the European installed FGD capacity.

Combustion modifications are a wide-spread technology for NO_x reduction. However, the application of these measures is generally insufficient to fulfil the emission requirements in some countries. Therefore, since the mid-1980s, power plants have been equipped with secondary measures; in the European OECD countries, an electric capacity of more than 36 000 MW has been installed at new and existing power plants. The secondary measure most commonly used for the removal of NO_x from flue gas is the selective catalytic reduction process (SCR). On the other hand, the scientists and engineers have searched for new cost - effective technologies for simultaneous removal SO_2 and NO_x . One of them, the electron beam dry scrubbing process is proposed to be employed in industrial scale.

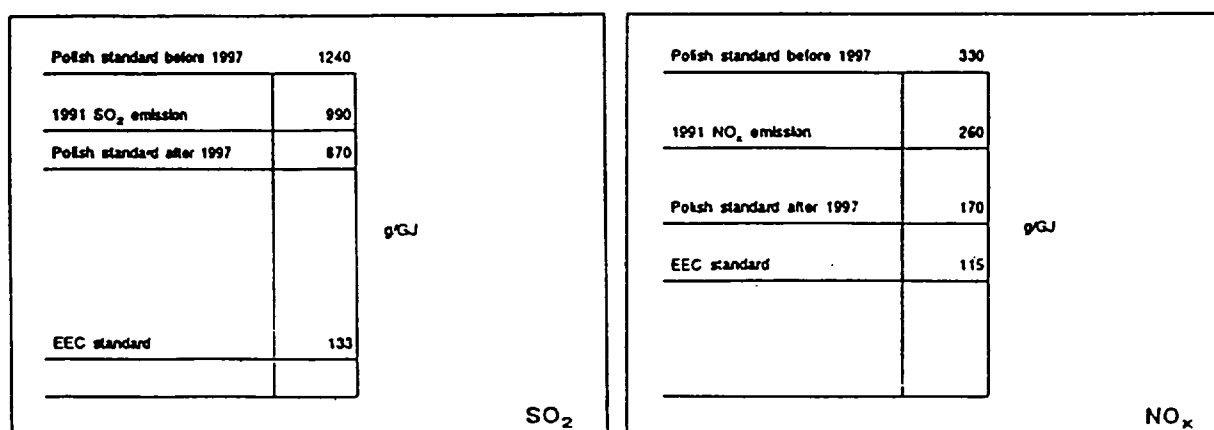


Fig.1. Comparison of Polish and EEC the emission standards for SO_2 and NO_x .

Evaluation of technology applying electron beam to energetic inducing of the outlet gas components should recognize that removal of boths SO_2 and NO_x is accomplished.

In Fig.2 comparison of the investment costs vs emitter capacity for different methods of removal of SO_2 and NO_x from the flue gases is shown [2].

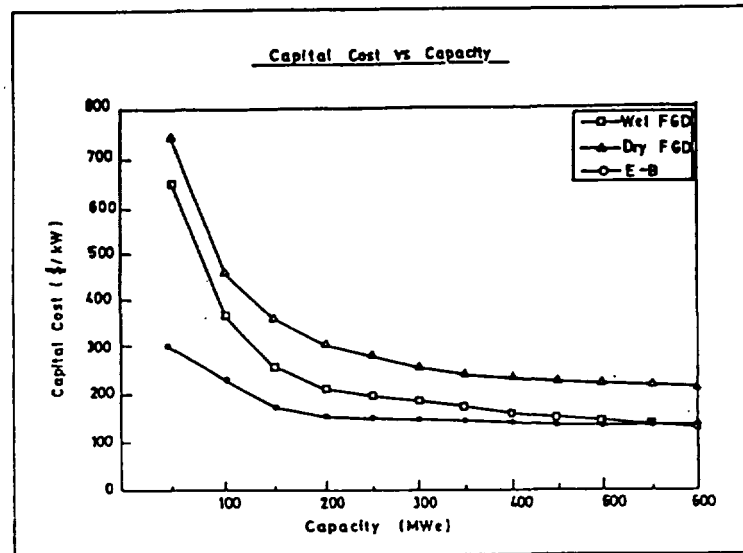


Fig.2. Comparison of the capital costs for different FGD technologies versus capacity of emitter.

As follows from quoted data, the investment cost of e-b technology is on the level 150-200 \$/kWe of the installed electric power. Significant competitiveness of the electron - beam technology to the another technologies is evident.

The investment and operation costs of FDG installation effect on the final price of electricity.

In the paper the economics analyse of e-b and others technologies for flue gases treatment introduced in Polish market are discussed.

It should be pointed out that the Electric Power Research Institute (USA) estimated that from among 70 checked technologies for simultaneous SO₂ and NO_x removal from the flue gas, application of electron beam is one of the four most promising second - generation methods recommended for simultaneous removal of SO₂ and NO_x [3].

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INFLUENCE OF DOSE DISTRIBUTION AND FLOW PATTERN BETWEEN IRRADIATION STAGES ON REMOVAL OF NO_x

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In case of multistage gas irradiation in industrial conditions it is expected that dose distribution as well as mixing between stages have influence on NO_x removal efficiency. In this paper these problems were analysed by computer calculations. The calculations of NO_x removal were performed on, base of Witting's formula [1]:

$$\alpha = \frac{[NO_x]_0 - [NO_x]}{[NO_x]_0} = k_1 [1 - \exp(-k_2 \bar{D} / [NO_x]_0)] \quad (1)$$

where: α - efficiency of NO_x removal
 $[NO_x]_0$ - concentration of NO_x at the inlet to irradiation vessel
 $[NO_x]$ - concentration of NO_x at the outlet of irradiation vessel
 \bar{D} - dose absorbed in the gas [kGy]
 k_1, k_2 - constants

Witting's formula (1) describes removal efficiency in one stage irradiation process and case of uniform dose distribution.

Experimental dose distribution in Kawęczyn pilot plant process vessel is presented in form of map with 24 isodoses. Real removal efficiency of NO_x was calculated as weighted mean efficiency for removal efficiency in each of 24 zones between isodoses. For each zone mean dose absorbed was determined and NO_x concentration of the outlet of irradiation stage was calculated according following modification of Witting's formula:

$$[NO_x]_k^i = [NO_x]_{ok}^i [1 - k_1 (1 - \exp(-k_2 y_{ik} z_k \bar{D} / [NO_x]_{ok}^i))] \quad (2)$$

where: $[NO_x]_k^i$ - NO_x concentration at the outlet of k-stage for i - zone of dose distribution
 $[NO_x]_{ok}^i$ - NO_x concentration at the inlet of k-stage for i-zone of dose distribution
 z_k - dose delivery ratio for k-stage
 $z_k \bar{D}$ - dose absorbed in the k-stage
 y_{ik} - ratio of dose absorbed in i-zone of k - stage to dose absorbed in k-stage.

Values of constants k_1 and k_2 were calculated from experimental NO_x removal data of one stage irradiation in process vessel of pilot plant in Kawęczyn.

Results of calculations of NO_x removal for one stage irradiation for real dose distribution (curve 2) and uniform dose distribution for the same mean dose (curve 1) are presented in Fig. 1. From comparison of both curves it can be assumed that nonuniform dose distribution reduces significantly removal efficiency of NO_x. Another calculations of removal efficiency of NO_x for case approximation of real distribution dose by 3 zones (curve 3) were made. The results of calculations are very similar as for 24 zones of irradiation (curve 2). Therefore for next calculations 3 zones dose distribution model was used. If gas in process vessel is irradiated

from both sides with the same dose distribution is more uniform and curve 4 is very close to curve of 1 for uniform dose distribution.

The problems of mixing in case of two stage irradiation was analysed for 2 opposite cases: an ideal mixing and a segregation flow.

As a reference case calculations for uniform dose distribution in both irradiation stages were made, Fig. 2 curve 1. In this case the mixing between irradiation stages have no influence on effective removal efficiency of NO_x . For case of ideal mixing between irradiation stages and regarding of dose distribution, the removal efficiency is much less (curve 3).

In case of the segregation flow two cases was analysed: 1-st when irradiation was from the same side (curve 4) and when first irradiation stage was in opposite side to the second stage (curve 2). In this case irradiation is more uniform and real removal efficiency of NO_x significantly higher.

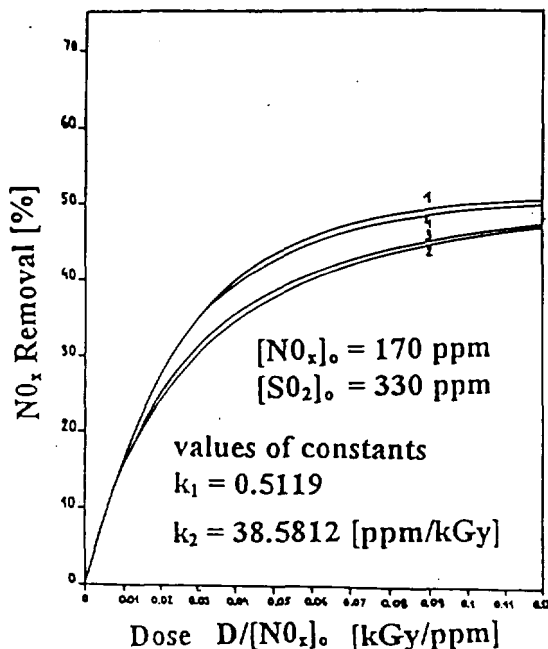


Fig. 1. Estimation of NO_x removal for single stage irradiation

1. uniform dose distribution
2. with regard to dose distribution (24 zones)
3. with regard to dose distribution (3 zones)
4. irradiation from both sides (3 zones)

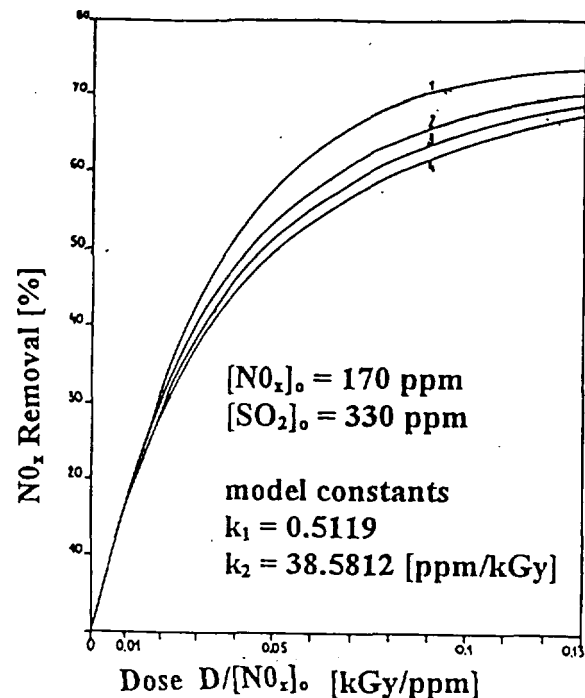


Fig. 2. Estimation of NO_x removal for double irradiation

1. without regard of dose distribution in the process vessel
2. with regard to dose distribution in the process vessel and crossing the opposite gas streams
3. with regard to dose distribution in the process vessel and ideal mixing between stages
4. with regard to dose distribution in the process vessel and segregation flow pattern between stages

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ENERGY CONSUMPTION OF THE SO₂ REMOVAL FROM THE HUMID AIR UNDER ELECTRON BEAM AND ELECTRIC FIELD INFLUENCE

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The kinetic of SO₂ oxidation in humid air under influence of electron beam and electrical field was investigated by computer simulation method in steady state and pulse mode. SO₂ oxidation process was stimulated by radicals and ions reactions. The calculation model has included 46 different particles and 160 chemical reactions. Gas mixture containing 1000 ppm of SO₂ concentration was investigated at temperature $T = 67^{\circ}\text{C}$ and pressure $p=1$ at. Water content was within the range 2 - 12 %. Electron beam parameters were as follow : average beam current density 0,0032 - 3,2 mA/cm² , pulse duration 400 μs , repetition rate 50 Hz. Electrical field density was $E/n=10^{-15}$ Vcm². Electrical pulse duration was changed within the range $5 \cdot 10^{-7}$ - 10^{-5} s.

The influence of the parameters of synchronized electron beam and electrical field pulses was under consideration. Energy cost of SO₂ removal on 90 % level was estimed in steady state and pulse modes. It was found that total electron beam and electrical field energy loses in pulse mode are 6 times lower to compare with steady state conditions. The optimum of electrical field pulse duration from point of view minimum energy cost of SO₂ removal was found for different electron beam pulse current levels.

PROSPECTS OF UTILIZING ELECTRON BEAM IRRADIATION TECHNOLOGY TO AUGMENT CONTROL OF SO₂ AND OTHER EMISSIONS FROM CHILEAN COPPER SMELTING PLANTS

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EXTENDED SYNOPSIS

Investigative work and a technical evaluation study has been conducted to analyze, verify and evaluate potential utilization of electron-beam processing for sulfur removal from reduced-SO₂-strength, copper smelter off-gases, characterized by SO₂ contents higher than 3,000 ppm, a complex chemical composition, highly oxidizing conditions, along with generation in a cyclical and fluctuating manner.

This work conducted by the Chilean Nuclear Energy Commission, CCHEN, is based on information supplied by principal smelter companies in Chile. It has been supported by the sponsorship of the International Atomic Energy Agency, IAEA, with the advisory assistance of experts from IAEA and the Institute of Nuclear Chemistry and Technology of Warsaw, Poland, whose laboratory unit equipped with electron accelerator of beam energy 800 keV and a flow rate of 20 Nm³/h, has been used for testing.

This assessment has addressed available SO₂-removal means, including electron beam irradiation, for incrementally improving overall abatement of SO₂ / SO₃ emission from existing copper smelting facilities in Chile. Processes were technically evaluated in detail considering the unique, severe characteristics of such smelter service.

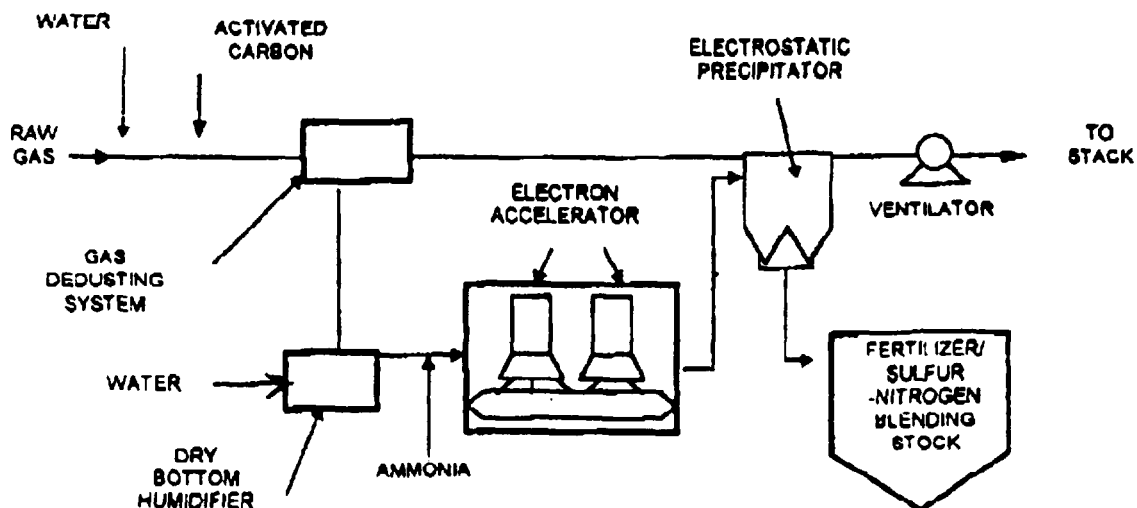
A generic schematic design, shown in Fig. 1, has been devised to address performance requirements. It encompasses upgrading of in-plant ventilation to the extent required by health standards for workers, together with gas cleaning system design based on the Electron Beam Process. The arrangement of the facilities provides for gathering and treating off-gas from selected fugitive emission sources on a continuous basis, at the same time in-drafting a minimum amount of tramp air. The introductory dry dedusting stage uses conditioned activated carbon injection in conjunction with a metals sorption contactor followed by a fabric filter to efficiently treat raw gas to remove heavy metals, including arsenic, along with particulate matter.

The main conclusion of the two major stages of this work, i.e. experimental laboratory tests and engineering-oriented studies, is that the Electron Beam Process is a simple and appropriate chemical process means that will, on a site-specific basis, optimally augment plant-wide Chilean copper smelter SO_2 emission control as required. This conclusion is based on the following considerations:

- Through specific laboratory tests conducted with simulated off-gases, electron beam irradiation with ammonia injection has been proved technically feasible for off-gases with SO_2 contents even higher than 10,000 ppm.
- The proposed generic design affords minimum total cost per tonne of SO_2 emission reduction.
- The Process efficiently removes gasborne SO_3 , a significant pollutant present in the off-gases, as well as SO_2 , thereby minimizing system stack discharge opacity.
- The Process generates a usable ammonium sulfate by-product yield of high intrinsic value, marketable for fertilizer production and use worldwide.
- Use of this dry system operation in copper smelter service is expected to be free of the severe reliability problems typically impacting alternative wet scrubber technology use in the electric utility industry in equivalent harsh duty.
- Secondary environmental benefits afforded by smelter application of the Electron Beam Process include no throwaway solid-waste generation other than that formed in upstream, conditioned, dry removal of smelter particulate and heavy metals, and no liquid effluent discharge.

A field pilot plant program is foreseen, replicating anticipated gas cleaning service conditions, and providing a necessary reference for commercial application of the Process. The principal purpose of the pilot plant is to collect data characterizing process operation and performance and serving as a basis for conceptual design of site-specific commercial installations.

Fig.1.- Generic schematic of electron beam process application for smelter off-gases



IMPROVEMENT ON CONVENTIONAL PARAMETERS OF ACTUAL INDUSTRIAL EFFLUENT BY ELECTRON BEAM IRRADIATION

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The ordinary process to treat wastewater from dye, textile, chemical, pharmaceutical and paper mill industries do not degrade easily the colored substances and organic compounds. A study on the improvement on this treatment using high energy electron irradiation was carried out [1].

Experiments were conducted using samples from Governmental Wastewater Treatment Plant (WTP) that receives about 80% of wastewater from industrial sources and 20% from domestic sources. A large amount of industrial wastewater comes from chemical and textile industries changing every day the quality, quantity and color, these characteristics depend on the production line of each particular industry.

Samples from WTP influent and effluent were collected every 15 days and irradiated in a batch system, the delivered doses were 3.0kGy, 4.0kGy, 6.0kGy, 8.0kGy and 10.0kGy. For the non irradiated and irradiated samples the following parameters were analyzed: chemical oxygen demand (COD), total and filterable solids, absorption spectrum (300 -700nm) and gas chromatography, this process was repeated three times. The gas chromatography analysis were made just to observe the degradation of the organic compounds and not to identify the byproducts.

The effluent sample COD had an average value of 1000 mgO₂/L and the influent sample had an average value of 300 mgO₂/L. After irradiation in all performed tests the effluent sample presented a higher reduction than the influent sample. For irradiated samples with lower solid concentration the reduction of COD was more significant, 50% of influent and 30% of effluent samples. This reduction of COD was at 3kGy dose, no change were observed for higher doses.

The figure 1 shows the absorption spectrum UV-VIS of irradiated and non irradiated effluent samples that presented more colored substances, the delivered doses were 3kGy and 10kGy. The reduction of color is visible with 3.0kGy dose and for higher doses it was not significant

The figure- 2 shows the gas chromatogram from the irradiated and non irradiated sample of WTP effluent, the sample was irradiated with 3kGy, the degradation of organic compounds can be observed by the reduction of the peaks.

The quality of the results obtained showed that this technology is a promissory to treat industrial effluent containing organic compounds and colored substances.

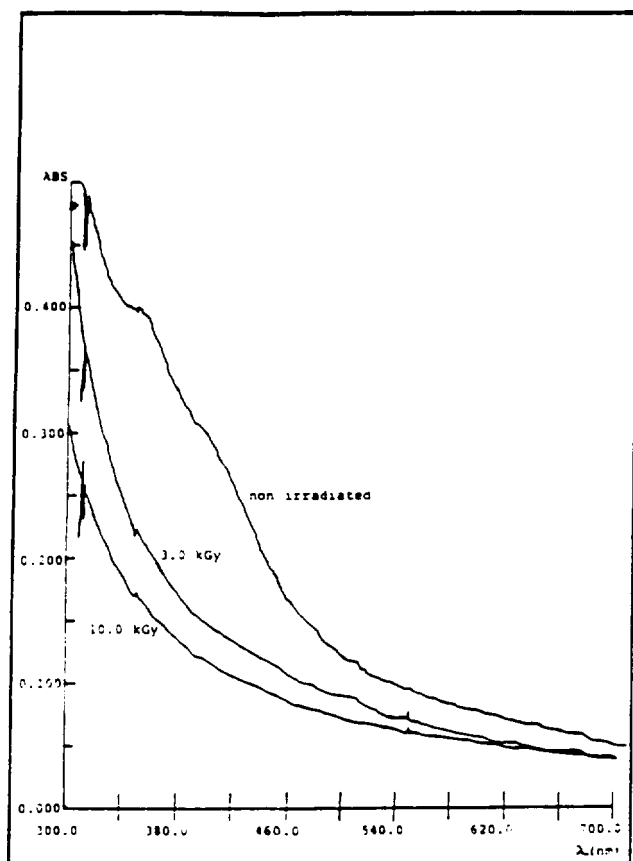


Fig. 1 Absorption spectrum of samples from effluent of WTP

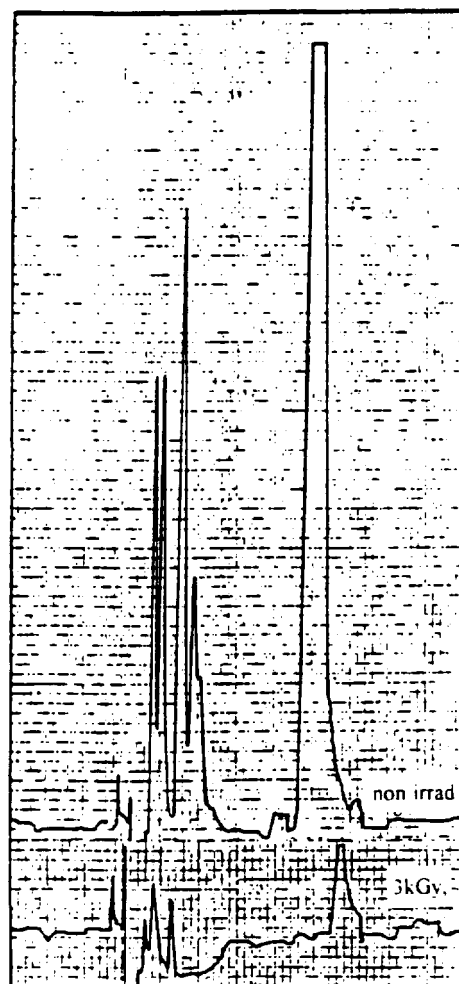


Fig. 2 Chromatogram of samples from effluent of WTP

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Effect of Addition of Heavy Metal Ion upon Decolouration and Degradation of Azo Dye in Aqueous Solution by Gamma Irradiation Combined with Ozone

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In decomposition of azo dyes by simultaneous application of gamma-ray and ozone treatment, the effect of addition of heavy metal ion upon decolouration and decomposition was studied. It has been well known that dyes are not readily biodegradable and make little contribution to BOD[1], On the other hand, some of the heavy metal ions had been also known to promote the decomposition as catalyst when it reacts with organic compounds [2,3].

This study is a preliminary report on the effect of cupric ion upon decomposition and degradation of azo dye in water with ionizing radiation combined with ozone(gamma ray/O₃/Cu²⁺).

Five experimental systems studied were as follows : (1) gamma irradiation with oxygen(gamma/O₂), (2) gamma irradiation with ozone(gamma/O₃), (3) gamma irradiation with ozone and Cu²⁺ (gamma/O₃/Cu²⁺), (4) ozone only (O₃), (5) ozone with Cu²⁺(O₃/Cu²⁺). About 1000 ml of water soluble and disperse azo dye aqueous solution(TOC : 44-50 mg/L) with or without Cu(II) ion (concentration : 1 mmol/L) was placed in 10 cm diameter x 15 cm length pyrex reaction vessel, respectively, and was irradiated with Co-60 gamma ray at room temperature. At the same time as the irradiation was started, ozonized oxygen gas from an ozone generator was made to bubble up through a porous ball at the bottom of the vessel. The dose rate was 4.1 kGy/hr. The gas flow rate was 190 ml/min and ozone concentration was 1.3 w% in O₂. The irradiated solution with ozone was purged with nitrogen gas to remove the remaining ozone in solution. After treatment, TOC, COD, BOD, pH and absorption band were analyzed.

A Dohman model DC80 TOC analyser was used to determine the TOC value. BOD and COD were measured according to standard method. The absorption band for decolouration was measured with a Shimadzu UV 365 spectrophotometer.

The Kayaku Acid Brilliant Red BL(KABL) solution showed a clear absorption at 529 nm , 552 nm and 340 nm in the UV-visible spectra as shown in Fig.1 (curve a). The former two absorption bands are considered to be the

main absorption band assigned to the conjugated system of the dye molecules.

The optical density of curve (a) at 552 nm in experimental system with gamma and ozone was decreased from 2.16 to 0.1, 0 with irradiation. When the cupric ion was added, however, the optical density was decreased from 2.16 to 0.3, with irradiation. Therefore, it is clear that the addition of cupric ion plays a negative role in acceleration of decolouration.

The change of total organic carbon (TOC) of Disperse Red 1 (DR1) with irradiation before and after addition of cupric ion are shown in Fig. 2. At the initial stage of irradiation, TOC content after addition of cupric ion was increased, but it was remarkably decreased at the irradiation time of 60 min. It was thought that increase of TOC content was due to increase of soluble component of colloidal particles of the disperse dye by irradiation, and reduction of TOC content was due to effect of cupric ion.

In order to clarify the effect of cupric ion on decomposition of dye solution, further work is now in progress.

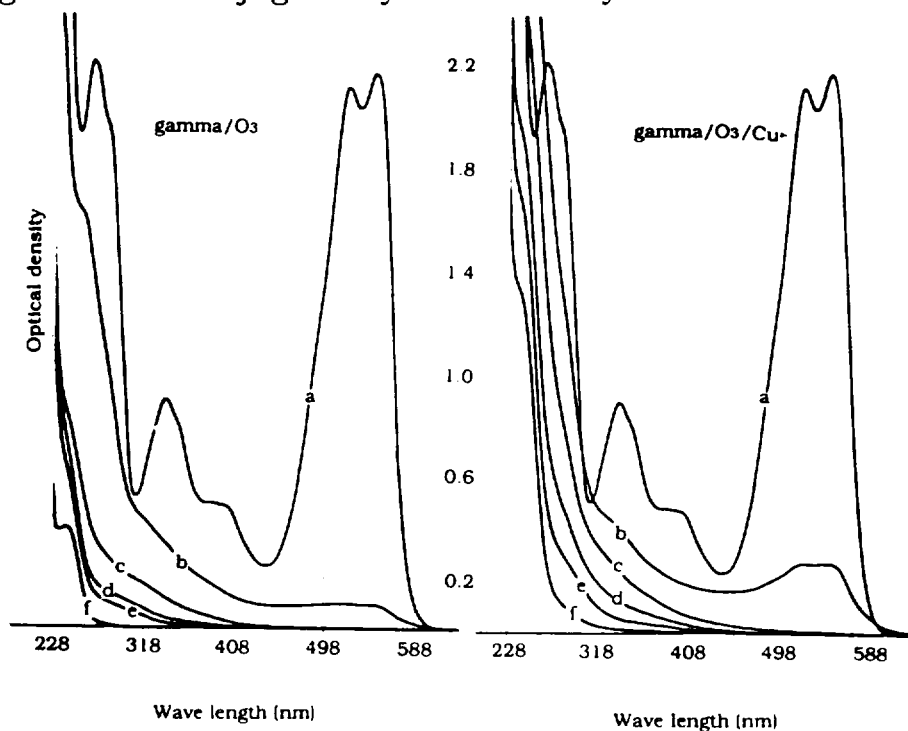


Fig. 1 The spectra change with gamma irradiation dose in water soluble azo dye solution (a: 0 min irradiation, b: 10 min, c: 20 min, d: 30 min, e: 40 min, f: 60 min, dose rate: 4.1 kGy/hr)

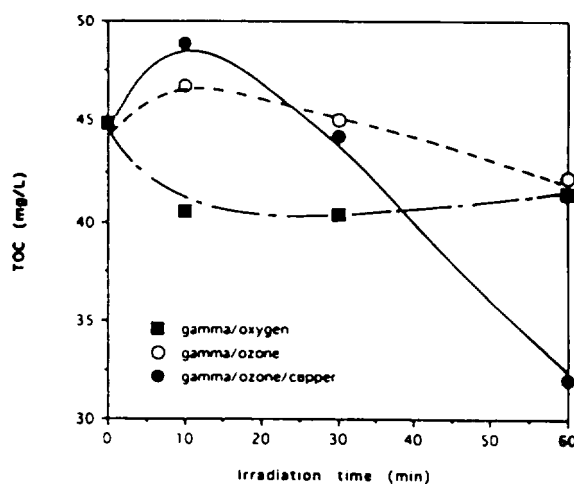


Fig. 2 TOC change of water disperse azo dye solution in each experimental systems with irradiation time (dose rate: 4.1 kGy/hr)

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TREATMENT OF COFFEE WASTEWATER BY GAMMA RADIATION

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The irradiation treatment of industrial wastewaters offers a new alternative to preserving environment and eliminating a potential hazard to public health, like halogen organic compounds, poisonous substances and viruses [1].

A preliminary survey of the effect of gamma radiation on wastewater from coffee wet depulping was carried out. Samples were collected from Wajay Coffee Treatment Plant in Havana. The depulping wastewater contains normally about 16 g/L COD (Chemical Oxygen Demand), 10 g/L BOD (Biological Oxygen Demand), and a high concentration of phenols (120 mg/L) which negatively influence the biological treatment of such wastes.

The samples were irradiated by a batch procedure, using 1L volume capacity Pyrex glass vessels at 25 °C with doses ranging from 0.5 to 100 kGy. For the irradiation of

the samples a ^{60}Co MP-γ-30 (10.5 KCi activity) installation was used. The dosimetry control was carried out using Fricke and Cerium dosimeters.

Table 1 shows the effect of gamma radiation on conventional parameters of wastewaters. It should be noted that the major influence of radiation on phenol content is observed at lower doses rather than at greater ones. In fact about 50-60 % of phenols is degraded up to a dose of 1 kGy and from that value on the phenol content undergoes only a slight decrease. This is well established by [2]. It was also noted that between 5 and 50 kGy an intensification of the colour of the samples was observed.

As reported in [3] a thorough organic degradation is already observed at doses of 20-30 kGy. Table 2 shows the effect of gamma radiation of the samples at 25 kGy. The simultaneous action of chemical treatment ($\text{Ca}(\text{OH})_2$ -precipitation followed by $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ -coagulation) is compared to the combined treatment (chemical treatment + simultaneous irradiation), being the last more efficient. It is probably due to structural changes of molecular aggregates and ions, as well as the activation of the coagulant under radiolysis.[4].

Some works as well as the combination of radiation treatment with anaerobic digestion should be further investigated.

Table 1. Effect of gamma radiation on different parameters of wastewaters

Dose (kGy)	0	0.5	1	5	10	25	50	75	100
DQO (g/L)	16.0	11.2	8.0	6.4	5.6	4.8	4.0	3.2	3.2
Total suspended solids (mg/L)	8.66	0.56	0.87	-	-	-	-	-	-
Phenol (mg/L)	120	84	50	42	39	30	32	34	32

Table 2. Effect of irradiation dose on sample organic content at 25 kGy.

	Turbidity (% removed)	BOD (% removed)	COD (% removed)
Chemical treatment	56.7	47	23.0
Irradiation followed by chemical treatment	87.5	70	32.5

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Radiation Degradation of Some Commercial Dyes in Wastewater

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ABSTRACT

In the present study, a try was made to explain the degradation kinetics due to irradiation of aqueous solutions of some commercial dyes, in the absence of other specific pollutants of the textile and dyeing industry. These dyes are: two acid dyes, namely Nylomine Blue AG (Acid Blue 25) and Erionyl Red 2B (Acid Red 116). A combined treatment of gamma irradiation and conventional methods was applied to some waste solutions in manageable volumes. Factors affecting the radiolysis of the dye such as dye concentration, irradiation dose, dose rate and pH of the solutions were studied. The effect of different additives such as nitrogen, oxygen, hydrogen peroxide and sodium hypochlorite on the degradation process were investigated. The effect of irradiation dose on the different dye solutions at various concentrations, showed that the acid dye (Acid Red 116) was very sensitive to gamma radiation. Using a low dose rate (0.3 Gy/Sec.) resulted in more degradation of the dyes than using higher dose rates (0.61 and 1.22 Gy/Sec.). The effect of the pH of the dye solutions proved to vary according to the type of the dye.

Synergistic treatment of the dye solutions by irradiation and conventional methods showed that the saturation of the dye solutions with nitrogen did not enhance the radiation degradation of this dye. On the contrary, addition of oxygen resulted in a remarkable enhancement of the radiation degradation of the dye solutions. Also, the addition of sodium hypochlorite (5%) and the oxidation by hydrogen peroxide of concentration between 2 mM and 10 mM resulted in more radiation degradation. The radiochemical yield of the degradation process (G-value) for the dye solutions with different additives was calculated.

The effect of the additives on the degradation process was in the following sequence according to more degradation of the dye molecules ($\text{NaOCl} > \text{H}_2\text{O}_2 > \text{O}_2 > \text{Air} > \text{N}_2$). Adsorption purification of the dyes onto GAC and Strong Cation Exchanger Merck I showed the best adsorption at pH = 3 followed by the neutral medium. GAC showed the highest adsorption capacity for the two acidic dyes compared with the ion exchangers. It may be concluded that radiation degradation of the toxic dye pollutants and their removal from wastewater down to concentrations not exceeding the maximum permissible concentration (MPC) according to international standards, proved to be better than the conventional methods of purification alone and more economical as well.



RADIOLYTIC DEGRADATION OF CHLOROPHENOLS FOR THEIR REMOVAL FROM POLLUTED WATERS

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Wastewaters containing high levels of phenol and chlorophenols are produced in numerous petrochemical and fermentation processes. Efficient removal of those pollutants from effluents is of great importance for environmental protection. This can be carried out using physical, biological or chemical methods of wastewater treatment.

The first reports on radiolytic decomposition of dyes and detergents were published in the beginning of seventies with use of γ radiation from ^{60}Co . Recently, several papers have been published on the use of a high energy electron beam for the removal of halogenated alkyl hydrocarbons, benzene, toluene, xylenes and chlorobenzenes from water and wastes and also dyes and detergents from textile industry wastes.

The aim of this study was to investigate the possibility of radiolytic decomposition of chlorophenols in aqueous solution using a high energy electron beam in a Russian made electron accelerator type LAE 13/9 with electron beam energy 13 MeV. The beam current was 6 μA and the irradiation was carried out at room temperature using doses up to 15 kGy. The irradiation with smaller doses up to 1 kGy was carried out with γ radiation from a Russian made ^{60}Co source ISSLEDOVATEL. In both cases the irradiation was carried out using 15 ml sample solutions placed in polyethylene bags with about 10 mm layer of irradiation solution formed.

The efficiency of radiolytic degradation of phenol and chlorophenols was monitored by reversed-phase HPLC. The products of radiolytic degradation were preconcentrated using solid - phase extraction with 3 ml BAKERBOND spe phenyl columns.

The most difficult to decompose is the simple phenol, which is also a product of radiolysis of all chlorophenols except for pentachlorophenol. Doses up to 2.0 kGy have not decomposed it completely. Degradation of chlorophenols in synthetic aqueous solutions takes place almost completely at 0.2 kGy dose, however, for the river water matrix containing scavengers such as carbonates or oxygen it requires a larger dose. For the same dose used for degradation of higher chlorophenols in river water smaller amounts of difficult to decompose phenol are produced.

In radiolysis of phenol, products such as hydroquinone, resorcin and catechol were identified, whereas for irradiation of 2-chlorophenol only a low level of resorcin and catechol were found. Several other products separated by HPLC were not identified as yet.

Radiation Induced Decomposition of Chlorinated Benzaldehydes in Aqueous Solution

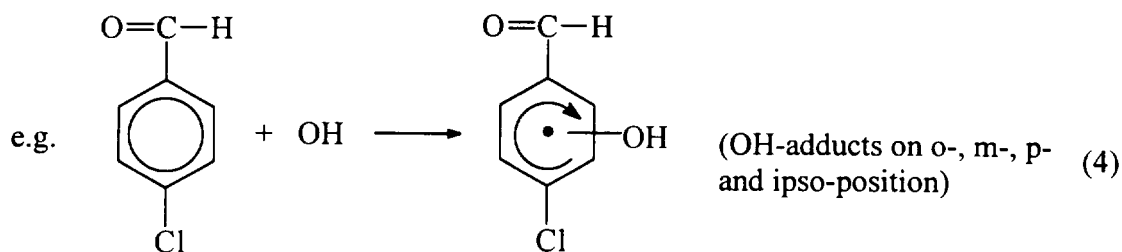
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The most of the biologically resistant water pollutants are chlorinated organic compounds, originating from the chemical, pharmaceutical and other industries. The paper describes the radiation-induced degradation of 2-, 3- and 4-Cl-benzaldehydes in water solution in the presence of oxygen ($1.25 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ O}_2$) at pH~6.5. The yields (G_i -values) of the major degradation products (Cl^- ions, aldehyde, carboxylic acids) formed under these conditions were studied as a function of absorbed dose.

In the presence of oxygen in the solution, both e^-_{aq} and H-atoms are converted into peroxy radicals, which, together with the OH-species, are leading to degradation of the chlorinated substrates.



The resulting OH-adducts (eq.4) are adding oxygen under formation of the corresponding peroxy radicals, which are unstable and decompose or undergo hydrolysis resulting in the above mentioned final products. Based on their G_i -values it could be established that the substrate degradation, Cl^- ions and aldehyde are increasing in the sequence: 3-ClBzA: 2-ClBzA: 4-ClBzA. On the other hand those of the acid formation are: 2-ClBzA: 3-ClBzA: 4-ClBzA. The ratios of the above mentioned G_i -values are given in the following Table 1.

Table 1: Ratios of the G_i -values for the substrate degradation, formation of Cl^- ions, aldehyde and acids of the three studied chlorinated benzaldehydes.

Substrate	Ratio for G_i -values for:			
	Substrate degradation	Cl^- ions	Aldehyde	Acids
2-ClBzA	2.0	1.6	1.26	2.65
3-ClBzA	1	1	1	1.85
4-ClBzA	3.7	3.24	2.7	1

Probable reaction mechanisms for the formation of the radiolytic products are presented.

Hydroxyl-Radical Induced Dechlorination of Pentachlorophenol in Water [1]

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The dechlorination of pentachlorophenol (PCP) in water induced by hydroxyl radicals generated ionizing-radiolytically has been investigated at low PCP concentration under various conditions (different atmosphere or different pH). As shown in Figure 1, PCP consumption and chloride ions release occur simultaneously, both of which increase linearly with the increasing absorbed dose. At relative high absorbed dose PCP could be decomposed almost completely and almost all chloride atoms on PCP molecules (*i.e.* five times of initial amount of PCP) are eliminated. (Fig. 1). From the slope of such linear plots, $G(-\text{PCP})$ is calculated to be 0.4 (air) and 1.5 (N_2O), and $G(\text{Cl}^-)$ 1.7 (air) and 7.1 (N_2O). G values also depend on pH of the solutions.

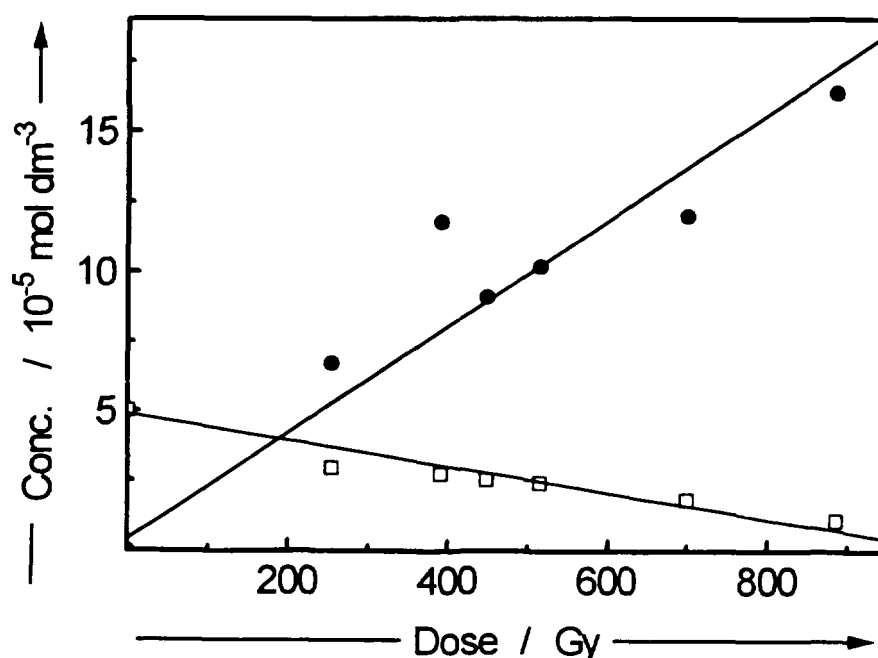


Fig. 1 Dose dependent consumption of pentachlorophenol and release of chloride.

$[\text{PCP}]_0 = 4.8 \times 10^{-5} \text{ mol dm}^{-3}$, pH 9, air saturated, dose rate: $0.3\sim 1.6 \text{ Gy s}^{-1}$.

Terzian *et al.* [2] has reported that hydroxyl radicals react with PCP by attacking the benzene ring to generate dihydroxypentachlorocyclohexadienyl, pentachlorophenoxy and semiquinone radicals, and at pH 8 the phenoxy radicals prevail (77%). Phenoxy radicals often react very slowly with O_2 but usually react with $O_2^{\cdot -}$ very fast [3,4]. $O_2^{\cdot -}$ can add to phenoxy radicals and subsequently regenerate phenols by O_2 elimination or result stable adducts. The very low yield of PCP decomposition in air saturated solution (where hydrated electrons are converted into $O_2^{\cdot -}$) indicates that $O_2^{\cdot -}$ react with PCP derived phenoxy radical mainly to regenerate PCP. In the present work pulse radiolysis of PCP has been done to reveal the possible effect of pH on the composition of PCP derived radicals and on their decay kinetics.

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Radiation Induced Decomposition of Pentachlorophenol in Water

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The decomposition of PCP in water induced by γ -irradiation has been studied at low PCP concentration under various conditions (different atmosphere or different pH). PCP is consumed linearly with increasing dose. At the later stage where most PCP are consumed and the remaining couldn't compete for $\cdot\text{OH}$ radicals with products efficiently, thus the consumption rate (G value) decreases. PCP could be consumed almost completely by γ -irradiation at relative high doses. Chloride ions are eliminated simultaneously with the consumption of PCP. The amount of chloride eliminated increases also linearly with the increasing absorbed dose. At relative high absorbed dose, almost all chloride ions (*i.e.* five times of initial amount of PCP) are eliminated. The G values of PCP consumption and that of chloride ion formation are compiled in Table 1.

Table 1 The compilation of G values for PCP consumption and Cl^- elimination

pH	air		N_2		N_2O	
	$G(\text{PCP})$	$G(\text{Cl}^-)$	$G(\text{PCP})$	$G(\text{Cl}^-)$	$G(\text{PCP})$	$G(\text{Cl}^-)$
5	-0.22	1.1	N.D.	2.4	N.D.	2.7
9	-0.37	1.7	-1.2	4.8	-1.5	7.1

Note: G values in the units of $10^{-7} \text{ mol J}^{-1}$; N. D. not determined.

Chemical oxygen demand (COD) has also been measured after irradiation. The results are shown in Table 2. These results suggest that at the early stage the benzene ring open is

negligible in the consumption of PCP induced by OH radicals though O_2 is present, which agrees to the low reactivity of phenoxyl radical towards O_2 . [1]

Table 2 COD_{Mn} values of irradiated PCP. $[PCP]_0 = 6.3 \times 10^{-5} \text{ mol dm}^{-3}$, pH 5.3, air-saturated, dose rate 0.3~1.2 $Gy \text{ s}^{-1}$.

Dose / Gy	0	530	1600	2500
$COD_{Mn} / \text{mg dm}^{-3}$	10.5	10.5	9.4	3.4

O_3 itself can decompose PCP at pH 8.6. After saturation of $4.81 \times 10^{-5} \text{ mol dm}^{-3}$ PCP aqueous solution with O_3 for 20 min, $[PCP]$ drops $2.6 \times 10^{-5} \text{ mol dm}^{-3}$ while $1.56 \times 10^{-4} \text{ mol dm}^{-3}$ chloride is formed. This indicates that O_3 induced dechlorination of PCP might be in a cooperative way. When the ozonolysed PCP is subjected to γ irradiation, the G value for PCP consumption is measured to be $0.2 \times 10^{-7} \text{ mol J}^{-1}$, while the G value for chloride formation is $0.8 \times 10^{-7} \text{ mol J}^{-1}$. Comparing to the results obtained when PCP solution is γ irradiated without ozonation, the G value for the formation of chloride decreases markedly. This is reasonable however when one considers the high reactivity of Cl^- towards OH radical. [2]

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RECYCLING OF SEWAGE SLUDGE : *NILE TILAPIA* FEEDING WITH IRRADIATED AND DRIED
SLUDGE FROM BEER INDUSTRY.

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Recycling of sewage sludge from wastewater treatment plant from beer industry for fish feeding at commercial scale were conducted. Sewage sludge from activated sludge wastewater treatment plant of beer industry were irradiated at 3.32 kGy gamma irradiator carrier type, JS 8900, ^{60}Co activity at 187,088.121 Ci at 6 June 1995. For fish production study, it is needed to change the wet sludge to dry powder form by Rotadics dryer, type Stord TST 3.4 C, Stord (Thailand) Co. Ltd. at the capacity of 15-20 T/24 hr.. The moisture content of finished product was at 8-10%. Recycling of irradiated dried sewage sludge from beer industry were then replaced at 60% of control diet to become as test diet.

Nile tilapia, Oreochromis niloticus (Linn.) fingerlings averaging 0.67 g. in body weight were stocked into earthen ponds of 400 square meters. Fish were fed with two diets, control diet and test diet (60%) replaced with irradiated and dried sludge at the density of 5 fishes per square meter for 154 days. There were no statistical differences in specific growth rate, quality of the fish flesh (Cd and Pb concentration, edible portion and off flavor) also water quality in the pond. Survival rate and feed conversion efficiency of the diet feed was higher than control diet ($P < 0.05$). Replacement of irradiated sewage sludge could decrease the cost of fish production and resulted in better benefit than that of control diet.



AGRICULTURE REUSE FEASIBILITY STUDIES OF SLUDGES FOR THE SEWAGE SLUDGE IRRADIATION PLANT IN ARGENTINA.

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The Argentine Sewage Sludge Irradiation Project, conceived by CNEA in 1992, decided the construction of an industrial-scale irradiation plant for disinfection of liquid sludges coming from a sewerage treatment plant and their recycling as fertilizers. This Plant is being constructed and installed in Tucuman City in an agricultural zone of NorthWestern Argentina. It is based on a gamma radiation process by batches of six cubic meters and using Argentine made Cobalt-60 sources^[1].

The radiation treatment is a reliable method of disinfection to eliminate pathogen microorganisms in the sludges, and therefore to protect the public health, thus allowing the re-use in agricultural land ^[2,3]. But costly technologies such as a gamma irradiation facility become an option only if a profitable use can be found for irradiated sludge, in addition to the sanitary conditions improvement.

The feasibility studies on the Tucuman's Sewage Treatment Plant sludges involves:

1. Technical parameters and chemical characterization of the sludges.
2. Microbiological test to verify disinfection by irradiation
3. Toxic elements evaluation, both inorganic elements (heavy metals) and organic compounds (pesticide traces). These pollutant concentrations should meet the criteria set by the environment regulations.

Many of the experiments have been conducted within two Research Coordinated Programmes organized by the IAEA and the Joint FAO/IAEA Division.

Another important aspect is the bioavailability of soil nutrients (N and P) from the sludges: it will determine the real economic value of sludges as fertilizers. Further studies on the behaviour of toxic elements accumulation on soil and plants, and also the capability of sludges to improve soil properties, will lead to the environment impact assessment of the application on land.

1. Technical parameters and chemical characterization of the sludges:

The Sewage Sludge Irradiation Plant will treat the sludges generated by the treatment plant of Tucuman City (400,000 inhabitants served). After the primary treatment of wastewaters, the concentrated sludges are anaerobically digested: 140 m³/day of digested sludges, 8% total solid concentration, are available for the

irradiation. The advantage of the digested sludges, compared to the raw sludges, is the stabilization grade which is shown by the chemical data. The design parameters of the Irradiation Plant are suitable to treat all the amount of sludges, producing an annual treated volume of 46,600 m³/year.

2. Microbiological tests:

It is proved that irradiated sewage sludge are safe, from a public health point of view, for its use in crop production. The environment legislation in Argentina does not include specifically the limitations in the case of food crop fertilization by sludges. Thus, other countries regulations, mainly U.S.E.P.A. regulations are observed.

The analyses of sludges as well as the analyses of sludge fertilized soil have shown that an irradiation dose of 2 kGy is enough to meet the criteria of the law concerning to the pathogenic bacteria and the parasite ova. But the recommended irradiation dose has to be increased to at least 3 kGy due to the viruses inactivation requirements.

3. Toxic elements evaluation:

The inorganic toxics such as heavy metals are the primary limitation for the agriculture re-use. The evaluations of sludge monthly samples throughout a year have proved that the concentration of heavy metals are far enough the maximum tolerable by EPA regulations, being lead the only element that has to be under control. Also the metal accumulations on soil are being tested year by year in the experimental fertilizations started in 1995. No differences were detected yet.

The organic toxics were also analyzed by Gas Chromatography screening comparing them to the most commonly used pesticides. Only one compound was repeatedly detected, it does not seem to be a problem due to its low concentration and its eventual decomposition in the soil.

After the feasibility studies, long-term field experiments are being carried out to evaluate the equivalence of sludge in soil nutrients with the chemical fertilizers and to assess environmental impact related to the behaviour of toxics accumulation and soil characteristics changes.

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Irradiation treatment of sewage sludge

— History and Prospects

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This paper first reviews the history of irradiation treatment of sewage sludge in the world. First sludge irradiation plant was built in Geiselbullach, West Germany in 1973 which used ^{60}Co as irradiation source in batch operation mode [1]. The solid content of sludge was 4%, irradiated dose was 3 kGy, capacity was 5700L/batch. In the United States, a 8-ton/day irradiator was constructed in 1978 by Sandia National Laboratory in Albuquerque, New Mexico. At this facility, ^{137}Cs was used as irradiation source and the operation was in continuous mode. In 1976, an electron beam irradiation system was put on line at Boston's Metropolitan District commission waste water treatment plant at Deer Island. The facility handled up to $15.8\text{m}^3/\text{hr}$ of liquid sludge, delivered a dose of 4 kGy. Electrons were generated by a 750 kV, 50 kW commercial electron accelerator. Based on the research at Deer Island, a sludge irradiator using accelerator electron at Virginia key wastewater treatment plant, Miami, Florida officially began operation in 1984. The electron energy is 1.8 Mev. The applied dose is 3.5--4.0 kGy. This sludge handling system allows a flow of 27 m³/hr. The sludge entering the irradiator has a concentration of 2% dried solids. In India, a pilot irradiation plant for sludge treatment as part of commercial waste treatment plant was built in Boroda, a city in west India in 1985[2]. The intensity of ^{60}Co γ -ray source in plate form is 500kCi. The treatment dose is 3.0--3.5kGy. The Indian scientists also investigated the potential application of sludge. It could be used as soil conditioner, fertilizer complement and animal feed. The electron beam irradiation of sludge was also carried out in Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute[3]. The design and cost analysis for irradiation--composting plant of sewage sludge were made with capacity of 25--200 ton sludge/day. The accelerating voltage of electron and the capacity of the accelerator are 1.5 Mev and 15 kW, respectively with a dose of 5 kGy. Composting of the irradiated sludge is made at 50 °C for 3 day (conventional composting

needs 10--12 day). Total volume of the ferment is about one third of that of conventional composting process because the irradiation makes the time of composting shorter. For a plant with treatment capacity ≥ 50 ton/day, the cost of sludge treatment is slight less than that of conventional method. For a large scale plant with capacity of 200--300 ton sludge/day, the cost of sludge treatment will be much lower than that of conventional method.

In China, especially in Shanghai, sludge treatment is also a big problem. This paper presents a proposal for irradiation treatment of sewage sludge from suzhou river of shanghai. The outline of the proposal is as follows:

1. Basic research on irradiation of sewage sludge from suzhou river including component analysis (organic substances, trace elements, variety of bacteria), irradiation method (γ -ray and electron beam, irradiation and heat, irradiation and ozone et al), and comprehensive treatment (irradiation + composting, irradiation + chemical denaturation, irradiation+precipitation).

2. Technological research including flowsheet design and accelerator manufacture. We proposed that a accelerator with electron of 1.5 Mev, 30 mA should be manufactured. If the water content of the sludge is 50% and the dose is 3--5kGy, the capacity could be 50--100 ton/day.

3. The application of irradiated sludge: Mainly it could be used as composite fertilizer, soil additive and animal feed.

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GAMMA RADIATION DISINFECTION OF MUNICIPAL WASTE FOR REUSING AS A CARRIER FOR BIOINOCULANT

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The study aims at the analytical evaluation for heavy metals, phenols and microorganism as well as fungus contamination in municipal waste from Hanoi (Vietnam) City in term of reuse of it as a carrier for bioinoculant. For this purpose gamma radiation was applied to disinfect the material.

The experiments have been conducted with the waste which was primarily processed at a waste treatment station to remove major inorganic construction as well as nondecomposed materials such as brick, plastics etc. Sampling of preprocessed waste makes sure that samples to be studied were statistically mixed over a huge amount of collected municipal waste.

The main components of the waste such as total organic carbon, nitrogen, phosphorus, kalium, silica, moisture content and pH_{KCl} were evaluated by appropriate chemical or physical methods and they are found to be 36.8, 5.7, 0.45, 0.81, 1.25, 25.4, 25.0 and 6.6, respectively.

Heavy metals content of the waste was analysed by XRF technique using a ^{109}Cd source of 4 ~mCi activity and a Si(Li) detector. The spectra processing program is the EMCALUS provided by the International Atomic Energy Agency.

Phenols originating from either agrochemicals contaminated with food residues or industrial ones in the waste were analysed by gas chromatographic method using a capillary column and FPD detector.

Total aerobic microorganisms and fungus population in the waste were count by dilution method on appropriate media.

45

Analytical data show that the phenols content was lower than detection limit of FPD (0.01 ppm) and the total aerobic microorganisms and fungus population were found to be $1.4 \cdot 10^8$ and $0.54 \cdot 10^6$ c/g, respectively. At the same time pathogen was not found.

Obviously, the municipal waste has high content of nutrition and is suitable for using as a carrier in bioinoculant such as nitrogen fixation and phosphorus solubilizing ones. However, the high contaminating microorganisms and fungus population will compete with the useful microorganism strains.

Radiation disinfection was carried out using the Co-60 facility with various absorbed doses in order to determine the effective dose (D_{eff}) to reduce the initial contaminating microorganism and fungus population down to $\leq 10^3$ c/g. The D_{eff} was estimated as high as 50-54 kGy.

It appeared that municipal waste from Hanoi city with its high nutrition content followed by irradiation disinfection is quite capable to partially replace conventional materials such as peat soil in production of biofertilizer for agricultural uses. The irradiated disinfected municipal waste based inoculant is able to store for a long period of time before the contaminating microorganisms and fungus could recover.

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THE USE OF DIFFERENT TYPE OF ELECTRON BEAM RADIATION EQUIPMENT FOR BIOTECHNOLOGICAL MATERIALS PROCESSING

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The potential of using electron beam radiation and bremsstrahlung for some biotechnological materials treatment it is presented. There are comparatively discussed different types of electron accelerators used to process biotechnological materials as: cell culture; microbial strains; enzymes and some metabolites.

The presented results are obtained from an extensive R & D programme established in 1993 at the Institute for Lasers, Plasma and Radiation Physics, Bucharest, concerning the electron-beam processing in biotechnology, biomaterials, agro-food, medicine and environmental protection. In the Electron Accelerator laboratory of ILPRP Bucharest there were designed, developed and improved different type of electron accelerators as: betatron, linear and microtron-type, in order to fulfil the requirements of radiation processing in biotechnology and environmental protection. There is also a real interest to develop a dedicated electron accelerator [1].

The linear electron accelerator has the following main parameters: electron mean energy 6 MeV; average beam current 5 μA ; pulse length 3.5 μs ; frequency 100 Hz. The microtron is adapted for radiation processing in order to scan the electron beam in the vertical direction and to generate bremsstrahlung, as well. It has the following characteristics: 17 orbits; electron energy in the first accelerating mode 10 MeV; average beam current in the first accelerating mode 50 μA ; pulse length 3 μs ; frequency 400 Hz. The dedicated electron accelerator could be a promising solution for the biotechnological materials processing, both in continuous and batch

modes, if it has the following characteristics: electron energy approximately 5 MeV; beam power between 5 and 10 kW; vertical and horizontal electron beam; electron beam and bremsstrahlung irradiation possibility; controlled material conveyor; adjustable dose rates in order to achieve in a wide range of irradiation doses in an economic effective term [1, 2].

The studies are oriented on irradiation of biotechnological items [3] as:

- a) cell cultures, to obtain real information on different cell lines radioresistance which will be useful for further applications in biotechnology; environment protection; medical supplies sterilisation and food irradiation;
- b) microbial strains, especially *B. subtilis* and *Monascus rubens*, in order to obtain a higher biosynthesis potential for specific biotechnologies;
- c) enzymes and other biomolecules, to obtain more effective biopreparates and to achieve the required qualities of these preparates;
- d) different materials, as cellulose-based wastes or other biopolymers-based wastes, in order to develop the appropriate methods for their degradation or re-use.

There are presented the main research results and some consideration in cost-benefit terms, for: dose-effect relationship and radioresistance parameters for different cells; the biotechnologies and characteristics of *B. subtilis* (enzyme-producing) and *Monascus rubens* (red/orange pigments producing) strains; the enzyme preparation for both crude extracts and immobilised ones and a method for radiolytic degradation of cellulose-containing wastes.

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FORMATION OF FREE-STANDING STERILIZED EDIBLE-FILMS FROM IRRADIATED CASEINATES.

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INTRODUCTION

γ -irradiation was used to produce free-standing sterilized edible films based on milk proteins. The nature of the counter-ion as well as the protein and glycerol concentrations were examined. The use of physical treatments, such as irradiation, can increase the cohesive strength of the protein by the formation of crosslinks. Indeed, the irradiation of aqueous protein solutions generate hydroxyl radicals (\bullet OH) that produce stable compounds [1]. Tyrosine is sensitive to (\bullet OH) attack. Tyrosyl radicals may react with other tyrosyl radicals or with tyrosine molecule to form several stable biphenolic compounds, where the phenolic moieties are linked through a covalent bond [2].

RESULTS

Irradiation of solution based on calcium-caseinate produced more crosslinks than solution based on sodium-caseinate. As a consequence, films based on calcium-caseinate showed a better mechanical strength. Glycerol was found to play a double role in enhancing the formation of crosslinks within caseinate chains, accounting for the increase of the puncture strength, and acting as a plasticizer, being responsible for the improved film extensibility and viscoelasticity. Moreover, the effect of the irradiation on the mechanical properties were strongly dependent on the glycerol/protein ratio, i.e. the formulation of the films. Films of high quality and a satisfactory mechanical behaviour were generated with at a glycerol/protein ratios of 0.5 and 0.67.

The highest amount of bityrosine, i.e. crosslinks, occurred at a ratio of 0.33 leading to very high puncture strength values and very low puncture deformation values. Indeed, the highest effect of the irradiation dose on the puncture strength was observed at a ratio of 0.5. The puncture strength was found to be affected by the irradiation process: an increase of 80% was noticed

between the non-irradiated and irradiated sample at 20 kGy. On the other hand, the most important effect of the irradiation on the deformation was observed at a ratio of 0.67: an increase of 45% was measured after irradiation at 20 kGy. These findings can be explained by the fact that the lowest amount of crosslinks were produced at a ratio of 0.67, as confirmed by puncture strength values. As a consequence, films behave more similarly as elastomers. Among formulations investigated, films obtained upon irradiation process exhibited the best mechanical strength and flexibility at glycerol/protein ratios of 0.5 and 0.67.

ACKNOWLEDGMENTS

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TABLE I: Effects of the glycerol/caseinate ratio on the mechanical behaviour of films irradiated at 20 kGy.

glycerol/caseinate ratio mechanical property	0.33	0.5	0.67	1
puncture strenght	+ 10%	+80%	+30%	+15%
puncture deformation	2%	+30%	+45%	+25%

- + indicates an increase of the mechanical property measured after an exposure to ionization corresponding to 20 kGy.
- indicates a decrease of the mechanical property measured after an exposure to ionization corresponding to 20 kGy.

FORMATION OF STERILIZED EDIBLE-FILMS BASED ON CASEINATES:

EFFECTS OF CALCIUM AND PLASTICIZERS.



XA9745215

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Edible films based on milk proteins were found to possess satisfactory mechanical properties [1][2]. The crosslinking of caseinates with calcium ions [3] were reported. More recently, gamma-irradiation was also reported to be an effective method in enhancing the cohesion within caseinate [4]. Our assumption was that the combination of both calcium ions and gamma-irradiation would generate films with an improved cohesion, making them suitable for packaging and/or coating purposes. The addition of plasticizers and calcium ions was also assumed to enhance the mechanical strength of films and gels based on caseinate.

Gamma-irradiation was used to produce free-standing sterilized edible films based on caseinate. The effect of calcium ions (Ca^{2+}) and two plasticizers, namely propylene glycol (PG) and triethylene glycol (TEG) were investigated, as well as the effect of the irradiation on both the gel formation and mechanical properties of the resulting films. Gamma-irradiation provoked formation of bityrosine, i.e. crosslinks (fig.1). The presence of PG or TEG enhanced the formation of crosslinks, leading to an improved mechanical strength of films (fig.2,3). TEG was found to interact more favorably with the caseinate than PG, being responsible for the improved film extensibility. Addition of Ca^{2+} caused the formation of gels (fig.4). Moreover, high irradiation dose seemed to affect the protein structure, accounting for the decrease of the breaking strength of gels and for the depreciation of the mechanical behaviour of films (fig.2,4).

The formation of bityrosine upon gamma-irradiation lead to a branching of polypeptide chains to form a three-dimensional network and interactions between the protein and plasticizer molecules contribute to the mechanical behaviour of the films. However, inadequate irradiation period will strongly affect the structure of the film, and thus its mechanical behaviour.

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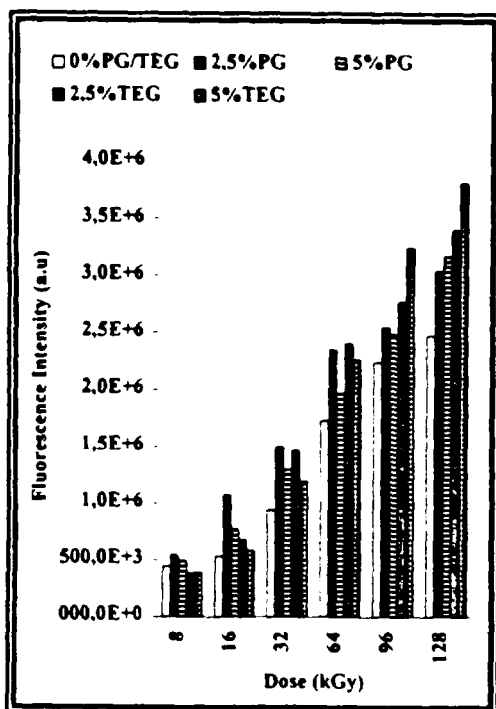


Fig. 1 Formation of bityrosine as a fonction of irradiation dose.

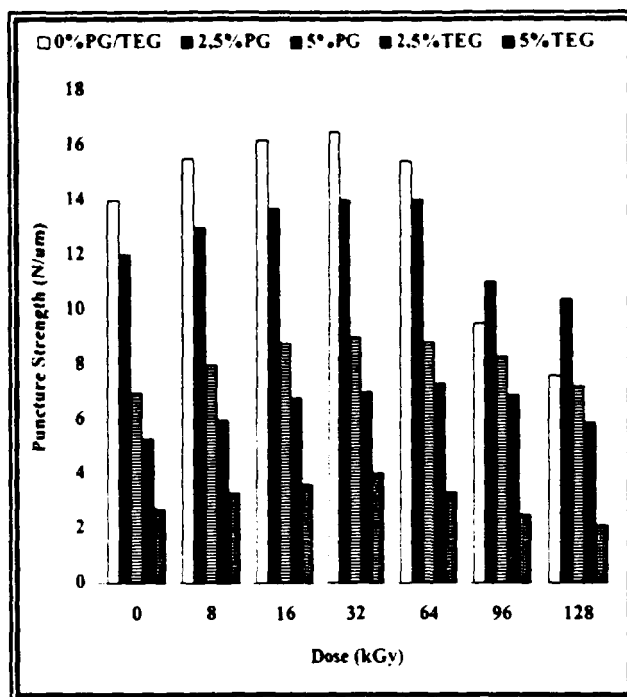


fig.2 Effect of irradiation dose on the puncture strength of films.

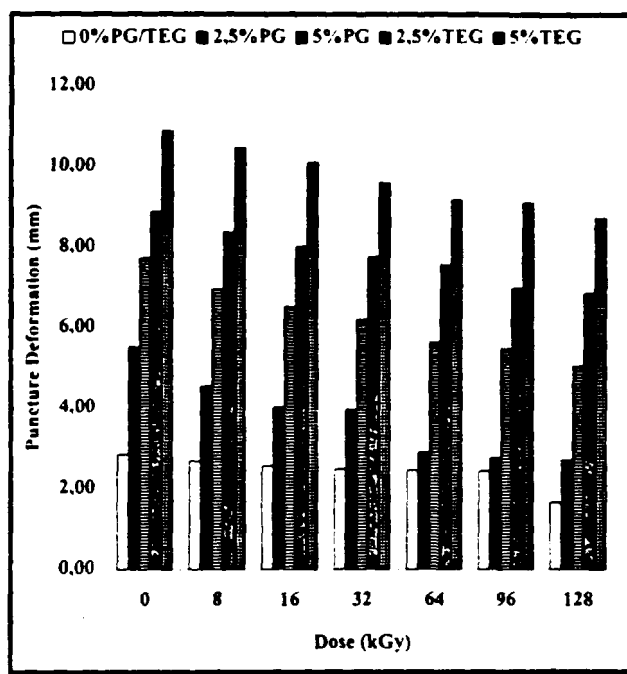


Fig.3 Effect of irradiation dose on the puncture deformation of films.

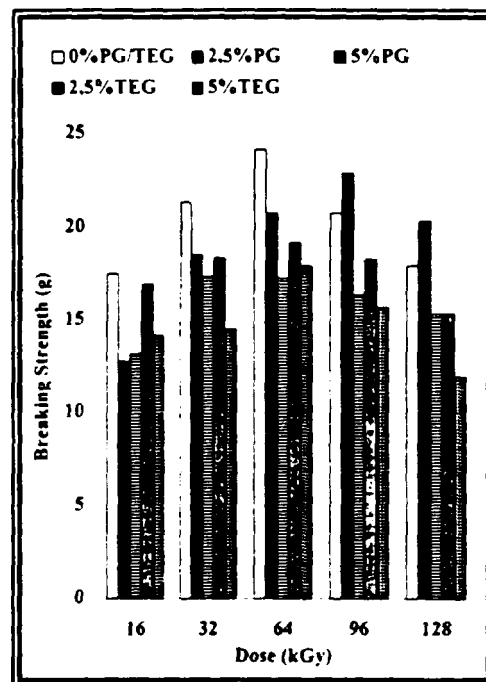


Fig 4. Effect of irradiation dose on the puncture strength of gels.

IRRADIATION AS AN ALTERNATIVE ENVIRONMENT FRIENDLY METHOD FOR MICROBIOLOGICAL DECONTAMINATION OF HERBAL RAW MATERIALS

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Microbiological contamination of herbals raw materials causes serious difficulties in the production of therapeutical preparations. A good quality of this materials, according to the pharmaceutical requirements may be achieved by different methods of decontamination.

Each of decontamination treatments should be:

- a/ carried out safely and fast;
 - b/ effective against all microorganisms
 - c/ able to penetrate the packaging and product in order to act against all the microorganisms present;
 - d/ adaptable to large quantities of material with high efficiency
- and
- e/ must not reduce the sensory and technological qualities of the treated commodities.

In the paper, the results of comparative investigations on the microbiological decontamination herbal raw materials by chemical and physical methods are presented

Decontamination with ethylene oxide is very effective method. It gives bacteriostatic or bactericidal effect without substantial changes in biological active substances in raw herbals materials. However, a ethylene oxide is consider as a human carcinogen, and the use ethylene oxide for fumigation is prohibited in EU. In the near future, the same situation will be in Poland.

Decontamination by methyl bromide is not a process allowing to obtain the high microbiological purity of herbals raw materials. This process causes a decrease essential oil in particular fumigated materials. Because, the methyl bromide destroys the ozone layer at atmosphere, the total prohibition of the usage this compound will be introduced in the EU from 2005.

Radiation treatment the herbals raw materials at the doses up to 10 kGy effectively reduce to the acceptable level contamination this materials. Content of biological active substances in many herbals raw materials did not change in a significant degree after irradiation.

It seems, that radiation decontamination of herbals raw materials is a method by choice. It is a technically feasible, very effective and friendly to environment process. Radiation treatment can be applied to hermetically packed product, thereby excluding recontamination.

Effect of combination of irradiation and zeolite on pyrolysis of polymer materials

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To recover of available materials from wasted plastic as chemical recycling, pyrolysis of propylene (PP) and polyoxymethylene (POM) by combination of irradiation and zeolite have been investigated. Irradiated PP in the present of zeolite initiated pyrolysis at lower temperature as shown in Figure 1. The initial temperature of pyrolysis of PP irradiated to 220 kGy in the present of zeolite was observed at 220 °C and the temperature is lower at 100 °C compared with unirradiated PP. Depression of initial temperature of pyrolysis depended on component of zeolites. According to this study, Na⁺ type was most effective in reducing of initial temperature for pyrolysis of PP. Product identification in pyrolysis at relatively lower temperature, 350 °C are shown in Table 1. Hydrocarbon of shorter molecular chain were identified and some products contained

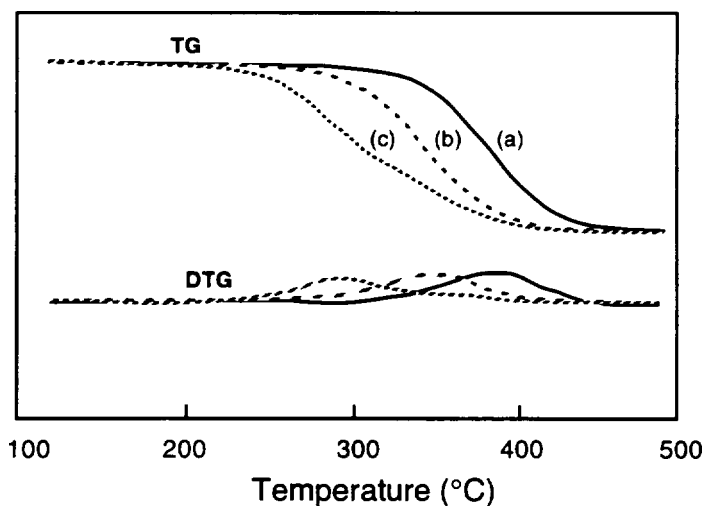


Fig. 1 TGA and DTG curves of PP irradiated in the presence of zeolite. 640NAA zeolite is mixed in molten state of PP:(a) without irradiation; (b) irradiated to 60kGy;(c) irradiated to 220kGy

oxidized compounds. It implied that production of oxidized materials are due to increment of oxidation by zeolite during irradiation. Unirradiated PP did not initiate pyrolysis at such temperature, 350 °C.

Furthermore, effect of zeolite on pyrolysis of irradiated POM is shown in Figure 2. T_i and T_f are estimated from TGA curves. T_i and T_f are initial and end temperatures of pyrolysis, respectively. T_i and T_f of unirradiated POM were 280 °C and 312 °C, respectively. T_i of pyrolysis of irradiated POM was depressed to 180 °C, while T_f was rather increased. Furthermore, addition of 320NAA or 320HOA zeolite, achieved significantly lower T_f s compared to the case without zeolites. It means that pyrolysis of irradiated POM is accelerated by catalytic function of zeolites. Both of 320NAA and 320HOA zeolites are classified as Y type, and the others as different types such as L, Mordenite and so on. Thus, it is suggested that structure of zeolite is an important factor to reduce T_f in pyrolysis of irradiated POM.

Table Products identified in pyrolysis of irradiated PP-zeolite mixture(Film containing 5% 640NAA irradiated in air to 340kGy at a dose rate of 10Mrad/h, pyrolyzed at 350°C)

Peak number	Retention time(min)	Composition	Possible structure	Yield (mol%)
1	1.139	C_3H_6 , C_3H_8		19.49
2	1.364	C_3H_6O		17.65
3	1.438	C_3H_6O		4.02
4	1.606	C_4H_6O		3.21
5	1.792	$C_2H_4O_2$		10.85
6	2.164	C_4H_8O		2.57
7	3.680	C_6H_{12}		2.29
8	4.438	$C_5H_8O_2$		8.52
9	4.647	$C_5H_8O_2$		2.40
10	5.190	$C_6H_{12}O_2$		3.30
11	5.515	C_9H_{18}		2.90
12	5.592	C_9H_{20}		2.21
13	8.992	$C_9H_{19}O$	not identified	6.90
14	11.958	$C_{12}H_{24}$		2.88
15	12.022	$C_{12}H_{26}$		2.35
16	12.580	not identified	not identified	3.29
17	16.954	$C_{15}H_{30}$	not identified	5.19

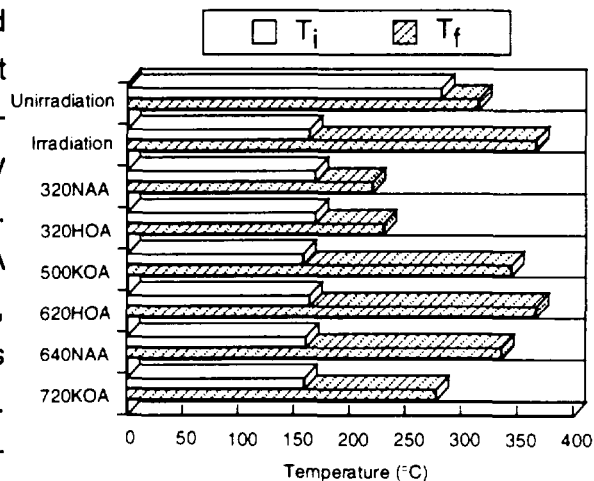


Fig. 2 Effect of zeolite on pyrolysis of irradiated POM (220 kGy)

Development of Radiation Processes for Better Environment

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India is one of the major producers of natural rubber latex with an annual production of over 300,000 tons. A significant part of this is used for producing dipped goods such as rubber gloves, teats and soothers. The conventional sulphur vulcanization method results in the formation of considerable amounts nitrosamines, both in the product as well as in the factory environment. A Co-60 gamma radiation based pilot plant has been functioning since April 1993 to produce sulphur free radiation vulcanized natural rubber latex (RVNRL) using acrylate monomers as sensitizer. The role of sensitizer, viz *n* - butyl acrylate in the vulcanization process has been elucidated using the pulse radiolysis technique. The results show that polymerization of the sensitizer is initiated by electrons and the vulcanization is mainly a grafting reaction¹

The viscose rayon industry is an important industry in India. This industry is now facing stiff regulations from environmental pollution control agencies primarily due to the emission of toxic sulphur-containing gases. It is in search of ways to reduce the pollution levels associated with the process. The irradiation of cellulose with ionizing radiation results in cellulose activation and reduction in the degree of polymerization (DP). These effects can considerably reduce the solvents required to dissolve the paper pulp. There is a keen interest in utilizing radiation technology in viscose rayon production. We have utilized the electron beam accelerator for reducing the degree of polymerization (DP) of paper pulp. Laboratory and pilot plant scale tests have been carried out to standardize the conditions for production of pulp to produce fiber of requisite quality. Our studies show that irradiation of paper pulp with only 8-10 kGy radiation dose can reduce the DP of pulp from 1200-1500 to 400-500 and $\approx 40\%$ reduction in the consumption of CS_2 and hence also in its emission from the effluents, can be achieved by using irradiated paper pulp instead of the conventionally aged paper pulp. This can be beneficial in reducing the inevitable pollution associated with the process.

The third process is the conversion of PTFE waste into a low molecular weight (1×10^4 - 1×10^5) microfine powder², that has considerable industrial demand. It has been demonstrated that, even PTFE filled with carbon or metal can be recycled using the EB process. A dose of 1 to 2 MGy was selected depending upon the end use of the product.

"Environmentally sensitive polymers", are being studied worldwide as energy saving materials for a number of novel applications such as concentrating protein/enzyme

solutions near room temperature. Electron beam irradiation has been utilised to create inhomogeneous crosslinking in poly(vinyl methyl ether) to produce fast response hydrogels³, these hydrogels exhibit different swelling behaviour and faster response in comparison to hydrogels obtained by gamma irradiation.

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The regeneration of polluted active carbon by radiation techniques

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Active carbon is already used during many years for removal of organic pollutants from different wastes. However, it lost the sorption capacity after some working period and should be regenerated periodically. The traditional method of regeneration is the treatment in special ovens at 900--1000°C. In this case the absorbed pollutants will escape from active carbon into air. Also high temperature operation is a big problem in large scale.

In 1972 the low temperature method of destructing organic substances absorbed at carbon surface by irradiation was proposed by Case and Ketchen[1]. However, because the concentration of the pollutants was too high, the low temperature regeneration was not a continuous process. Shubin and others (1980) found that considerably better results can be obtained by combination of radiation treatment with biological and chemical treatment [2]. They further observed that for the maintenance of absorption activity of the carbon at sufficiently high level the wastes were passed through column under continuous irradiation of active carbon by ^{60}Co γ -rays.

Active carbon is also popularly used for treatment of industrial and municipal waste in China. The most difficulty for its use in large scale is limited absorption capacity and high temperature in its regeneration. We are starting our work on municipal waste water in batch manner. First the polluted active carbon is treated by irradiation, then waste water is passed through irradiated active carbon and analysis for oxidization, transparency, COD,

PH and bacteria has been made. The active carbon without irradiation has been used for comparison. Both ^{60}Co γ -ray and electron beam used as irradiation sources. Some parameters which should effect treatment efficiency (such as dose rate, total dose et al) have been tested. On batch basis, continuous radiation-absorption method has been carried out. In this case, waste water is passed through active carbon column under the condition of continuous irradiation of sorbent by ^{60}Co γ -ray and electron beam. After the irradiation, waste water is analyzed. Some experiment without irradiation is also needed for comparison. Our work is still in progress.

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Research Activities of Samsung Heavy Industries on the Conservation of Environment

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Research activities for accelerator fields at Samsung Heavy Industries (SHI) could be categorized into the accelerator development and its industrial applications. As the initial step of the efforts, high voltage industrial electron accelerators are developed, and development of synchrotron light source and other accelerators are also investigated. The research activities for the applications of accelerator include waste water treatment, combustion flue gas purification, semiconductor treatment, and other radio-chemical processing. The treatment of industrial waste water with electron beam is one of the actively studied subject for the environmental application in Central Research Institute. The method for the removal of heavy metals from waste water and other technologies [1,2] are developed with the joint works of Central Research Institute of SHI and Institute of Physical Chemistry (IPC) of Russian Academy of Sciences. The development of flue gas purification process is also actively studied. Pilot scale tests using the flue gas with the flow rate of 500Nm³/hr in Central Research Institute proves the simultaneous reduction of SO₂ and NO_x up to 90% and 80%, respectively. A actual plant operation in Kaweczyn, Poland with the collaboration of Institute of Nuclear Chemistry and Technology shows that this method is one of the most prominent methods for the treatment of the flue gas from incineration plants and coal power plants.

An electron beam pilot plant for treating 1,000m³/day of dye waste from 60,000m³/day of total waste water is under construction in Taegu Dyeing Industrial Complex (TDIC). TDIC includes more than hundred factories and requires high consumption of water (60,000m³/day), steam, and electric power, being characterized by large amount of high colored industrial waste water. Purification of the waste water in present is performed by Union waste water treatment facilities using conventional methods. Because of increase in productivity of factories and increased assortment of dyes and other chemicals used, substantial necessity appears in re-equipment of purification facilities by application of efficient methods of waste water treatment. The existing purification system is close to its limit ability in treatment of incoming wastes. The studies have been carried out regarding the possibility of electron beam application for purification of waste water. With the co-works of SHI Central research Institute and IPC, the experiments on irradiation of model dye solutions and real waste water samples (from various stages of current treatment process) have been performed [3]. The results showed the application of electron beam treatment of waste water to be perspective for its purification. The most significant improvements

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consist in decoloration and destructive oxidation of organic impurities in industrial waste water. Irradiation on the stage of chemical treatment or immediately before biological treatment results in appreciable reduction of chemical reagent consumption, in reduction of the treatment time, and in increase in flow rate limit of existing facilities by 30-40%.

A pilot plant for a large-scale test (flow rate 1,000 m³ waste water per day) of electron beam treatment is under construction with 40kW, 1MeV electron accelerator. At present time the shielding room for accelerator and equipment are under construction and the installation of reactor and other instruments will be finished by November 1997. The waste water from various stages of the existing purification process can be treated by e-beam in this plant to expand the experimental possibilities and it will give rise to elaborate the optimal technology of the electron beam treatment of waste water with increased reliability at instant changes in waster composition.

Actual plant for re-circulation of waste water with electron beam from papermill company is also under construction in S-paper Co. S-paper co. is located in Cheongwon city, 120km south of Seoul, and consumes 18,000 m³ of water per day. The major product of this company is papers for newspaper printing (450t/day) and are made of recycled paper (91%) and pulps. Purification of waste water is now performed by chemical and biological treatment facilities. For the economical point of view, this company tried to recycle the treated water to production lines, but to use only 20-30% of total water since the organic impurities of water from treatment facilities are high and some of them are accumulated during re-circulation. In order to develop the most efficient method for re-circulation of waste water, the experiments were conducted with samples in various stages of treatment. The best result obtained is irradiation of water after biological treatment combined with coagulation and filtration. Irradiation in this stage, the additional removal of impurities are up to 80% in TOC (Total Organic Carbon) values.

On the base of data obtained by SHI and IPC the suitable doses in this case are determined as around 1 kGy for the flow rate of 15,000 m³ waste water per day. Therefore, four accelerators with the total power of 320kW and treating systems are designed and will start construction in September 1997 to finish by the end of June 1998. After the successful installation of these electron beam treatment facilities, up to 90% of waste water could be re-used in paper producing process.

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A NEW SEMI-MOBILE PLANT FOR RADIATION PROCESSING OF WASTE

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A new pilot/demonstrative semi-mobile irradiation plant, named TRIRIS (TRIsaia-Rifiuti-Sterilizzazione, namely "Trisaia Res. Center - Wastes - Sterilization"), has been designed and erected in order to propose and explore new technological opportunities, based on an "in-situ" effective cleaning process. The main general goal is to face increased problems and concerns related to the treatment /disposal of different solid-liquid wastes, particularly with reference to emergency situation (e.g. need of a quick environment restoring operation following an accident with groundwater pollution).

The project, which was jointly carried out by ENEA and Hitesys Co., an Italian electrons accelerators manufacturer, foresees a LINAC type EB-machine (s band) having 4-6 MeV and till 1000 W as beam features. A highly flexible automatic system allows materials (solid or liquid wastes) transporting and handling, being equipped with a belt conveyor and a piping net.

Scattered radiation shielding is performed by a water pool surrounding the EB-machine head, filled up before operations. Auxiliary systems, control console and analytical chemical laboratories are hosted in suitable containers near the plant and easily transportable.

The whole plant and annexed systems disassembling and reassembling in a new site can be easily carried out in a short time (few days).

The plant, that is located by the ENEA-Trisaia Res. Center (Basilicata, southern of Italy), allows a large operative flexibility: groundwater and wastewater decontamination (1800 to 70 kg/h in the 1 to 25 kGy dose range), organic and chlorinated waste streams (25 kg/h at 75 kGy), solid hospital wastes (50 kg/h at 35 kGy) or hazardous wastes like polycyclic aromatic compounds (180 to 35 kg/h in the 10 to 50 kGy dose range).

The paper describes and illustrates the plant in details and presents first available operating results so far performed by the installed plant.

TRIRIS Plant during testing operations by the HITESYS Co machine shop in Aprilia (Rome) before disassembling for shipping to ENEA-Trisaia Research Center (Basilicata, southern of Italy)



Fig.1 - External view

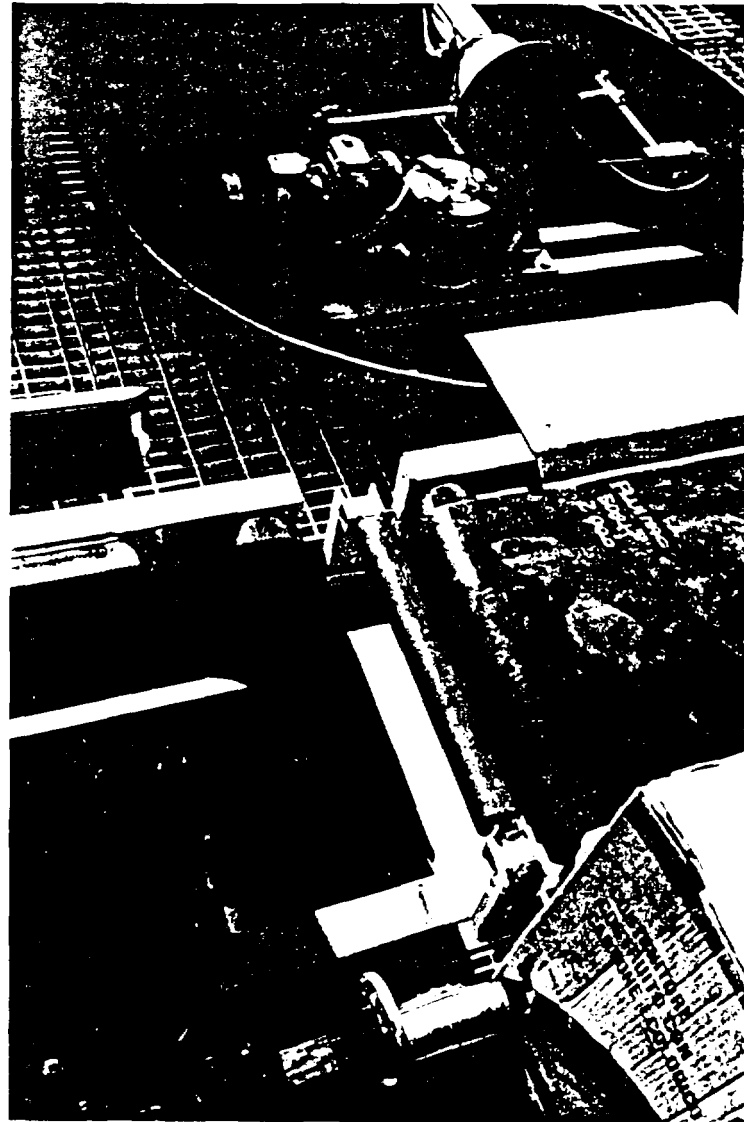


Fig.2 - EB-machine top area / Irradiation channel

"High Repetition Rate Accelerator MILLING for Radiation Technology"

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The results of the study of 200 kV prototype accelerator MILLING-1/3 are presented. This prototype is as a scaled model for a 1 MeV, high repetition rate (15 - 20 kHz), high power accelerator MILLING for radiation technologies.

MILLING-1/3 accelerator produces the electron beam with the energy up to 200 keV, peak current up to 1.0 A, pulse duration of about 6 - 8 microsecond and repetition rate up to 18 kHz.

The high frequency electronic inverter (50Hz/18kHz) is used as the power source. Accelerating voltage up to 200 kV is formed with high voltage transformer. The electron pulses are produced by a cold sheet cathode (dimensions 300 cm+2) with the threshold of volt-ampere characteristics.

The main aims of the present step of investigations are verification of novel technical solutions for obtaining electron beams with high average power and high electron energy (up to 1 MeV), study of critical parameters of the design and optimization of the operation regimes. The results of investigation have proved a possibility of constructing high power, cheap electron beam source for radiation technologies.



Economical aspects of radiation sterilization with electron beam

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A radiation sterilization plant equipped with electron accelerator Elektronika 10 -MeV/10 -kW was put into operation in the Institute of Nuclear Chemistry and Technology (INCT) in 1993. So there is now reasonable time to summarize the real costs of running this plant. The costs of this investment were covered by the government money but also some funds were provided by INCT.

The economical effects of radiation sterilization installation may be influenced by many factors.

The most important are the following:

- A. Investment costs
- B. Exploitation costs
- C. Utilization of electron beam
- D. Dose setting

The investment costs are always high for any electron beam facilities. Mainly because of the accelerator's price and costs concerning building with special biological shielding. There is also ancillary equipment needed like conveyer, cooling cycle, monitoring system and it has to be taken into account the costs concerning accelerator's maintenance, calibration and validation.

The exploitation costs can be divided into two parts - the first part is fixed and does not depend on the production scale (amortization, credit repayment, etc.), the second part is increasing proportionally with the standard and scale of service.

When the utilization of electron beam is concerned the following factors are to be taken into account: dose distribution (as a function of energy and beam current), type of irradiated items

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(complex product geometry, material interfaces and nearby surfaces), uniformity of conveyer speed, and the design of the carrier system [1].

Regarding the dose setting the bioburden and type of sterilize devices have to be considered. Dose setting is of great importance for the quality assurance level of radiation sterilization process and also influence on economical factor. A dose of 25 kGy was established during validation studies as the minimum dose required to sterilize medical devices. However, some countries (Scandinavian countries) have decided to use higher sterilization doses based on evidence of higher radiation resistance in some environmental isolates. On contrary, in the USA, Food and Drug Administration has allowed to use lower sterilization doses based on product specific dose setting studies and the need to irradiate some health care products at lower doses.

According to standard EN 552 the manufacturer must substantiate the effectiveness of 25 kGy as an irradiation dose. The costs of verifying 25 kGy as a sterilization dose might be quite high because it requires the use of large numbers of items in the initial study to establish the verification dose [2].

Operating costs are significantly influenced by the initial capital costs. Radiation sterilization carried out with electron beam requires quite high capital expenditure. The only way to lower the irradiation costs of single unit is to obtained the intensive plant-utilization times. When the plant is carried out with the high throughput the radiation sterilization is competitive with another sterilization techniques.

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Electron Processing Systems for Environmental Applications

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Electron Beam processing is widely used in a variety of fields. Examples are: crosslinking of plastics and rubber materials, curing of coatings, and so on. Nissin-HighVoltage (NHV) has been supplying many types of beam accelerators for many application fields.

Recently the demand to use Electron Beam Technology for environmental applications has arisen. DeSO_2 and deNO_x by Electron Beam treatment and decontamination of water are most promising. Under the circumstances, NHV installed several EB units for deSO_2 and deNO_x applications. Currently NHV will be supplying two 800KV - 300KW \times 2 heads units to IAEA. The system will be installed in Poland. This system is called "Demo Plant of deSO_2 and deNO_x ."

The paper will describe the requirements of the EB System for flue gas treatment applications and also the unique design parameters of the system.

APPLICATION OF FLUORIMETRY FOR DOSIMETRY PURPOSES

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A dosimetry method based on the measurement of fluorescent light, originating from organic or inorganic samples exposed previously to ionizing radiation, is applicable in radiation processing, radiation therapy and radiation protection.

Fluorimetry is often used to measure low concentration of fluorimetric compounds produced upon irradiation. These products then yield photostimulated luminescence by excitation of UV or visible light, since the emission of the absorbed energy takes place in the form of visible light soon, i.e. 10^{-9} - 10^{-6} sec, after excitation. The resulting fluorescent light intensity is related to the concentration of the fluorescent compound and thus can be related to the dose absorbed in the system. The advantage of this method is its applicability in a wide dose and dose rate range with great sensitivity [1].

In our investigations we have studied the fluorescence intensity of different type organic compounds in solid and liquid phase before and after irradiation. The absorption and emission spectra were analyzed by spectrofluorimetry. Increasing fluorescence light intensity was observed in the 1 - 100 kGy dose range studying the aqueous solution of naphthalene - 1 -, and naphthalene - 2 - carboxylic acids as well as that of 3 - (4 - hydroxyphenyl) - propionic acid.

Detailed investigations have been carried out studying the effects of solute concentration, presence of additives, dose and dose rate range in the case of the naphthalene - 2 - carboxylic acid, and its dose dependence is shown on Fig. 1.

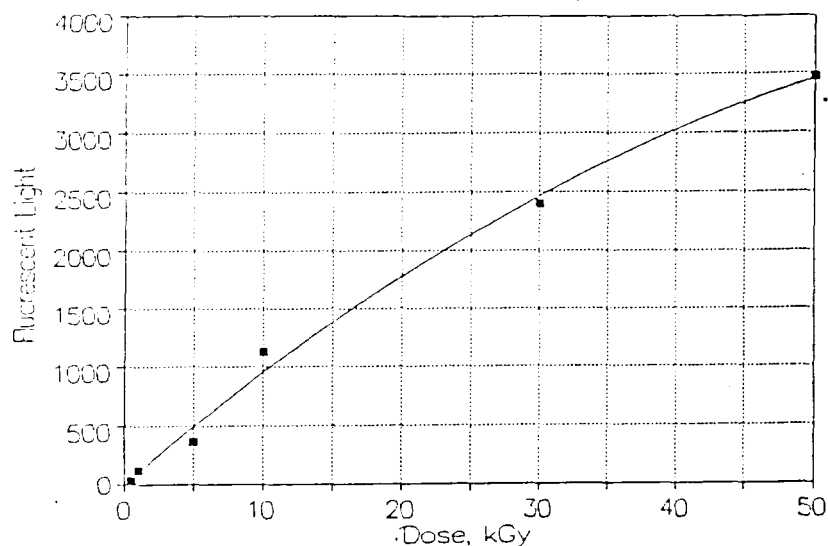


Fig.1.

Yield of fluorescent light of irradiated aqueous naphthalene-2-carboxylic acid as a function of absorbed dose

We have also studied the possible applicability of originally fluorescent compounds which - due to the decreasing concentration of the fluorescent compound - show decreasing fluorescent light intensity with increasing dose. The fluorescein containing compounds (like dibromine-fluorescein) are applicable in the low dose range, i.e. 0.01 - 1 kGy. The pyrazoline and flavone containing compounds [2], on the other hand, can be applied in the 1 - 100 kGy dose range according to our investigations.

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APPLICATION OF RADIOISOTOPE TRACER TECHNIQUES IN EVALUATION OF IRRADIATION VESSEL OF FLUE GAS TREATMENT SYSTEM

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The dry process to purify flue gases using electron beam accelerators was developed and is now in the status of industrialization. In addition to technical advantages, economic competitiveness to conventional processes is very important to accelerate the industrialization of the process. A few percent of electrical output of the power plant is used for the process and most of the energy is consumed to supply high energy electron beam to irradiation vessel where chemical reactions are initiated by the beam [1]. Getting high energy efficiency is very important in reducing operating cost as well as investment for electron accelerators. The proper design of the irradiation vessel and resultant gas flow pattern is very important to get high removal efficiency of toxic materials from flue gases.

Radioisotope tracer technology which is a powerful tool to obtain essential information for the optimization of various reactors in industry is applied to the irradiation vessel. Radioisotope tracer experiments were conducted to study the residence time distribution of gas flow in a cylindrical irradiation vessel (27cm in diameter and 118cm in length). The tracer injection point and the arrangement of detectors for the experiments are as shown in Fig. 1.

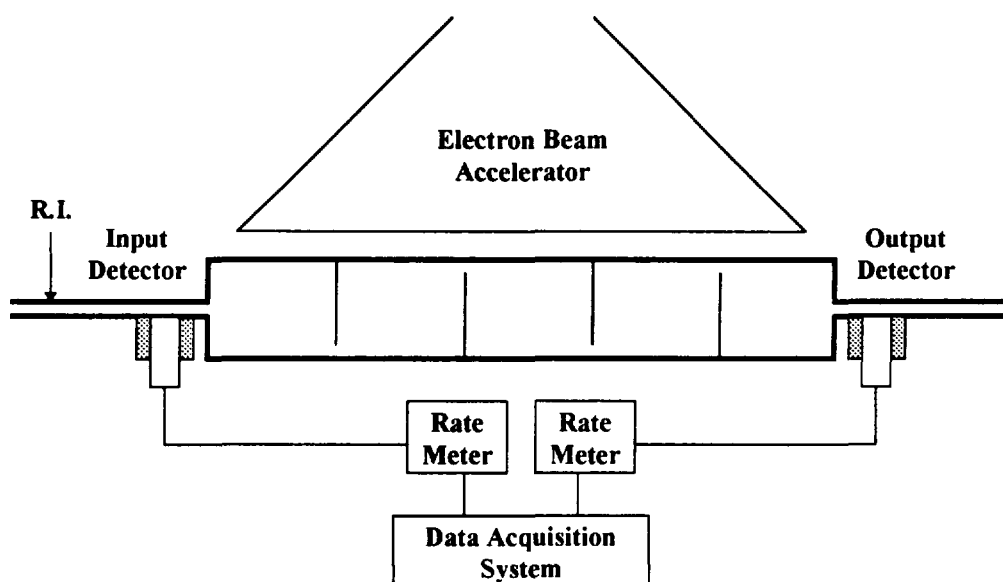


Fig. 1. Arrangement for RTD study using radioisotope as tracer

A few mCi of gaseous radioisotope tracer Ar-41 was injected to the upstream of the vessel and the input and output response (Fig. 1-a) were measured with the NaI scintillation detectors. The same experiment was conducted after modification of the

vessel by introducing 4 baffles(Fig. 2-b). The experimental data were analyzed to calculate mean residence times and mixing characteristics of each system using a RTD analysis software which was developed by Korean tracer group.

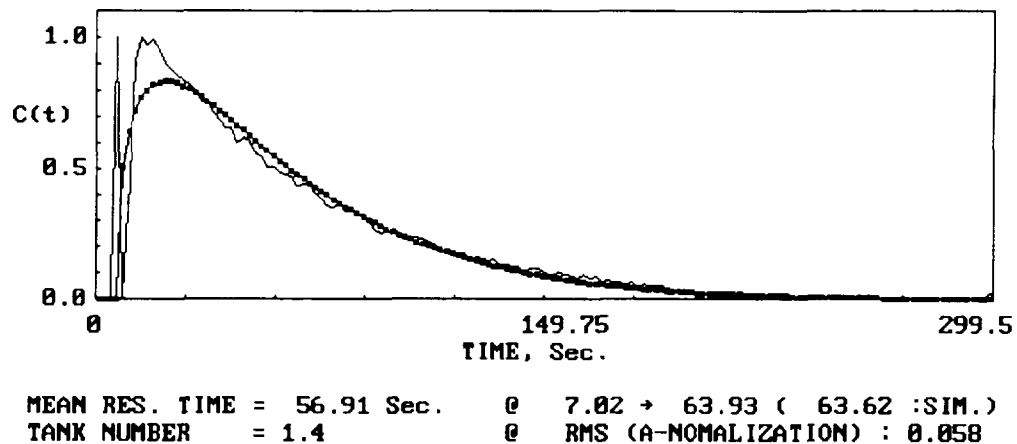


Fig. 2-a. RTD of flue gas in the cylindrical irradiation vessel with no baffle

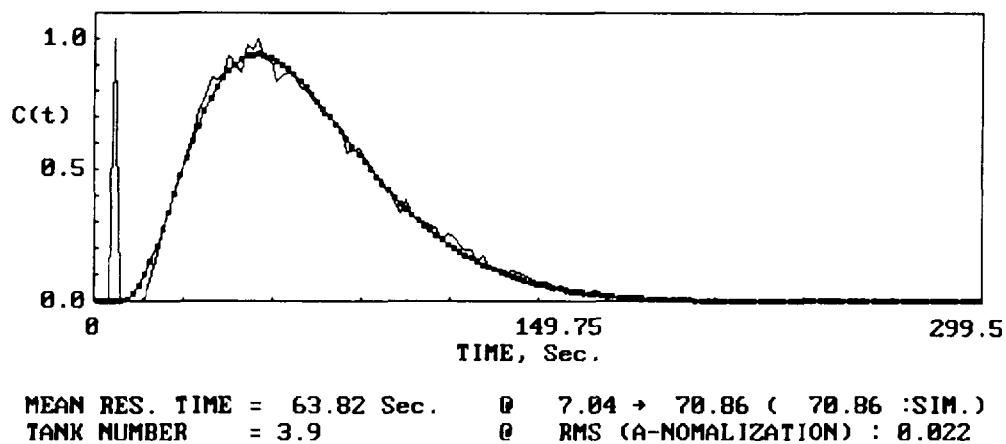


Fig. 2-b. RTD of flue gas in the cylindrical irradiation vessel with 4 baffles

A method to estimate pollutant removal efficiencies of a irradiation vessel from the residence time distributions measured by radiotracer experiments was suggested. The analytical results were compared to evaluate the effect of the baffles on the removal efficiency of the plant.

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Computerized PVC absorbance reader as the device for quick detection of dose distribution on, under and inside the electron irradiated objects

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One of the very important element of radiation technology is the investigation of dose distribution on the surface, back wall and frequently -inside irradiated object. These data are particularly important in the case of usage of standard electron beams (with penetrating range of several centimeters) for irradiation of discontinuous objects (e.g. comprehensive packages load with syringes or with another small medical devices).

For preliminary technological tests the usage of expensive commercial dosimeters (usually sold as small pieces of films with dimensions in the range from 1 x 1 up to 1 x 3 cm) causes the increase of costs and does not give the full range of needed information.

Commercially available PVC films are not recommended as the chemical dosimeters mainly because they depend on energy, dose rate and because the radiation generated colour is unstable with time. Nevertheless this polymeric film is quite cheap and can be used as the long strips which are put on, underneath and inside the irradiated packages.

The investigations which have been carried out many years ago at INCT [1] have shown that after thermal treatment these films get more stable and intensive colour and can give the valuable information about the dose distribution. This allows for parameters optimalization and cut down the

time of irradiation technology elaboration. The key issue was a quick absorption measurement (immediately after thermal treatment) linked with the data visualization and collection.

In this paper we propose to use the PVC film commercially available and computerized equipment for quick absorbance readings of irradiated films.

The description of prototype of this kind of equipment is presented.

The dose reader operates on the principle of attenuation of light beam from a light source. The degree of light attenuation is the measure of dose absorbed by the dosimetric foil. Two light sources are employed as the light beam a halogen and a deuterium lamp covering the measuring range from UV to IR. The lamps are selected depending on the light wavelength requested. The light beam from the light source is chopped 100 times/second then passes through a monochromator to obtain monochromatic light beam, after that the light is split into two beams serving as measuring and reference beams. Focused measuring beam incident on the dosimetric foil through 5 x 1 mm aperture is detected by a photodiode. The photodiode signals are amplified and processed by a standard personal computer. The reference light beam detected by another photodiode is employed to correct indication of measuring channel depending on the variation of light intensity of the light source. Computed absorbance from the signals in measuring channel is the measure of radiation dose. To move dosimetric foil in a form of a long band 7 x 1000 or 7 x 5000 mm across the light beam, a step motor drive is used. Number of steps is the measure of the length of foil moved. To move the foil by 1000 mm approximately 2500 steps are executed, thus the dosimetric foil movement can be adjusted with an accuracy 0.04%. The speed of foil movement can be selected in the range 0.6 ... 5.0 cm/sec.

Reference

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THERMAL DEFECTS OF WATER, GRAPHITE AND POLYSTYRENE AFFECTING CALORIMETRIC RESPONSE

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In order to measure accurately the amount of energy deposited by radiation in the absorber of the calorimeter, it is necessary to know so called thermal defect. It is the quantity of the heat that may have been either lost or gained as the result of radiation-chemical reactions and also as the change of the crystal lattice energy.

For very large doses of reactor mixed radiation they are directly observable: among others as the swelling of nuclear graphite or as hardening of previously soft aluminium wires.

In the range of typical doses of E.B. dosimetry (10-50 kGy for radiation processing) the defects effect it is most pronounced in plastics [1], where it might amount to a 5-10% level.

Our own measurements, using water calorimeters and the same polystyrene vessels as calorimetric ones - filled (instead pure water) with the Fricke's solution indicates thermal effect of water of about 6-8%. Obtained results are higher in comparison to 3.5% an excess heat production in a water calorimeter - observed by Domen [2].

In the case of domestic polystyrene we observed two different thermal defects. The first one is connected with the radiation-induced polymerisation of relict remaining styrene monomers and free radicals present in commercial polystyrenes. The value of thermal defect is equal to several percent only during the "virgin" irradiation. The second effect is related to large doses (several hundreds of kGy), which slowly degrades polymer and the heat defect is about 0,1%. It is worth to point out that the thermal effect of polystyrene depends strongly on properties of particular batch of the polymer.

We have investigated the radiation behaviour of the nuclear graphite (used in our calorimetry - Russian manufactured material) for evaluation of the thermal defect mechanism. Powdered samples of graphite blocks were irradiated in air using 10 MeV linac EB. After doses greater then 80-100 kGy there is an observable radiation-induced wettability with water, and as results graphite powder sinks in water-in contrary to unirradiated samples which permanently float. On the other hand

irradiated graphite powder is sensitive to an oxidation in air with mellitic acid as product. (the characteristic yellowish colour of water extract).

Moreover, 10 MeV electrons - besides ionisation of graphite as main effect also generate vacancies and interstitial carbon atoms. The overall thermal effect in of graphite nuclear purity can be estimated as about of 0,1%. This result lies between extremal literature data, i.e. 0 and 2% [3].

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POTENTIAL FOR RADIATION PROCESSING AS A TECHNIQUE FOR THE CONSERVATION OF THE ENVIRONMENT IN GHANA.

Abstract

Environmental pollution in developing countries such as Ghana transcend many fields of human activity. Rivers that serve urban communities as sources of potable water encounter challenges of pollution as a result of agricultural, industrial and domestic activity.

The wood processing industry leaves in its trail huge amounts of sawdust. Urban sewage also creates environmental problems if not manage adequately. Contaminated imported foods become sources for the introduction of new microflora into developing countries. Such new microflora can result in health problem on such societies.

This paper discusses the enormity of these problems in Ghana with a proposal for minimising them by the application of radiation processing technology.

AN OVERVIEW OF ENVIRONMENTAL POLLUTION STATUS AND WASTE TREATMENT TECHNOLOGY USED IN PAKISTAN

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There is little pollution consciousness in Pakistan. Rapid growth in population and unplanned disposal of untreated industrial, agricultural and domestic wastes has caused severe pollution problem of air, soil, drinking water and coastal marine water environments in Pakistan. To date, no systematic approach is being used in the domestic & industrial sectors of Pakistan for continuous processing and decontamination of solid, liquid and gaseous wastes prior to disposal. The two large industrial and population centers in Pakistan, namely, the cities of Karachi and Islamabad are using a few small scale wastewater treatment facilities consisting of trickling filters and activated sludge process respectively. Most of the industrial plants have installed electrostatic precipitators to control particulate emissions, for example, of cement dust [1]. However, in practice, only a few are actually using them. Presently, no accelerator is being used in Pakistan for decontamination of hospital, industrial or domestic wastes. However, the prospects of Radiation Technology for waste treatment are well realized and the Charged Particle Accelerator Laboratory (CPA) at the Pakistan Institute of Nuclear Science & Technology (PINSTECH) has developed a 250 keV ion accelerator for research, development and training purposes [2]. The main emphasis of CPA-Laboratory is now to locally design and fabricate user dedicated electron beam machines (and related devices which include sources, lenses, beam separation, diagnostic of vacuum systems) for radiation curing and decontamination of domestic, industrial and hospital wastes. This paper presents an overview of the characteristics of domestic, agricultural and industrial effluents, performance of existing sewerage treatment plants, and highlights of accelerator developments in the CPA-Laboratory at PINSTECH for environmental conservation in Pakistan.

References:

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IRASM - A MULTIPURPOSE IRRADIATION FACILITY IN ROMANIA

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Abstract

A multipurpose irradiation facility is in construction at IPNE, Bucharest, under the IAEA T.C. Project: ROM/8/011. It will be the first industrial facility in Romania.

This paper presents the philosophy standing behind the design, the short and long term managing plans. Some dose calculations are added in the view of use the empty spaces in the irradiation room for cultural heritage conservation. An economical study is presented aiming to provide basic estimations for further management strategy. At the start the facility will be a state enterprise. The implications, advantages and disadvantages of this situation are discussed.

Industrial gamma irradiation facility with a wet storage source in Syria

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Atomic energy commission

Damascus, Syria

A. MOUSSA

Atomic Energy Commission

Damascus, Syria

D.G. STEPANOV

Techsnabexport, Russia

V. ERMAKOV

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Abstract

INDUSTRIAL GAMMA IRRADIATION FACILITY WITH A WET STORAGE SOURCE IN SYRIA.

A gamma radiation facility was built in Damascus-SYRIA. The plant (ROBO) is a Co-60 wet storage, batch/continuous facility with

nominal capacity of 1.85×10^{16} Bq. The initial activity is 3.7×10^{15} Bq. The ratio of maximum absorbed dose to the minimum one within an irradiated materials is round 1.3 ± 0.03 . The irradiator consists of two sections to select required sources for irradiation. Two pools were constructed. The main pool to serve as biological shield for the main sources frame. The second pool host a fixed circular frame to be used as calibration source or to irradiate small samples to low doses. The conveyor consists of chain facility move along trucks. A repair section is provided on the conveyor route in the load -unload area for carrying out inspection, repair etc. The trucks are holed with a rectangular frames. Loading, unloading and rearrangement of the products is carried out automatically. This mechanism is carried out by seven pneumatic cylinders, lifting devices and roller conveyors. Many safety futures were included, push-back platform, followed by pit used as a physical barriers. Interlocks are connected to the platform, pit cover and to ionization chambers. In case of failure of power or any overriding of interlocks the irradiator come to emergency dropping. Ventilation system, fire system, emergency power and closed water purification system are indicated on control panel. The facility will be utilized for medical products sterilization, research and calibration.

1. INTRODUCTION

The need for a radiation -sterilization facility in Syria was recently recognized with demand from growing industry of pre-sterilized, ready for use medical products.

Improvement on Conventional Parameters of Actual Industrial effluent by Electron Beam Irradiation

C.L. Duarte, M.H.O. Sampa, P;R. Rela, C.G. Silveira

Brazil

IONIC MEMBRANES OBTAINED BY RADIATION GRAFTING FOR THE USE IN WASTE WATER TREATMENT.

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ABSTRACT

The preparation and characterization of synthetic membranes obtained by radiation-induced graft copolymerization of Styrene/ Maleic anhydride (Sty/MAn) binary monomers system onto low density polyethylene films were investigated. The optimum conditions at which the grafting process proceeded homogeneously were determined. To elucidate the possibility of practicable use of the prepared membranes, some selected properties and investigations were carried out using TGA, UV, FTIR, X-ray fluorescence (XRF), atomic absorption and differential scanning calorimeter (DSC). The structure and composition of the grafted chains were also determined. The selectivity of grafted membranes toward different heavy metals such as Fe, Cu, Cr, Cd and Pb was studied for its possible use in waste water treatment. Improvement in the chelation of the prepared membranes is also carried out by further chemical treatment with hydroxylamine-HCl and thiosemicarbazide. It was found that the introduction of thiosemicarbazide groups in the Sty/MAn grafted chains resulted in changing the selectivity from Fe^{+++} to Cu^{++} . Also in feed solution containing Fe^{3+} , Cu^{2+} and Cr^{3+} , the selectivity of untreated grafted films towards Fe^{3+} is pronounced. However, the selectivity of the treated grafted films with hydroxylamine-HCl towards Cr^{3+} is remarkable. Meanwhile, the treated films with thiosemicarbazide preferred Cu^{2+} . These grafted membranes possessed good properties toward metal chelation and of practical interest for the waste water treatment from heavy and toxic metals.



RADIATION GRAFT COPOLYMER OF ACRYLAMIDE ONTO
POLYPROPYLENE FIBERS AS METAL UPTAKE FOR WATER
SOLUBLE

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ABSTRACT

RADIATION GRAFT COPOLYMER OF ACRYLAMIDE ONTO POLYPROPYLENE FIBERS AS METAL UPTAKE FOR WATER SOLUBLE. In an attempt to modify polypropylene (PP) fibers for ion exchanger , grafting of acrylamide (AAm) monomers by the pre-irradiation method in inert medium (N_2) has been studied. Grafting was carried out in water and methanol solvent system . The percentage of grafting has been determined as a function of total dose, monomer concentration, temperature and period of grafting reaction. Water was found to be the best solvent for affording high percentage of grafting but along with it a high concentration of homopolymer was formed which was difficult to separate. The addition of small amount of methanol reduced effectively the formation of acrylamide homopolymer. The results showed the best condition of grafting were total dose 20 kGy, 10% methanol /water as a solvent, temperature 50° C , and reaction period of 2hours. The yield of grafting was found 210 %. The study of the effect of reaction temperature revealed that the calculated activation energy for the grafting process is 5,0 kkal/mol . The PP-g-AAm fiber was characterized with FTIR and DSC. It was found that PP-g-AAm fibers showed high selectivity toward Cu(II) compared with Co(II) and Fe(III) ions.

RADIATION RESPONSE OF PHILIPPINE NATURAL RUBBER LATEX

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Philippine Nuclear Research Institute, Diliman, Quezon City 1101 PHILIPPINES

Radiation vulcanization of natural rubber latex (RVNRL) is an emerging technology aimed towards replacing sulfur and various accelerators for the vulcanization of natural rubber latex (NRL). Studies have shown advantages with obvious environmental impacts of RVNRL over sulfur vulcanization (1).

Our earlier work has shown that the NRL produced and processed in the Philippines is suited for radiation vulcanization (2). The cast films from NRL with 50% TSC exhibited maximum tensile strengths of 25 - 32 MPa at 15 kGy, which is the vulcanization dose or D_v . The irradiated natural rubber latex (INRL) was stable during the experimental period of 12 months having physical properties within values acceptable to the latex industry.

In the manufacture of dipped NRL products, certain specifications such as %TSC, protein content, and tensile properties must be met to ensure an acceptable product. RVNRL, if it is to be accepted as an alternative process, must also meet these requirements. Thus this paper presents some data on the radiation response of local NRL at different total solids content, leachable proteins from NRL films as a function of dose, and thermal activities of INRL.

NRL at different %TSC levels were mixed with the monomer, nBA. The

concentration of nBA used was the maximum concentration that can be added without affecting the stability of the latex. In effect, the sample with 60%TSC can only tolerate 1 phr of nBA, while the sample with 52% TSC can be mixed with 5phr of nBA. As shown in Fig.1 the DV increases with increase in total solids content. The DV ranges from 15 kGy to 40 kGy as the %TSC increases from 52% to 58%. In fact, maximum tensile strength was not obtained for latex with 60% TSC even at a dose of 45 kGy. This difference in response could be attributed primarily to a lower concentration of

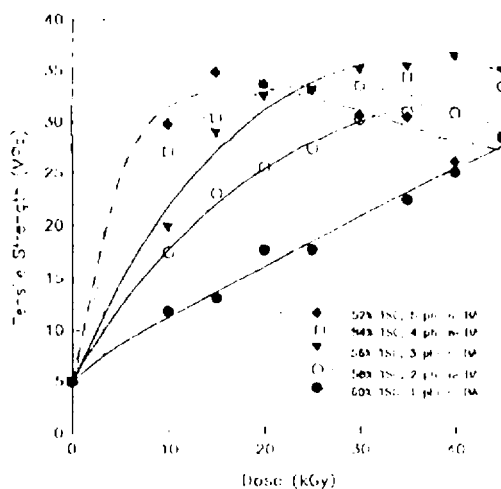


Fig. 1. Dose Response Curve of RVNR at Different TSC and nBA Concentrations

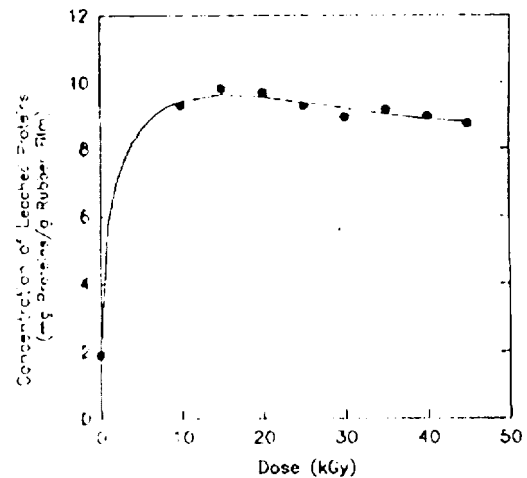


Fig. 2. The effect of Dose on the Leachable Proteins of RVNR

nBA in the latex sample with higher %TSC. These data indicate that the radiation treatment required will be dictated by the intended application of the INRL.

Fig. 2 shows the effect of radiation dose on the leachable proteins of INRL. The cast films from INRL were leached with 1% NH_4OH overnight. Protein determinations were performed using the bicinchoninic acid protein assay. Upon

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irradiation, the amount of proteins leached from the latex films increased significantly from 2 to 9 mg/g latex film. As observed by other workers, radiation increased the leachability of latex films. At doses ≥ 30 kGy, however, denaturation of proteins occurs resulting in their decreased solubility, and a decrease in their leachability. There is maximum leachability of proteins at 1Dv which is of great advantage for RVNRL because the resulting dipped products would have lower protein content, thus less allergic reactions to sensitive users.

Table 1 shows the thermal activities of INRL at different doses. The thermogravimetric data indicate greater stability of INRL to thermal oxidation relative to the unirradiated NRL, which correlates directly with their tensile properties.

Scale up mixing and irradiation of NRL has been undertaken. The performance of INRL in the production of dipped products is presently being conducted by the local industry. The potential of RVNRL in the Philippines is discussed.

Table 1. THERMAL ACTIVITIES OF NRL AT DIFFERENT RADIATION DOSES

PARAMETERS	RADIATION DOSE (KGy)					
	0	5	10	15	20	30
Temperature (°C) at Initial Mass Loss	276.74	309.18	285.71	311.224	275.510	292.86
Temperature (°C) at 10% Mass Loss	337.96	346.939	354.082	356.122	353.061	356.122
Temperature (°C) at Constant Mass Loss	368.89	373.84	371.66	369.78	377.11	377.83
% Mass Left at 500°C	6.89	1.01	8.51	6.16	6.31	6.26

References:

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EFFECT OF IONIZING RADIATION ON PROPERTIES OF ACRYLIC PRESSURE SENSITIVE ADHESIVES

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Pressure-sensitive adhesives for technical application are widely produced. The biological properties of adhesive depend mainly on the type of monomers used. The enclosed literature review as well as the experience of the authors in such area as pressure-sensitive acrylic adhesive, polymers used in medicine, polymerisation in aqueous media, radiation sterilization, allow to believe that present work will be a starting point to elaborate the technology of production of pressure-sensitive adhesives in aqueous emulsion for medical application.

The research on phenomena influencing the adhesive properties, especially its adhesion, cohesion, tack and durability is of great importance. The control of polymers structure is technologically possible by means of adequate selection of conditions of synthesis and parameters of radiation sterilization. The authors investigate the influence on the final products of such factors as the type and amount of monomers used, their mutual ratio as well as the preportioning between monomers and the dose of ionizing radiation. There is no available literature information concerning the investigation of resistance of acrylic emulsion adhesive to sterilisation by high energy radiation. It is known mainly from unpublished research data that some adhesives are resistant to radiation, while others undergo destruction. It depends probably on the composition of emulsion and specifically on the additives which modify properties of adhesives.

The selected glue samples were irradiated with various doses from 10 to 100 kGy in a new electron beam facility for radiation sterilisation of medical devices for single use, equipped with electron linac: UELV-10-10-S70-1. Radiation induced radical processes in glue were examined by EPR method. All samples before and after irradiation were examined for the determination of:

adhesion, cohesion and tack in the Institute of Industrial Chemistry, Warsaw. The value of doses were determined using a graphite and polystyrene calorimeters with an accuracy better than 10%.

It has been found that the properties of irradiated glue are improved, the adhesive is not changing and the cohesion increases. The elaborated glue is suitable for sticking plaster or self adhesive tapes contacting living human tissue, ("Viscoplast" S.A. Chemical Factory).

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ELECTRON BEAM POWER PLANT FLUE GAS TREATMENT

Abstract

Among the processes in which fuel is used for energy generation coal burning plays leading role. On the other hand combustion of fossil fuels is the biggest source of air pollution. When burning fossil fuels pollutants such as particulate, sulfur oxides, nitrogen oxides, volatile organic compounds and others are emitted. Air pollution caused by these pollutants not only acts directly on environment but by contamination of water and soil leads to their degradation. The advanced technology for simultaneous SO_2 , NO_x and VOC removal is discussed in the paper. The technology is based on electron accelerators applications.

Many new solutions have been introduced in the new pilot plants which have been operated at coal fired power stations. 98 % SO_2 and up to 90 % NO_x removals were obtained at very moderate energy consumption (for de SO_x). Additional agricultural test have proved full applicability of byproduct in pure form or as a blending stock for NPK fertilizers. Two full scale industrial plant are being built in China (640 kW accelerators) and Poland (1.2 MW accelerators). These will be the biggest radiation processing units using accelerator technology all over the world.

The Decomposition of Polychlorinated Aromatic Hydrocarbons in the Offgas of a Municipal Waste Incinerator by Electron Beam¹

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Forschungszentrum Karlsruhe GmbH
Institut für Technische Chemie

Emissions of chlorinated aromatic compounds e.g. polychlorinated dioxins and furans (PCDD/F) have been reported recently from a large number of industrial processes such as waste incineration and metal smelters. Due to the toxicity of PCDD/F stringent emission limits have been imposed.

State of the art for emission control are adsorption processes, which have high removal efficiencies, but produce PCDD contaminated wastes. The incineration or disposal of these materials is rather costly. Therefore new technologies are being developed, which do not yield secondary wastes, such as catalysts, hydrogen peroxide injection or electron beam irradiation.

Here we report the results on the electron beam induced decomposition of PCDD/F in incinerator off gas. We used a mobile off gas cleaning plant (AGATE-M), which is equipped with a 200 keV electron accelerator (EB). The off gas was sampled upstream and downstream of the irradiation zone by a condensation method. Subsequent clean-up and GC-MS analyses were performed using standard analytical methods.

The analyses show, that very high decompositions for PCDD and PCDF are achieved depending on the experimental parameters. The german emission standards are exceeded. In addition chlorinated phenols and benzenes are destroyed. A computer model (AGATE-code) was developed to analyze the gas phase chemistry of the process. The experimental and the theoretical results are reported and compared.

The energy consumption of the process is in the order of 3 - 5 kWh per 1000 m³ of treated offgas. The process has a very low pressure differential. The industrial application of the technology will be evaluated in comparison to competing methods with respect to costs and technical aspects.

Radiation Chemistry and the Environment

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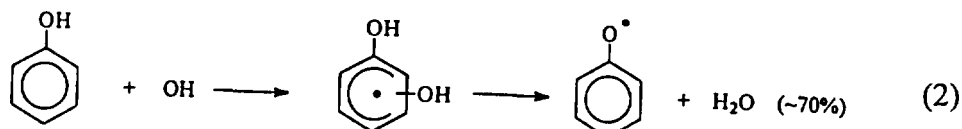
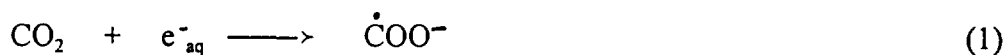
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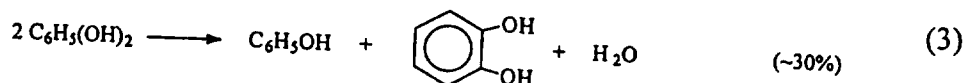
The various human activities in the last decades have caused very strong pollution of the environment (atmosphere, water resources, soil). As a consequence of this fact, health hazard for the population as well as environmental impact on a local and global scale are resulting.

Radiation chemical technologies have been developed for the solution of a number of environmental problems. These methods produce no radioactivity, no waste and they are safe for the public and the environment as well as highly efficient and economic. In addition to this several new and environmentally "clean" technologies have been developed on the base of radiation chemistry which are briefly mentioned.

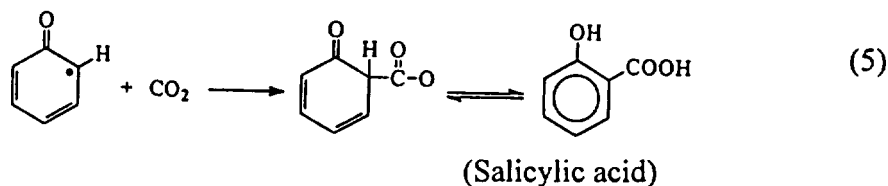
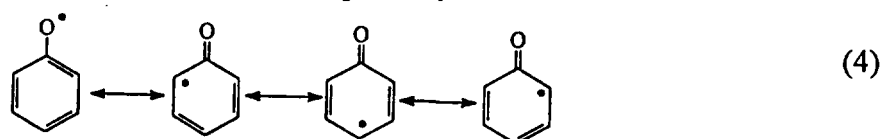
As a result of the usage of fossil fuels (coal, oil, natural gas) an emission of enormous amounts of CO_2 in the atmosphere causes a global climate change (greenhouse effect). However, CO_2 can be utilized under the influence of radiation. For illustration of this subject matter, two examples were selected: i) Formation of salicylic acid from phenol and CO_2 :



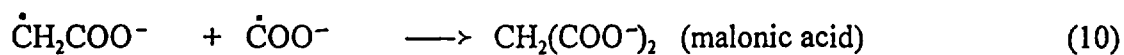
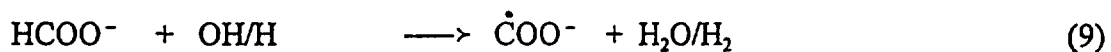
(OH-adducts on
o-, m-, p- and ipso-
position) (Phenoxyl radical)



Mesomeric structures of the phenoxyl radical:



ii) Formation of malonic acid from monochloroacetate ion in the presence of CO₂, CO and/or formate, e.g.



As mentioned above, the water resources are strongly polluted with biologically resistant compounds, e.g. chlorinated aliphatic, aromatic and heterocyclic substances. A general discussion on the degradation of such water pollutants by electron-beam processing in the presence of ozone (synergistic effect) is presented.

Invited Lecture by

T. Waite

College of Engineering, University of Miami, USA

NEW ENVIRONMENTAL APPLICATIONS OF RADIATION TECHNOLOGY

A.K.PIKAEV

Institute of Physical Chemistry of Russian Academy of Sciences, Moscow,
Russian Federation

The paper is a brief review of the new data on environmental applications of radiation technology obtained with participation of the author. It includes the results of the study on combined electron-beam and ozone treatment of municipal wastewater in the aerosol flow and on electron-beam purification of water from heavy metals (lead, cadmium, mercury, chromium).

The aerosol method for electron-beam treatment of wastewater [1] was developed to use comparatively cheap, low-energy electron accelerators. Fig. 1 shows the scheme of the respective pilot plant which was constructed to test the method. The electron accelerator utilized has the following parameters: electron energy 0.3 MeV, beam power 15 kW, beam cross-section 700 x 600 mm, size 1200 x 800 x 170 mm. The plant is equipped with 4 sprayers. In the plant, irradiated air containing ozone circulates through irradiation chamber. The output of the plant is 500 m³/day. The real municipal wastewater of small town Raduzhnyi (near Vladimir city) was treated by this method. The required level of purification and disinfection was found to be achieved at dose of several kilograys.

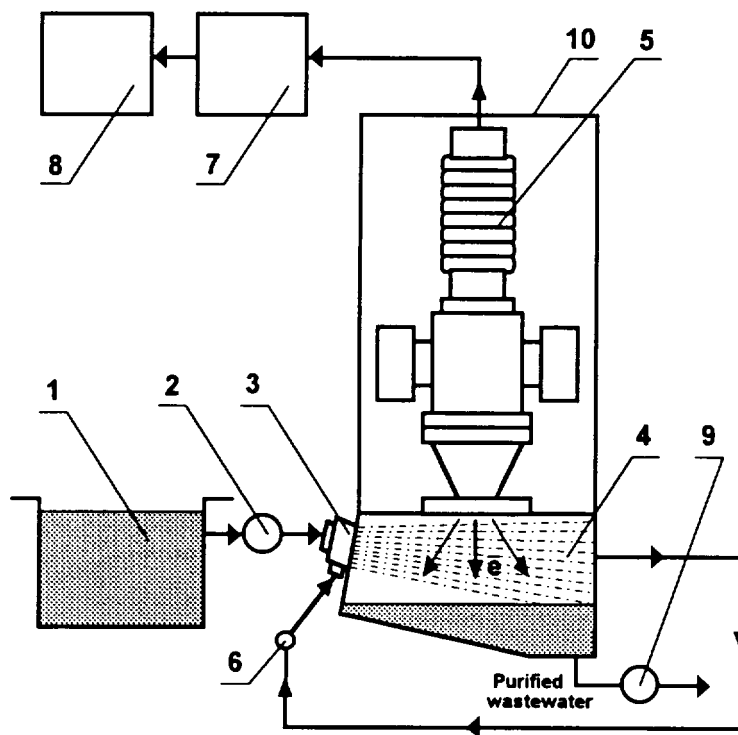


Fig. 1. The scheme of pilot plant for electron-beam and ozone treatment of wastewater: 1 is reservoir of wastewater intake, 2 is electric pump unit for wastewater, 3 is sprayer unit, 4 is irradiation chamber, 5 is electron accelerator, 6 is turboblower, 7 is power supply, 8 is control desk, 9 is electric pump unit for purified wastewater disposal, and 10 is biological shielding.

Two methods for the removal of heavy metals from water were developed. The first of them consists in electron-beam treatment of water, containing heavy metal ions, in the presence of formate and subsequent removal of precipitated metal powder by conventional procedure (e.g., by filtration) [2]. The formate is used as OH radical scavenger to prevent reoxidation of reduced metal ions and to increase the removal efficiency. The method was predominantly tested for the removal of lead and cadmium. As an example, Fig. 2 shows some data on cadmium removal. It was obtained that doses required for removal of mentioned metals to concentration less than 0.5 mg/l are equal to several kilograys.

The second method consists in the combined electron-beam and adsorption purification of water from mercury and chromium using materials of plant origin (cellulose, gluten, wheat flour and so on) as sorbents [3]. The best results were obtained with wheat flour. The removal degree reached 98% at doses of several kilograys.

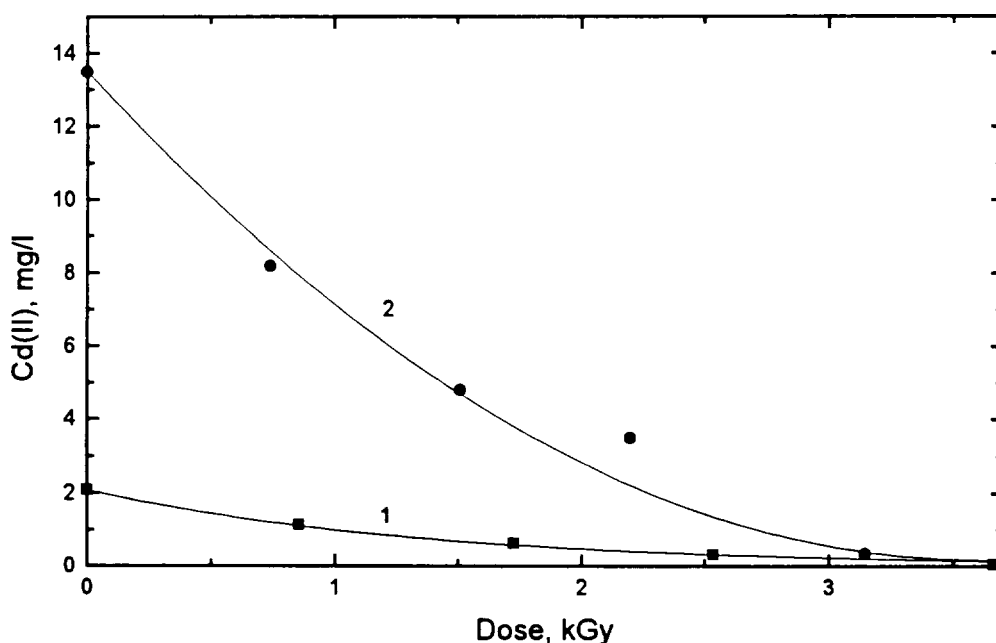


Fig. 2. Dependence of Cd(II) concentration in deaerated aqueous solution containing 5×10^{-3} (1) or 1×10^{-3} (2) mol/l formate on dose of electron radiation.

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SEWAGE SLUDGE IRRADIATORS BATCH AND CONTINUOUS FLOW

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Municipal waste waters and sludges are potentially hazardous to the environment due to their high content of pathogenic microorganisms. Growing aspirations for a cleaner environment is making it increasingly difficult to return these wastes back to nature, as they are, without pretreatment. Conventional waste water treatment processes are unable to sanitize these wastes to acceptable levels. Ionizing radiation, on the other hand, has the ability to inactivate microorganisms in such wastes effectively, rendering them safe for ultimate disposal. To demonstrate the role that radiation technology can play in the protection of environment, Department of Atomic Energy has set up Sludge Hygienisation Research Irradiator (SHRI) Project at Baroda, integrating it with an existing 22 MLD conventional sewage treatment plant to hygienize its sewage sludge by radiation treatment.

SHRI, a batch flow irradiator designed for 18.5 PBq (max.) of ^{60}Co , can process 110M^3 per day of digested sludge (4% solids) at 4 kGy dose. Effluents and raw sewage can also be drawn into the irradiator for treatment, if desired. Since its commissioning in December 1990, charged with initial activity of 5.5 PBq, the irradiator is continuously in operation. Numerous studies, related primarily to the inactivation of microorganisms in irradiated sludge have been carried out so far. With over six years of operating experience, the conclusions are as follows:

1. Microbiological Aspects: A dose of 3 kGy of gamma radiation with aeration is sufficient to hygienize the sludge to a pathogen-free and odour-free state, air functioning as a cheap sensitizing agent during irradiation. For raw sewage a dose of 1.6 kGy and for effluents a dose of 0.5 kGy is adequate to reduce the coliform counts below permissible discharge limit in surface waters. The treatment is suitable for protecting rivers like Ganga from pollution generated by the cities on the banks.

2. Engineering Aspects: For trouble-free operation of the irradiator, incoming sludge should be properly screened by wire mesh to remove clogging materials; fluid circuit should be simple and should not promote formation of the dead pockets.

Megacurie ^{60}Co irradiators have been very common in the past in applications like medical products sterilization. Waste water irradiator with sources of this order is well suited for processing the batches of low volume liquid sludge by constant

recirculation in radiation zone to maintain high fluid velocity. For higher continuous throughputs, as in case of effluent waters or raw sewage, choice of electron accelerators may be prudent. Some concepts of ^{60}Co irradiators operating in continuous flow mode are developed at BRIT. Vertical or horizontal flow irradiation vessel placed at an appropriate depth in water pool serving as biological shield, makes it a very simple and economical irradiator system. With a charge of about 74 PBq of ^{60}Co , expected throughputs are around 20 M^3 for sludge and 160 M^3 for effluents per hour. Cobalt-60 sources are fully shielded and cooled by clean water totally isolated from the waste water. It is easier to remove sources from the system under clean water for its maintenance.

Invited Lecture by

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Recycling and Treatment of Plastic Waste

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Radiation technology, using gamma or electron beams, develops its benefits at highest yield if *macromolecular* systems are treated. This is valid equally if *build-up* processes (polymerization, crosslinking) or *degradative* processes (chain scission, depolymerization) are initiated by radiation.

Radiation-induced degradation is used to convert polytetrafluoroethylene (Teflon) scrap into powder and low-molecular-weight products used in the production of other perfluoro compounds. Irradiation with several hundred kilograys in the presence of additives gives a fine powder of polytetrafluoroethylene. The powdered Teflon polymer has additional functional groups that are not present in the original polymer, e.g. carboxylic acid groups, if irradiation is carried out in the presence of oxygen or air. The pilot plants treating Teflon scrap use electron accelerators. The Teflon powder produced is blended with other materials for use as a lubricant, and the perfluorocarboxylic acids are employed as surfactants.

Radiation-induced chain scissions may find novel applications in converting *natural polymers* of biomass origin as well. EB treatment of *wood* and *cellulose* results in significant energy saving in *wood pulping* and in *viscose* (regenerated cellulose) *production*.

Radiation treatment of polymers could play an important role in the *recycling of polymer wastes* in case of natural and synthetic polymers as well. The non-selective energy transfer from gamma or electron sources to polymer systems produces many kind of reactive centers such as free radicals, oxydized and peroxydized active groups, on which further reactions may occur. In presence of monomer-like or oligomer-like reactive additives *graft-copolymerization* may take place, *compatibilizing* on that way the originally incompatible polymer components. Such a compatibilization is the key solution of recycling *commingled plastic waste*.

Radiation processed common recycling of synthetic and natural waste materials may result in *reinforced composite systems* as well. New procedures have been developed to produce wood-fiber-reinforced plastic composites from thermoplastic matrices and cellulosic fibers in the presence of selected reactive additives, using electron-beam processing.

Status of Industrial Irradiation Technology

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Abstract

The industrial radiation technology is in wide use since the beginning of the 1970s. Because of its advantages especially in economic and ecological aspects this technology became very customary for plastic industries, where powerful irradiation facilities with high security standards are used. Gamma rays and accelerated electron beams are the most important rays for these purposes. Their application fields are different according to their characteristics:

Sterilization, disinfection of medical articles need small doses and the objects may be very bulky. Here gamma-rays are preferred. Crosslinking of plastic products however needs high doses as well as high dose rates. In this case accelerated electron beams are optimal. The penetration of the material by these electrons depends on the power of accelerators (electron-beam machines). Essentially industry is using three categories of electron beam machines according to their application fields:

- low-energy electron beam accelerators (150 to 450 kV): Their penetration depth is very small, so they are mainly used for crosslinking of shrinkable films, surface treatment of papers, films, textiles etc.

- medium-energy electron beam accelerators (500 kV to 3 MeV): The penetration depth is rather large, so they are mainly used for crosslinking of plastic products e.g. cable and wire insulations or their sheathing, floor heating- or sanitary and drinking-water pipes, heat shrinkable tubes, polyolefin foams, and moulded articles. Furthermore there are some interesting special products e.g. semi-conductors, coloring of stones, degradation of polymers (recycling of PTFE waste), etc.

- high-energy electron beam accelerators (4.5 to 10 MeV): The penetration depth is very large. Therefore the application fields are suitable not only for crosslinking of big dimensioned plastic products but also for sterilization of medical products in shipping boxes. The sterilization with electron beam accelerators has been used since more than 30 years, so nowadays it is of increasing interest in hospital or pharmaceutical industries. The crosslinking especially of big dimensioned plastic products will be more and more interesting because of its ecological and economical advantages.

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