

Needs and Emerging Opportunities of Electron Beam Accelerators on Radiation Processing Technology for Industrial and Environmental Applications in South America

W. A. P. Calvo; C. L. Duarte; L. D. B. Machado; E. S. Pino; D. C. R. Poli; J. E. Manzoli; C. C. B. Tobias; M. B. Mathor; E. S. R. Somessari; C. G. Silveira; S. L. Somessari; N. M. Omi; P. R. Rela

IPEN-CNEN/SP - Institute for Nuclear and Energy Research, Brazilian National Nuclear Energy Commission, Radiation Technology Centre. Av. Prof. Lineu Prestes, 2242 - Cidade Universitaria - Sao Paulo/SP - Brazil. Zip Code: 05508-000. Telephone: (55-11) 3133-9762 - Fax: (55-11) 3133-9765

E-mail: wapcalvo@ipen.br

Abstract. The radiation processing technology for industrial and environmental applications has been developed and used worldwide. In South America there are 23 industrial electron beam accelerators (EBA) with energy from 200 keV to 10 MeV, operating in private companies and governmental institutions to enhance the physical and chemical properties of materials. However, there are more than 1,500 high-current electron beam accelerators in commercial use throughout the world. The major needs and end-use markets for these electron beam (EB) units are R&D, wire and electric cables, heat shrinkable tubes and films, PE foams, tires and components, semiconductors and multilayer packages. Nowadays, the emerging opportunities in South America are paints, adhesives and coatings cure in order to eliminate VOC's and for less energy use than thermal process; disinfestations of seeds; films and multilayer packages irradiation for low-energy EBA (150 keV - 300 keV). For mid-energy EBA (300 keV - 5 MeV), they are for flue gas treatment (SO₂ and NO_x removal); composite materials and carbon fibers irradiation; irradiated grafting ion-exchange membranes for fuel cells application; natural polymers irradiation and biodegradable blends production. For high-energy EBA (5 MeV - 10 MeV), they are for sterilization of medical, pharmaceutical and biological products; gemstone enhancement; treatment of industrial and domestic effluents and sludge; preservation and disinfestations of foods and agricultural products; lignocellulosic material irradiation as pretreatment to produce ethanol biofuel; decontamination of pesticide packing; solid residues remediation; organic compounds removal from wastewater; treatment of effluent from petroleum production units and liquid irradiation process to treat vessel water ballast. On the other hand, there is a growing need in South America of mobile EB facilities for different applications.

1. Introduction

The industrial uses of electron beam accelerators started in the late 1950's, with the crosslinking of polyethylene wire insulation. Nowadays, the number of electron accelerators in use for various radiation processing applications exceeds 1500. These accelerators are used mainly in plastics, automotive, wire and electric cables, semiconductors, health care, aerospace and environmental industries, as well as numerous research and development facilities around the world [1]. In South America and particularly in Brazil, there are 23 and 15 industrial electron beam accelerators, respectively, with energy from 200 keV to 10 MeV, operating in private companies and governmental institutions to enhance the physical and chemical properties of materials. These electron accelerators for radiation processing are presented in Tables I and II.

TABLE I: INDUSTRIAL ELECTRON BEAM ACCELERATORS WITH ENERGY FROM 200 KEV TO 10 MEV OPERATING IN SOUTH AMERICA [2].

Country	Organization	City	Units	Products	Additional Information
Brazil	IPEN-CNEN/SP	Sao Paulo	2	<u>R&D</u> : wastewater treatment, polymer modification, shrink tube and film, surface curing, food irradiation	Radiation Dynamics, Inc. (RDI), JOB 188, 37.5 kW, 1.5MeV, roller bed conveyor (batch), pilot plant for wastewater treatment (30 L/min)
				<u>Commercial</u> : wire and electric cables, semiconductors, sterilization of medical and pharmaceutical devices, PE foam	RDI, JOB 307, 97.5 kW, 1.5 MeV, continuous treatment system (300 m/min)
Ecuador	Escuela Politecnica Nacional	Quito	1	<u>R&D</u> : food irradiation, wires and electric cables	ELU-6U, 6-10 MeV
Mexico	Comision Nacional de Seguridad Nuclear y Salvaguardias	Tijuana	2	Polymer modifications (plastics and rubber)	RDI Dynamitron 300/46/1220, 3 MeV
	ICU Medical S.A.	Ensenada	1	Sterilization of medical devices, polymer modifications	Precision Scan, SB108, 10 MeV
	Cryovac	México City	1	Fresh food packaging	Nissin High Voltage, 2SP500, 500 keV
Costa Rica	BeamOne SRL	Alajuela	1	Sterilization of medical and pharmaceutical devices	Titan Corporation, 10 kW, 10 MeV
Dominican Republic	FENWAL International Inc. (BAXTER)	Haina	2	Sterilization of medical and pharmaceutical devices	Titan Corporation, TB-10/15, 10 MeV, 1.44 mA EL Surbeam/Varian, SB-1/5, 650 keV, 0.094 mA

TABLE II: INDUSTRIAL ELECTRON BEAM ACCELERATORS WITH ENERGY FROM 200 KEV TO 10 MEV OPERATING IN BRAZIL.

Company	Manufacturer	Model	Energy (keV)	Current (mA)	Applications
IPEN-CNEN/SP and Cofibam	Radiation Dynamics, Inc.	JOB 188	1,500	25	R&D and crosslinking
		JOB 307		60	
Bridgestone-Firestone	Energy Sciences, Inc.	EC/300 - 1 and 2	300	500	Crosslinking
Cryovac Brasil	Cryovac	ECLU - 1,2,3 and 4	500	30	Crosslinking
Unipac Embalagens	Energy Sciences, Inc.	CB200/060/070	210	168	Curing
Curwood Itap	RPC Industries	Broad Beam - 1 and 2	300	600	Curing
Acome do Brasil	Acome/ Radiation Dynamics, Inc.	DPC 1000	550	66	Crosslinking of wire and electric cables
Prysmian	Radiation Dynamics Inc.	JOB 307	1,500	60	Crosslinking of wire and electric cables
Aceletron	Titan Corporation/ EL Surebeam	LINAC - 1 and 2	10,000	1.8	Food irradiation, gemstone enhancement, radiosterilization of medical disables, cosmetics, polymer modification

2. Needed Technologies

The current use of the electron beam accelerators on radiation processing technology for industrial applications shows that polymers dominate the industry. While these technologies are well established in the industrialized countries, they are also needed in South America where their introduction and expansion would require assistance for technology transfer and financial support from the industrialized countries and international aid agencies. The established and needed technologies include the following [1,3]:

- a) Crosslinking of selected thermoplastics for enhancing their performance, through improvements in their mechanical and/or surface properties, electrical conductance and resistance, thermal stability, and imparting heat-shrink properties, including wire and cable insulation, multilayer packaging films, plastics tubing and foam sheets;
- b) Radiation vulcanization of elastomers, in addition to automobile tires;
- c) Radiation modification of semiconductor devices;

- d) Radiation sterilization of medical devices, cosmetics and pharmaceuticals products; and
- e) Decontamination of packaging for foods and pharmaceutical raw materials.

2.1. Wire and Cable Insulation

The electron beam crosslinking of the insulation jacketing for wire and cable is one of the most well established industrial electron-beam (EB) processing. Crosslinking prevents insulation from dripping off an over-heated wire, as could result from a short circuit, or when exposed to the high heat of an automotive engine or even a fire. Specialized under-beam transport system is shown in Figure 1. They have been developed to transport wire using multiple passes under the beam. The wire is slightly turned during each pass to assure the uniformity of exposure even if the copper conductor would be thick enough to prevent beam penetration. Pay-off and take-up equipment has been designed so that the entire process can run at several hundred meters per minute. Depending on the end-use requirements, wire jacketing is most often made from formulated polyethylene. Blends of polyethylene and ethylene-propylene rubber are used if greater flexibility is needed, especially as the diameter of the jacketing increases as for cables. When enhanced temperature resistance is required, polyvinylidene fluoride or other fluoropolymers are used [3].

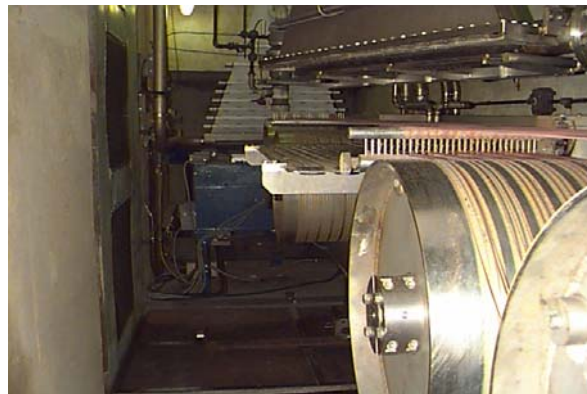


FIG. 1. Under-beam transport system for wire and electric cable irradiation at IPEN-CNEN/SP.

2.2. Semiconductors Treatment

Diodes and transistors have been irradiated under electron beam accelerators in order to induce permanent or transitory modifications in the electrical properties of these devices. For these applications, absorbed doses around 100 kGy are used in the electronic components. The results are property modifications of the components, such as, current (direct and reverse), capacitance, ideality factor (for the diodes as shown in Figure 2) and electric resistance. The usual analysis methods of these modifications generally are based on the direct measures of the current as a function of the tension, before and after the radiation processing. Recent results show that the alterations in the drift speeds of the load carriers are responsible by the reductions of the reversal recovery times of the devices. Thus, semiconductors become more suitable for applications in high power circuits [4,5].



FIG. 2. Irradiation of semiconductor diodes by EB.

3. Emerging Technologies

The success of the emerging technologies will be a function of not only products development and marketing, but also coordinated research effort. Any reduction in time and effort achieved through collaboration between industry, university and research institute could lead to faster and more economical commercialization. In most of the following emerging technologies in South America, applying electron beam accelerators with different energies for radiation processing, continued research and development would be needed to bring them to the maturity level needed to secure both the markets, and the required investment of capital, for their commercialization [1,3]:

- a) Low-energy (150 keV - 300 keV) - paints and varnishes for graphic arts, electronic circuits, optical fibers, adhesives for plastics and inks, and coatings for CDs, DVDs and wood finishes cure; disinfestations of seeds; films and multilayer packages irradiation;
- b) Mid-energy (300 keV - 5 MeV) - flue gas treatment; composite materials and carbon fibers irradiation; irradiated grafting ion-exchange membranes for fuel cells application; natural polymers irradiation and biodegradable blends production; and
- c) High-energy (5 MeV - 10 MeV) - sterilization of medical, pharmaceutical and biological products; gemstone enhancement; treatment of industrial and domestic effluents and sludge; preservation and disinfestations of foods and agricultural products; lignocellulosic material irradiation as pretreatment to produce ethanol biofuel; decontamination of pesticide packing; solid residues remediation; organic compounds removal from wastewater; treatment of effluent from petroleum production units and liquid irradiation process to treat vessel water ballast.

3.1. Radiation Curing of Composite Materials, Inks, Coating and Adhesives

Electron-beam (EB) curing has several advantages over conventional thermal curing methods: improved parts and material handling; ability to combine various materials and functions in a single operation, utilizing lower cost tooling; reduced cure times; energy savings, efficiency and environmental friendly. Figure 3 shows low-energy electron beam accelerators manufactured by PCT Engineered Systems, LLC and Energy Sciences, Inc. (ESI). The EB curing of composites has several advantages compared with conventional thermal processing.

Curing at ambient temperature allows greater control of part dimensions and eliminates internal stresses that otherwise occur during cooling, which can reduce material strength and durability. Curing time is significantly shorter, and the resins (which are not designed to cure thermally) are more stable and thus have longer shelf life. In addition, the EB process has environmental advantages in that the emission of volatile components is greatly reduced. This technology has been used in an aerospace application, in multi-layer tubes and is under investigation in numerous other areas, such as structural parts for use as automotive panels, and for electro-optical devices, healthcare products, and many other areas [6].

The faster curing times of radiation curing technology allied to the increase of production cycles (three times or higher) is an alternative for the current peroxide system cure used in the composites market. In South America it is still under development at some main composite producers. It demands investments in new equipments (lamps and ovens). However, it will be an interesting trend for the future due to the regulations regarding styrene emissions. The UV and EB energy saving curing technologies can be applied to processes like hand lay-up, spray-up, filament winding, gel coats and some applications in pultrusion, replacing thermal curing practices. The search for lower styrene emissions is one of the main concerns for the composite producers, mainly for safety, health and environmental reasons. Also, the final physical properties of the finished composite are enhanced, showing higher hardness and gloss. Market has become global. South America is part of this global market in spite of its economic situation. Therefore, all new development will affect significantly the use of UV&EB technology [7].

In August 2006, an agreement between the RadTech International North America and the ATBCR, the Brazilian Technical Association for Radiation Cure, turns ATBCR into RadTech South America. This new institution starts with already 10 years of history and pioneering technical experience and achievements in UV&EB radiation cure. Both RadTech institutions have asserted a whole cooperation and information exchange to continue with the initial ATBCR compromise in promoting UV and EB curing technology and to make it available to professionals, enterprises and other organizations. The RadTech South America has its headquarter at IPEN-CNEN/SP, from whom also gets sponsorship [7].



FIG. 3. Low-energy electron beam accelerators manufactured by PCT Engineered Systems, LLC (voltage: 70 to 125 keV and web widths: 914 to 1,727 mm) and Energy Sciences, Inc., ESI (web widths: 508 to 1,676 mm, speed capability: 335 m/min and thickness: 0.03 mm).

3.2. Irradiation as Pretreatment of Lignocellulosic Material for Ethanol Production

In recent years, there has been an increasing trend towards more efficient utilization of agro-industrial residues, such as sugarcane bagasse, as raw materials for industrial applications. Several processes and products have been reported that utilize sugarcane bagasse as a raw material. These include electricity generation, pulp and paper production, and products based on fermentation. Sugarcane bagasse generally contain up to 45% glucose polymer cellulose, 38% hemicelluloses, an amorphous polymer usually composed of xylose, arabinose, galactose, glucose, and mannose and 20% lignin.

The main obstacle to produce ethanol bio-fuel from cellulose is how to accelerate the hydrolysis reaction that breaks it down into starches and sugars suitable for fermentation. The major cellulose hydrolysis processes, as chemical or enzymatic reactions, are so harsh that toxic degradation products are produced and can interfere with fermentation. The radiation processing applying EB is a powerful technology to accelerate this hydrolysis reaction.

The main benefit of ethanol production from sugarcane bagasse is the environmental protection and recovery, reducing greenhouse gas emissions compared to oil derivatives and increasing ethanol production per planted hectare. In addition, as a large source of lignocelluloses biomass, sugarcane bagasse is a cheap and annually renewable resource suitable for producing natural cellulose fibers.

The obtained results demonstrated that the ionizing radiation with low doses can cleavage the external structure of sugarcane bagasse without destroy the cellulose or lost the sugar, that is desirable as pretreatment to enzymatic attack. The increasing in the conversion of cellulose to glucose by enzymatic hydrolysis in doses lower than 20 kGy is promising, and the maintenance of humidity even after irradiation is also very good to point out [8,9]. Figure 4 shows the sugarcane bagasse irradiation as pretreatment to produce ethanol biofuel.

The preparation and properties of new natural polymers from hemicelluloses and the use of cellulose and its derivatives in a diverse array of other applications, such as films, plastics, coatings, suspension agents and composites.

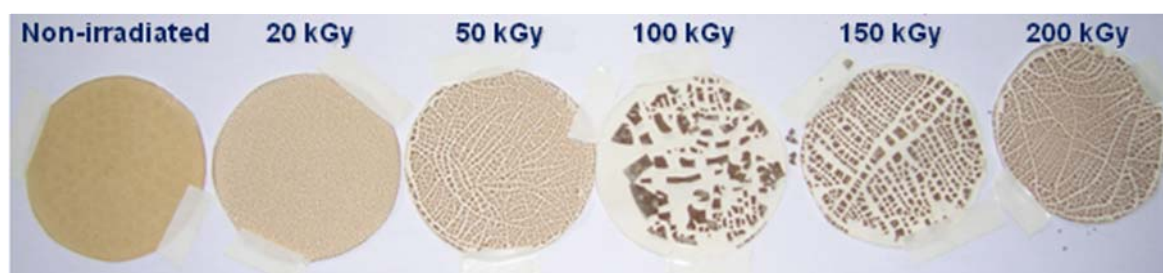


FIG. 4. Sugarcane bagasse irradiation as pretreatment to produce ethanol biofuel.

3.3. Solid Residues Remediation by Decomposition of Organic Pollutants Using Electron Beam Irradiation

There are numerous technologies potentially used for solid residues remediation and deactivation processes of hazardous wastes, mainly centered on biological and chemical treatments. Soil bioremediation in situ, appears to cause less impact to the environment. Nonetheless, considering that some waste components can be toxic to the microorganism consortium normally used in this remediation process and long periods of time may be necessary to achieve the target concentration of the contaminants in the soil. Ionizing radiation is an alternative technology for solid residues treatment by removal and degradation of toxic and refractory organic pollutants in solid residues using the Electron Beam Accelerator [10].

As a consequence of pesticides used in agriculture, the human population is constantly exposed to numerous chemical species present in the environment. The Brazilian agriculture activities have consumed about 288,000 tons of pesticides per year conditioned in about 107,000,000 packing with a weight of approximately 23,000 tons. The discharge of empty pesticide packing if done without inspection and monitoring, can be an environmental concern causing problems to human health, animals and plants. Since the uncontrolled burying and burning of waste it is no longer allowed, the only two options that remain are to dispose, or to recycle, in ways that protect the environment and human health. The ionizing radiation effectiveness on to evaluate pesticide degradation on commercial polymeric (high-density polyethylene, HDPE) packaging material, removal of the pesticides contamination in high-density polyethylene (HDPE) packaging and pesticides and petroleum residues (BTX) contamination in soil is evaluated [11].

Ionizing radiation was efficient in the removal of pesticides and other solvents from the polymeric packing, but the presence of water during the irradiation showed to be fundamental in this process. The pesticide removal yields using electron beam accelerator were similar to gamma rays. With 25 kGy absorbed dose a total removal of methomyl, dimethoate, carbofuran, and methyldathion, and more than 80% removal of triazine, thiophos and atrazyme; was reached. Lower removal rates were obtained for endosulfan (54%), chlorpyrifos (69%), thiazophos (79%), and trifluralin (74%) [12,13].

Ionizing radiation was efficient in the removal of pesticides and other solvents from contaminated soil, but the efficiency depends on the soil type, the pesticide physical chemical characteristics and humidity of the sample. Soil remediation using radiation processing showed efficient on removal pesticides, mainly for the higher water soluble pesticides, as atrazyme and ametryne [14,15].

3.4. Carbon and Silicon Carbide Fiber Modification

Composite materials are systems composed of two or more constituents differing in form and/or material composition that are essentially immiscible in each other. Polymeric composites are made of an organic matrix and a reinforcement material. Advanced composites materials are made from carbon fibers embedded in epoxy matrix. These materials are used in structural applications working under high mechanical loads.

An important factor to assure the good mechanical performance of carbon fiber based composite material is the adhesion properties between the carbon fiber surface and the epoxy matrix. Commercial carbon fibers have a sizing material on their surfaces in order to protect the filaments and also to improve the adhesion to the polymeric matrix.

The modifications induced by EB irradiation promote changes on the fiber surface, resulting in a better adhesion between the carbon fibers and the epoxy matrix used to prepare test specimens. This effect was an important factor that improved the mechanical performance of composite obtained from these materials. The improvement obtained was similar in the range of applied doses, from 50 kGy to 300 kGy, as shown in Figure 5. This mechanical improvement was only observed for composite prepared from irradiated carbon fibers, instead of applying EB radiation already on resin-impregnated composite. This behavior was observed for 6k and 12k commercial carbon fibers, independent of the differences in the sizing materials and number of filaments per roving [16-19].

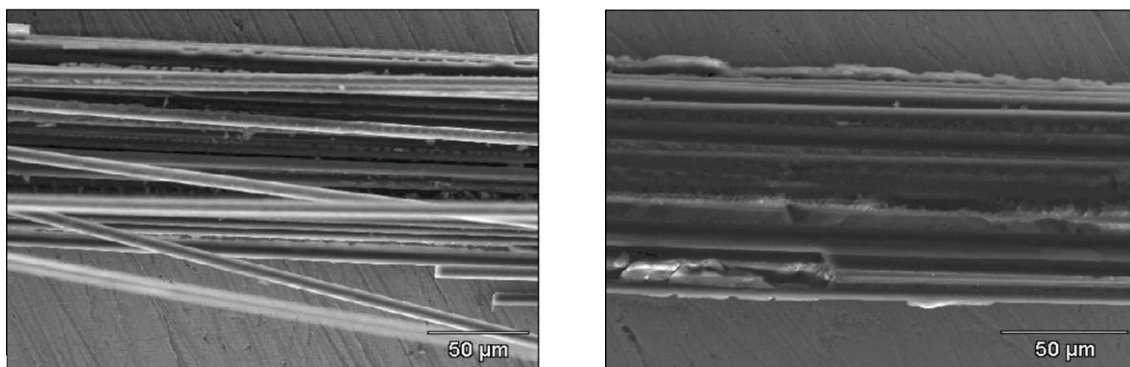


FIG. 5. Carbon fibers (12k) non-irradiated and irradiated by EB (50 to 300 kGy).

3.5. Fuel Cell Membranes

Grafting is a powerful surfacing modification process to produce new polymeric materials with an intimately molecular interaction, not present in simple processes like adhesion, traditional blending and co-polymerization. Grafting process by ionizing radiation has been more attractive lately due the fast free radicals production without chemical intermediates, like initiators.

These chemicals non rare needs long time periods to react and have high toxicity. Therefore, grafting by ionizing radiation applying EB is environmentally practicable to develop novel absorbents and membranes. The diffusional effects derived from ion exchange and other mass transport agents are studied in polymeric substrates irradiated and modified by monomer insertion or grafting, considering the measurements of its surficial, mechanical, thermal and chemical properties.

The evaluated properties are related to the applications of the modified polymer materials, such as, polytetrafluoroethylene (PTFE), polyvinyl difluoride (PVDF) and polypropylene (PP) films grafted by irradiation with styrene and lately sulfonated. Those applications will be ion exchange membrane in the PEM (proton exchange membrane, also called polymer electrolyte membrane) fuel cells, as shown in Figure 6, and plasticizer diffusion modification in PVC and monomers in other packaging films (sources of possible chemical food or

medicine contaminants) [20,21]. Another set of material use irradiation grafting of Dimethylaminoethyl Methacrylate (DMAEMA) monomer and Heparin into Polyvinyl Chloride (PVC) flexible film surface, and will be applied as a new packaging material to prevent thromboembolism when packaging in blood banks [22].

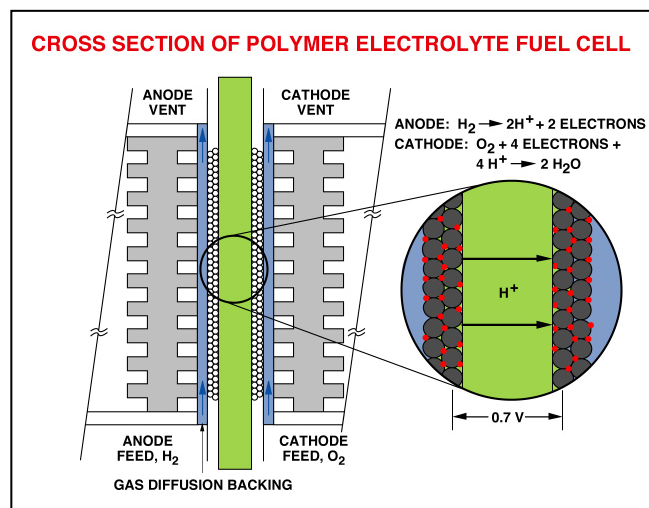


FIG. 6. Polymer electrolyte membrane fuel cell.

3.6. Catalyst Modification

Fuel cells convert chemical energy directly into electrical energy with high efficiency, low emission of pollutants and are extremely attractive as power sources for mobile, stationary and portable applications. In the proton exchange membrane fuel cell (PEMFC) the anodic oxidation of hydrogen and the cathodic reduction of oxygen should be catalyzed to occur at adequate rates at low temperatures. Carbon-supported platinum or platinum-based nanoparticles are the best electrocatalysts for anodic and cathodic reactions. However, the use of hydrogen as combustible continues to present problems especially for mobile and portable applications. Thus, there has been an increasing interest in the use of alcohols directly as combustible (Direct Alcohol Fuel Cell – DAFC). Methanol has been considered the most promising alcohol and carbon-supported PtRu nanoparticles (PtRu/C electrocatalyst) the best electrocatalyst.

The catalytic activity of PtRu/C electrocatalysts, as shown in Figure 7 is strongly dependent on the method of preparation and it is one of the major topics studied in Direct Methanol Fuel Cell (DMFC). Active carbon-supported PtRu nanoparticles is prepared submitting water/ethylene glycol solutions containing Pt(IV) and Ru(III) ions and the carbon support to electron beam radiation, with superior performance than commercial one.

The PtRu/C electrocatalysts is prepared with a nominal Pt:Ru atomic ratio of 50:50 and is characterized by energy dispersive X-ray analysis (EDX) and X-Ray diffraction (XRD) and tested for methanol electro-oxidation using cyclic voltammetry and chronoamperometry. After EB radiation the Pt(IV) and Ru(III) ions are reduced and deposited on the carbon support, obtained Pt:Ru atomic ratio of 80:20. The PtRu/C electrocatalysts has show the typical FCC structure of platinum-ruthenium alloys and the electrocatalytic activity depends on the water/ethylene glycol ration used in the preparation [23,24].

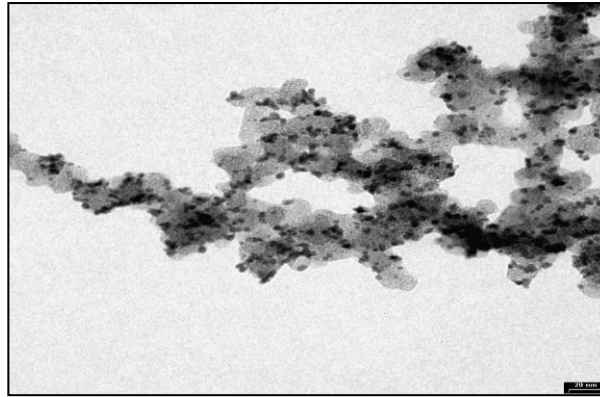


FIG. 7. PtRu/C electrocatalyst irradiation for Direct Methanol Fuel Cell (DMFC).

3.7. Seed Disinfestations

Among the man made activities agriculture plays a fundamental rule on the interference with environment. New alternatives for clean technologies are being searched in order to reduce the impact and degradation of the environment.

In the conventional chemical treatment, the insecticide/fungicide is mixed with the seeds inside a mixer (dry method) or the chemical solutions are applied by pulverization or immersion (wet method). The fumigation is another seed dressing methodology. However, it does not eliminate the pathogens inside the seed and neither avoid infestation of microorganism present in the soil.

The seed treatment technology applying ionizing radiation produced by electron beam accelerators presents as an environmentally friend alternative without the use of chemical treatments. New electron beam accelerators permit by controlling the accelerating field the adjustment of the electrons penetration power to not overpass the seed shell that normally ranges form 0.025 to 0.5 mm. The interaction of the ionizing radiation with the product is adjusted to occur only in the seed shell where the undesirable microorganism are present, preserving the inner part and the embrionary properties, without provoking the lethality or mutagenicity with reduction of the germinative properties. This technique was widely tested with wheat and barley seeds and it was successfully tested with maize seeds [25].

The association between the Fraunhofer Institut-FEP in Germany and the company Schimdt Seeger AG developed and built a movable demonstration facility using a low energy electron beam to bombard the seeds in a continuous flow drop off by gravity. Figure 8 presents the seeds, which are submitted to the bombardment of two EB emitted by two contraposed accelerators, with the energy ranging from 105 to 145 keV, permitting a uniformity interaction inside the thickness of seed shell. The results of these experiments compared with non treated seeds were that the chemical dressing showed an increasing of 5% in the production, while the seed treatment using low-energy electron beam increasing was 11% [26,27].

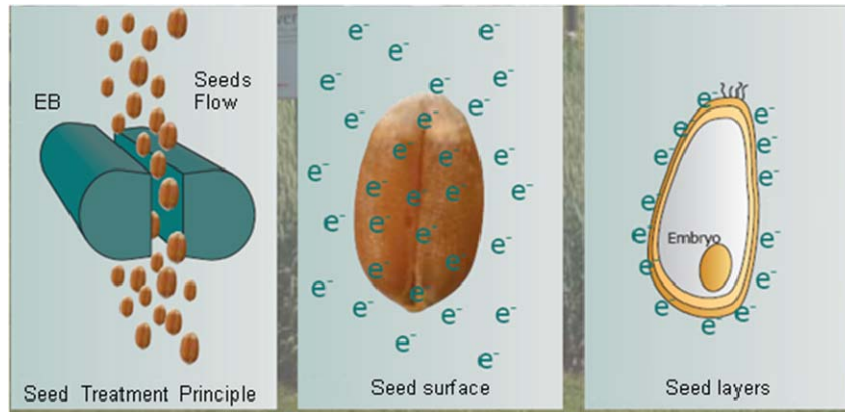


FIG. 8. Seed treatment technology applying ionizing radiation produced by EBA [26,27].

3.8. Soil Disinfestations

Inoculation of root nodule bacteria into legume seeds such as soybean [*Glycine max* (L) Merrill], common bean (*Phaseolus vulgaris* L.) and forage pasture has been effective and convenient as this simple procedure may introduce effective strains of *Bradyrhizobium/Rhizobium* into agricultural soils without a past history of successful cropping systems with the legume hosts. Peat-based substrates previously sterilized have been used for decades as bacteria carrier, protecting them from the prevailing harsh conditions in tropical soils and ensuring their survival with nutrient and protection against the soil antagonists.

All the peat-based substrates must be radiosterilized, prior the introduction of the root nodule bacteria into the package. The recommendation is doses up to 50 kGy for an effective suppression of pathogens and saprophytes, in order to avoid competition among the substrate microbiota. Recently, the use of electron beam accelerator has shown to be a new alternative for peat pre-sterilization, as this technique may promote reactive free-radicals which are efficient to suppress microbial contaminants. This fast EB technology is considered more environment and ecology friendly-sound and at high treatment dose, above 40 kGy, after long incubation periods (after 150 days), EB method is more efficient to suppress actinobacteria, one serious antagonist for *rhizobia* than gamma radiation treatment [28,29].

3.9. Human Tissue Sterilization

The industrial level ionizing radiation sterilization has been used for medical, pharmaceutical and cosmetic products treatment. Later on, this activity has extended to the sterilization of human tissues for graft. Most of the tissues transplanted, such as, skin, bone, amnion and other not viable tissues can be treated with electron beam ionizing radiation to minimize the immunogenicity, to kill bacteria and to reduce the contagious diseases transferring risk.

Besides implanting the irradiation services routine to the tissue banks of the country, the researchers developed irradiation devices for human tissues, implant dosimetric procedures for irradiation processes control, implant the quality warranty program for tissue irradiation, optimize type and dose to be supplied according to the preservation process of which the

tissue was submitted, collaborate with the implementation of quality systems of the Tissue Banks and experimental and clinical applications of irradiated tissues.

In the last few years, preserved tissue allograft, such as, bone and skin, have been used in reconstructive surgery in many clinical disciplines, like orthopedic and plastic surgery. The risk of transmission of infectious diseases by allograft, however, is a constant concern. To this end, many steps should be taken, including tissue sterilization.

Of the available sterilization techniques, the application of ionizing radiation deserves to be considered for its efficiency. The skin glycerol preservation has a bacteriostatic effect after certain time. On the other hand, skin sterilization by electron beam ionizing radiation may reduce the quarantine period for transplantation in patients and their safety is considered excellent. Skin samples were submitted to doses of 25 kGy and 50 kGy. The impacts of the irradiation on the mechanical properties through the analysis of stress-strain were evaluated and they were also accomplished by morphology and ultra-structure studies. The biomechanical and histological analyses have been used for the characterization of irradiated bones [30].

3.10. Flue Gas Treatment

The coal mines in Brazil are primarily located in southern part areas. The total coal reserves are approximately 32.8 billions tons, 89% of which are located in Rio Grande do Sul state. The Brazilian agriculture potentiality is very high, mainly due to the availability of flat land and the existence of industrial capacity to supply the main fertilizers needs.

Electron beam flue gas treatment process ensures simultaneous removal of SO_2 and NO_x from flue gases by single process. It is a dry process requiring no additional wastewater treatment system, most suitable for the installation in the thermal power plants under the present studies. The EBA process can transform SO_x (SO_2 and SO_3) and NO_x (NO_2 + NO) into a useful nitrogen fertilizer consisting of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ and ammonium nitrate NH_4NO_3 . The valuable collected by-products can be used to cultivate such crops as vegetables, corn and wheat in Brazil [31-33].

The overview of flue gas treatment in Brazil demonstrates the importance of reestablishing the partnership and works with the Thermal Power Plants in the South of Brazil, after the privatization process: Presidente Medici - CEEE (446 MW) and Jorge Lacerda - ELETROSUL (823MW) [34].

3.11. Wastewater Treatment

The effluent generate by the industries in Sao Paulo city are one of the main causes for the environmental pollution, most of these contaminants biodegrade very slowly, becoming dangerous for men, plants and animals. The conventional treatment and available technologies to treat such waste have low efficiency, and industries are searching for alternative technologies to degrade chemical compounds to get a better quality of effluent and consequently improve the environmental conditions.

The reactive species formed by the water irradiation are the reducing radical's solvated electron (e^-_{aq}), and H \cdot atoms and the oxidizing radical hydroxyl OH \cdot . The reactive species will react with organic compounds in the water inducing their decomposition. The use of ionizing radiation has great ecological and technological advantages, especially when compared to physical-chemical and biological methods. It degrades organic compounds, generating substances that are easily biodegraded without the necessity of adding chemical compounds. The purpose of the radiation treatment is the conversion of these substances to biodegradable compounds; sometimes the complete decomposition is not necessary for this conversion [35-36].

A study to combine beam irradiation process with conventional treatment was carried out. Experiments were conducted using samples from a Governmental Wastewater Treatment Plant (WWTP) that has predominance of industrial wastewater origin in Sao Paulo. Samples from WWTP Granular Media Filtration, Primary Sedimentation and Final Effluent after biological treatment were collected and irradiated in the electron beam accelerator in a batch system. The delivered doses were 5.0 kGy and 10.0 kGy. For the non-irradiated and irradiated samples the following parameters were analyzed: Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), solids, Total Organic Carbon (TOC), trihalomethanes (THM's), tetrachloroethylene (PCE), trichloroethylene (TCE), benzene-toluene-xylene (BTX), phenol and concentration of organic acids formed. After this evaluation, the best step of WWTP process for electron beam accelerator installation was suggested [37].

Concerning to the development of hydraulic system where the water is presented to the electron beam that governs the efficiency of the radiation processing the results are promising, allowing the processing of liquids with a competitive price. The hydraulic system can still be improved to be used with low accelerating voltage electron beam in order to reduce the processing costs [38].

The improvement of real industrial effluents related to the radiation process can be also shown by the toxicity removal obtained for 87.7% of the irradiated samples, which changed from very toxic to slightly toxic, except for produced water. This toxicity removal could significantly improve the efficiency of a post-biological treatment, after radiation process. The performed research carried out in the laboratory and in the pilot plant show that high-energy electrons are an effective treatment for many pollutants. However there is a lack of information concerning to the use of this technology by the environmental engineers. An extra effort must be done promoting this technology to the engineering community to understand the benefits of aqueous chemistry associated to radiation of water [37].

4. Conclusions

There is a growing use of low-energy electron beam accelerators (EBA) for the curing of inks, coating and adhesives for the eliminations of volatile organic compounds (environmental friendly), energy savings and efficiency. Lower cost and low energy EBA are commercially available. There is a growing need for mobile facilities for different applications, such as, industrial wastewater treatment and seed disinfestation in South America.

There is an increasing diversity of products and processes that require high and mid-energy electron beam accelerators for food irradiation, sterilization of disposable medical, pharmaceutical and cosmetic devices, crosslinking of wire and electric cables, multilayer packages, heat shrinkable tubes and films, tires and components, composite materials and carbon fibers, lignocellulosic and natural polymers irradiation, semiconductor modification, gemstone enhancement, grafting, solid residues remediation, wastewater and flue gas treatments. There is a need of improvements in the reliability of medium and high energy electron beam accelerators, with regard to window life time, power supply and cathode.

The future of the electron beam application for flue gas treatment depends on technical developments to make the radiation technology very competitive for environmental applications. Due to this fact it is necessary to establish new applications for EBA process in petrochemical complexes, incinerators and mines, to carry out R&D works in EBA systems and power supplies (capacity) supported by IAEA, including interregional projects, to promote fertilizer marketing for the valuable collected fertilizer (by-products), and to reach reliability, decreasing the power consumption and capital cost, optimizing the engineering technology and equipment to improve installation's stability.

Improved efficiency, with reduction in time and required dose, and effort achieved through collaboration between industry, university and research institute could lead to faster and more economical commercialization. Closer contacts with the polymer industries may open up new opportunities for radiation processing by electron beam accelerators.

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References

- [1] INTERNATIONAL ATOMIC ENERGY AGENCY, Report of a Consultants' Meeting on the "Recent development in electron accelerator technology and applications", Quebec, Canada (September 18-20, 2002).
- [2] INTERNATIONAL ATOMIC ENERGY AGENCY, Directory of Electron Beam Irradiation Facilities in Member States (July, 2008). http://www-naweb.iaea.org/napc/iachem/files/EBA_directory.pdf. Accessed in April 24th, 2009.
- [3] INTERNATIONAL ATOMIC ENERGY AGENCY, Industrial Electron Beam Processing, Consultants' Meeting on the "Preparation of the status report on low energy, self-shielded electron accelerators and of industrial scale electron/X-ray irradiators", Vienna, Austria (July 21-25, 2008). Working Material (CD-R Draft 10, Revision 1).
- [4] KRISHNAN, S. et al: "8 MeV electron irradiation effects in silicon photo-detectors", NIM B 264 (2007) 79-82.
- [5] KRISHNAN, S., et al., "Electron irradiation effects on the Schottky diode characteristics of p-Si", NIM B 266 (2008) 621-624.

- [6] MACHADO, L.D.B.; KAWANO, Y.; PINO, E.S.; GIOVEDI, C., "Research and development on electron beam curing of composites in Brazil: application perspectives". In: IAEA Consultant Meeting on Radiation Curing of Composites, 2005, Sao Paulo. Proceedings of the IAEA Consultant Meeting on Radiation Curing of Composites. Vienna: International Atomic Energy Agency, IAEA, Vol. 1 (2005) 16.
- [7] MACHADO, L.D.B.; ROTTA, A.C.; PETRIE, I., "Status of Radiation Curing in South America. In: RadTech Asia 2007", 11th International Conference and Exhibition on Radiation Curing, 2007, Kuantan. Conference Proceedings. Malaysia: PST Enterprise Sdn. Bhd., Vol.1 (2007) 31-37.
- [8] DUARTE, C.L.; CARDOSO, V.M.; NAGATOMI, H.R.; OIKAWA, H.; MORI, M.N.; FINGUERUT, J., "Studies of cellulose from sugarcane bagasse hydrolysis using electron beam accelerator". International Meeting on Radiation Processing - IMRP 2008. London, UK (2008).
- [9] CARDOSO, V.M.; MORI, M.N.; FINGUERUT, J.; NAGATOMI, H.R.; OIKAWA, H.; DUARTE, C.L., "Degradation of polysaccharides from sugarcane bagasse using electron beam accelerator". IRAP 2008 - 8th International Symposium on Ionizing Radiation and Polymers. Angra dos Reis, Rio de Janeiro, Brazil (2008).
- [10] DUARTE, C.L.; OIKAWA, H.; MORI, M.N.; SAMPA, M.H.O., "Present status of environmental application of electron beam accelerator in Brazil". In: IAEA ed. International Symposium on Utilization of Accelerators, Vienna, International Atomic Energy Agency (2006) 1-8.
- [11] DUARTE, C.L.; MORI, M.N.; OIKAWA, H.; SAMPA, M.H.O., "Simultaneous removal of various pesticides from contaminated HDPE packing using electron beam accelerator". In: Eighth International Topical Meeting on Nuclear Applications and Utilization of Accelerators, 2007, Pocatello. ACCAPP' 07 - Nuclear Applications and utilization of Accelerators. LaGrange, Park, Illinois: American Nuclear Society, Inc., V.1 (2007) 692-696.
- [12] MORI, M.N.; SAMPA, M.H.O.; DUARTE, C.L., "Study of the degradation of chlorpyrifos by ionizing radiation". J. Radioanal. and Nucl. Chem., **270**(1) (2006) 99-102.
- [13] DUARTE, C.L.; MORI, M.N.; SAMPA, M.H.O., "Decontamination of pesticide packing using ionizing radiation". Radiat. Phys. Chem., **76** (2007) 1885-1889.
- [14] DUARTE, C.L.; ANDRADE, D.C.; MORI, M.N.; MELO, R.P., "Decontamination of ametryne HDPE packaging using electron beam accelerator". Radiat. Phys. Chem., (2009) in press.
- [15] SANTOS, J.S.; OIKAWA, H.; MORI, M.N.; CALVO, W.A.P. DUARTE C.L., "Remediation of pesticide contaminated soil by ionizing radiation". International Conference on Recent Developments and Applications of Nuclear Technologies. Bialowieza, Poland, (September 15-17, 2008) 158.
- [16] GIOVEDI, C.; MACHADO, L.D.B.; AUSGUSTO, M.; PINO, E.S.; RADINO, P., "Evaluation of the mechanical properties of carbon fiber after electron beam irradiation", Nuclear Instruments and Methods. In Phys. Res. **B 236** (2005) 526-530.
- [17] GIOVEDI, C.; MACHADO, L.D.B.; PINO, E.S.; AUSGUSTO, M.; CARVALHO, O., "Effects of electron beam irradiation on carbon fiber tensile properties", 2nd International Symposium on Utilization of Accelerators, IAEA-CN-115-29, Dubrovnik, Croatia (2005).
- [18] PINO, E.S.; MACHADO, L.D.B.; GIOVEDI, C., "Improvement of carbon fiber surface properties using electron beam irradiation". Nuclear Science and Techniques, Vol. 18, No.1 (2007) 39-41.

- [19] GIOVEDI, C.; MACHADO, L.D.B.; PINO, E.S., “Thermal behavior of electron beam irradiated carbon fiber composite”. In: 2007 International Nuclear Atlantic Conference - INAC 2007, 2007, Santos-SP. 2007 INAC - International Nuclear Atlantic Conference, (2007), Contributed Paper (CD-ROM).
- [20] MUTO, F.; OSHIMA, A.; KAKIGI, T.; MITANI, N.; MATSUURA, A.; FUJII, K., SATO, Y.; LI, J.; WASHIO, M., “Synthesis and characterization of PEFC membranes based on fluorinated-polymer-alloy using pre soft-EB grafting method”. Advanced Research Institute for Science and Engineering (RISE). Waseda University, Tokyo, Japan (2005).
- [21] MANZOLI, J.E.; MAZZEI, R.; GERALDO, A.B.C.; MOURA, E.; BERMÚDEZ, G.G.; DEL GROSSO, M.F.; CHAPPA, V.C.; ARBEITMAN, C., “Cationic Membranes Produced by Swift Heavy Ions to be Applied in PEM Fuel Cells. 8th International Symposium on Ionizing Radiation and Polymers. Angra dos Reis/Rio de Janeiro, Brazil (October 12-17, 2008).
- [22] CHEN, J.; WU, Z.; YANG, L.; ZHANG, Q.; SUN, J., “Grafting copolymerization of *N,N*-dimethylacrylaminoethylmethacrylate (DMAEMA) onto pre-irradiated polypropylene films”. *Radiation Physics and Chemistry* **76** (2007) 1367-1370.
- [23] SILVA, D.F.; OLIVEIRA NETO, A.; PINO, E.S.; BRANDALISE, M.; LINARDI, M.; SPINACÉ, E.V., “PtRu/C electrocatalyst prepared using electron beam irradiation”. *Materials Research*, V. 10 (2007) 367-370.
- [24] SILVA, D.F.; OLIVEIRA NETO, A.; PINO, E.S.; BRANDALISE, M.; LINARDI, M.; SPINACÉ, E.V., “PtRu/C electrocatalysts prepared using electron beam irradiation”. In: 2007 International Nuclear Atlantic Conference - INAC 2007, 2007, Santos-SP. 2007 INAC - International Nuclear Atlantic Conference (2007). Contributed Paper (CD-ROM).
- [25] ZAGO, C.; RELA, P.R., “Technical feasibility for electron beam application on maize seeds disinfection for maize cultivation in Brazil”. In: 2007 International Nuclear Atlantic Conference - INAC 2007, 2007, Santos-SP. 2007 INAC - International Nuclear Atlantic Conference (2007). Contributed Paper (CD-ROM).
- [26] Fraunhofer Institut FEP and Schimdt-Seeger AG. E-ventus Pure Innovation. <http://www.e-ventus.de/index.php?setlang=en>. Accessed in July 14th, 2008.
- [27] BORCEAN, I., Results obtained at the University of Agricultural Science and Veterinary Medicine of the Banat in Timisoara, Romania. <http://www.e-ventus.de/index.php?setlang=en>. Accessed in July 14th, 2008.
- [28] TSAI, D.; RELA, P.R., “Application of electron beam radiation for peat sterilization and suppression of microbe contaminants”. Master of Science in Nuclear Technology – Applications. Sao Paulo University (USP) and Institute for Nuclear and Energy Research (IPEN). Coordinator: Dr. Paulo Roberto Relá. Sao Paulo, Brazil (2006).
- [29] TSAI, S.M.; OLIVEIRA, W.S.; TSAI, D.; RELA, P.R.; SAMPA, M.H.O., “Inoculants have promoted economy in the soybean production”. *Visao Agricola* No 5 (3), (2006) 31-34.
- [30] BOURROUL, S.C.; HERSON, M.R.; PINO, E.S.; MATHOR, M.B.. “Sterilization of skin allografts by ionizing radiation”. *Cellular and molecular Biology* **48**(7), (2002) 803-807.
- [31] JAPAN CONSULTING INSTITUTE, “Feasibility Study Report on Installation Project of Air Pollution Control Plant at Jorge Lacerda and at Presidente Medici Thermal Power Plants in Federative Republic of Brazil). Tokyo, Japan (November, 1997).
- [32] POLI, D.C.R.; LIMA, W.; CALVO, W.A.P.; ALY, O.F.; ANSON, J.M.A.; NETTO, N.F.A.; FRANK, N.W., “Pre-feasibility study for an electron beam flue gas treatment demonstration plant to Eletropaulo's Piratininga Power Plant”. In: Symposium on

- Radiation Technology for Conservation of the Environment, 1997, Zakopane, Poland. IAEA-TEC-DOC-1023. Vienna: International Atomic Energy Agency (1997) 97-103.
- [33] ALY, O. F., "Air pollutants conversion study of combustion gas generating by oil fueled thermoelectric power plant to fertilizer byproduct". Master of Science in Nuclear Technology – Applications. Sao Paulo University (USP) and Institute for Nuclear and Energy Research (IPEN). Coordinator: Dr. Dora de Castro Rubio Poli. Sao Paulo, Brazil (2001).
- [34] CALVO, W.A.P.; POLI, D.C.R.; DUARTE, C.L.; OMI, N.M.; LIMA, W.. International Atomic Energy Agency (IAEA). Technical Meeting on "Prospects and Challenges in Application of Radiation for Treating Exhaust Gases (TM 32927)". Overview of flue gas treatment in Brazil. Institute of Nuclear Chemistry and Technology (INCT), Warsaw, Poland (May 14-18, 2007).
- [35] SAMPA, M.H.O., BORRELY, S.I., VIEIRA, J.M.; RELA, P.R.; CALVO, W.A.P.; NIETO, R.C.; DUARTE, C.L.; PEREZ, H.E.B.; SOMESSARI, E.S. The use of electron beam accelerator for the treatment of drinking water and wastewater in Brazil. *Radiat. Phys. Chem.*, **46** (4-6), (1995) 1143-1146.
- [36] SAMPA, M.H.O.; DUARTE, C.L.; RELA, P.R.; SOMESSARI, E.S.; SILVEIRA, C.G.; AZEVEDO, A.L. Remotion of organic compounds of actual industrial effluents by electron beam irradiation. *Radiat. Phys. Chem.*, **52**(1-6), (1998) 365-369.
- [37] SAMPA, M.H.O.; RELA, P.R.; DUARTE, C.L. Industrial wastewater treatment in Brazil using an electron beam accelerator. In: COOPER, J.C.; CURRY, R.D.; O'SHEA, K.E. eds. *Environmental Applications of Ionizing Radiation*. New York, John Wiley & Sons, Inc. (1998) 521-530.
- [38] RELA, P.R.; SAMPA, M.H.O.; DUARTE, C.L.; COSTA, F.E.; SCIANI, V. Development on an up-flow irradiation device for electron beam wastewater treatment. In: 11th International Meeting on Radiation Processing - IMRP, Melbourne, Australia, 1999