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SOLID WASTE ELECTRON BEAM TREATMENT

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Solid Waste Electron Beam Treatment

The possible applications of electron accelerators for solid waste treatment are discussed in the report. The elaborated technologies allow to recycle of materials (e.g. cellulosic materials in municipal waste), improve their hygenic standards (agricultural usage of sludge from municipal waste water treatment) and reduce harmful to environment chemicals usage (cellulose degradation). These are environment friendly advanced technologies which meets demands concerning waste recycling.

Zastosowanie wiązki elektronów do obróbki odpadów stałych

W raporcie omówiono technologie wykorzystujące wiązkę elektronów do obróbki odpadów stałych. Opracowane technologie pozwalają na wtórne użycie materiałów (np. odpadów celulozowych zawartych w śmieciach komunalnych), higienizację odpadów (umożliwiającą np. rolnicze użycie osadów z biologicznych oczyszczalni ścieków) oraz redukcję zużycia szkodliwych chemikaliów (degradacja celulozy). Są one przyjazne dla środowiska i zgodne z trendami dotyczącymi wtórnego zagospodarowania odpadów.

CONTENTS

1. ORGANIC SOLID WASTE GENERATION AND POTENTIAL USE

Tremendous amounts of biomass in the form of waste are produced due to various activities of man. Many wastes orginate from agriculture and forestry; additional wastes are produced as municipal solid waste or sludge from communal wastewater treatment plants.

These wastes can be valuable resources in the production of materials, chemicals, fuels and foodstuffs [1].

In the OECD, in which 24 of the most technologically advanced countries belong, $9x10^6$ tons of municipal wastes were generated in 1990. Per capita in the end of 1980s 826 kg of municipal wastes were produced in the U.S. 394 in Japan, OECD (Europe) 336, and OECD (all countries) 513 [1].

In the U.S., municipal wastes on average are comprised of 35-50% paper, 8-18% glass, 10-20% yard, 10-17% miscellaneous, 9% metals, 8-12% food wastes and 7% plastics. In 1986, paper and paperboard, wood, and plastics accounted for approximately 65, 5.8 and $10.3x10^6$ t, respectively. By the year 2000, these figures are expected to increase to 86.5, 6.1, and $15.7x10^6$ tons annually [1, 2]. In addition to the wood fiber in the municipal solid wastes stream, vast quantities of low-grade wood, wood residues, and industry-generated wood waste in the form of sawdust, planer shavings, and chips are now being burned or otherwise disposed of.

Another potential source of cellulose or compost are agriculture wastes which were for example, totalled to $24x10^6$ tons/year (1989) in England and Wales only. In the U.S. 1974 this number was $412x10^6$ t/y. In predominantly agricultural countries the amounts of agricultural wastes are 5-10 times greater than municipal refuse.

Cellulose-containing materials are the single most important component of solid wastes. Utilization of waste cellulose is greatly simplified if cellulose is first hydrolyzed to its monomer glucose; this general reaction scheme is shown in Fig.1 [3]. Via this pathway cellulosic wastes can be converted into many chemicals (Fig.2) [3] now produced from hydrocarbons.

An other tremendous source of biological wastes are wastewater treatment plants using biological treatment. Sludge generated in municipal wastewater treatment plants, if they do not contain hazardous pollutants, can be a source of valuable fertilizer (after composting) or soil conditioner. The sludge produced from sewage treatment amounted to around 5.5 million (dry) tons in the U.S. in 1992 and the total produced in the original 12 EU countries amounted to 6.3 million tons. The sludge produced in the U.K. was 1.1 million tons in the early 1990s, but is

expected to rise to 2.2 million tons by the year 2006 [2]. The amount of sludge is increasing each year; this trend in Tokyo is illustrated in Fig.3 [4]. Sludge of course requires disposal and the main options for this are limited: land application, dumping at sea, landfilling and incineration.

The EU has banned the sea disposal of sewage and sludge from the end of 1998 and many other countries are also phasing it out.

There are great opportunities for organic waste processing using technologies, mainly based on electron beam applications. These opportunities are connected mostly with biological waste hygienization and cellulosic waste processing.

2. ELECTRON INTERACTION IN LIQUIDS AND SOLIDS

Electrons which are used for radiation processes (0.1-10 MeV) carry quite a high quantity of energy. Each particle initiates, for example, ionization, creating hundreds or thousands ion pairs. Secondary electrons are liberated in the ionization process with greatly varying kinetic energy. If the energy of these secondary electrons is relatively low (<100 eV) their range in liquids and solids is short and the ionizations and excitations caused by these electrons take place close to the primary ionizations, leading to the formation of small spurs containing ionized and excited species. Tracks of their own branches are formed by secondary electrons with high kinetic energy. For primary electrons in the range 10^4-10^7 eV, the secondary electrons (δ-rays) with the following energies are formed, approximately 40% - <3.4 eV, 20% - 3.4÷6.8 eV, 18% - 6.8÷13.5 eV and 12% - 13.5÷27.1 eV [5]. The ionizations and excitations caused by the secondary electrons take place close to the primary ionizations, leading to the formation of small spurs containing ionized and excited species. The spurs are distributed in a chaotic way along the track in smaller and bigger groups; for the secondary electrons with higher energies, the track may deflect from the main one caused by the primary electron (Fig.4). The radius of the core at low electron velocities is of the order of 1 nm. The energy of the fast electron is consumed by the formation of spurs (6-100 eV), blobs (100-500 eV) and short tracks (500-5000 eV). A blob is a spur from a secondary electron, including 1-3 ion pairs and 3-10 excited atoms per 500 nm track length.

Physical phenomena caused by radiation are followed by physicochemical and chemical processes. The electron excitation occurs in the range shorter than $\sim 10^{-10}$ s and vibrational

excitation in the range of 10^{-14} to 10^{-11}. Molecular dissociation takes place in the range of 10^{-14} to 10^{-6} centered to 10^{-10} s. Reactions governed by diffusion take place in the range of $\sim 10^{-10}$ to $\sim 10^{-6}$ s. In a liquid system, it takes an ion pair about 10^{-5} s to separate and become free ions. The time scale of events is presented in Table 1 [5].

Following these primary events, the ions, secondary electrons and excited molecules undergo further transformations, exchanging charges and energy and reacting with surrounding molecules, thereby producing free radicals and other reactive species which finally evolve into new stable products (Fig.5) [6]. The most important chemical reactions are listed in Table 2 [6]. Reactions which lead to biopolymer degradation and microorganism deactivation are of interest from the point of view of process applications for waste processing.

2.1. Microorganism deactivation

Biological effects are the final phenomena following physical and physicochemical reactions which occur in the living cell. There is a big quantitative difference between energy absorbed and its biological effect. A dose of 10 kGy which kills almost all mammalian cells corresponds to an absorption of energy of 10^{-4} J/g in tissue (equivalent to a rise in temperature of 0.002^0C). It is equal to 2×10^6 ionizations per cell (of mass 10^{-9} g). As a cell contains about 10^{13} larger molecules, the proportion of molecules which suffer ionization is very small, it is enough, however, to result in significant damage. This chain of physical events and chemical transformations results in damage to these large molecules, which are essential for the life of a cell. Due to the fact that water represents about 80% of the weight of living organisms, water radiolysis plays the most important role in radiation induced biological effects (Table 3).

The ionization event of water molecule:

$$H_2O \rightarrow H_2O^+ + e^- \qquad (1)$$

is very fast ($<10^{-16}$ s) and the positive ion formed is very unstable and so reacts with water, forming an OH radical and H_3O^+. The electron is liberated with sufficient kinetic energy before its energy falls below the ionization threshold of water (12.61 eV). The electron thereafter loses the rest of its energy by causing vibrational and rotational excitation of the water molecules and, finally, becomes solvated. The solvation process occurs within 10^{-12} s. The excited states dissociate within 10^{-14}-10^{-13} s to form H, OH and H_2. The physical and physicochemical processes are thus completed within 10^{-12} s. The radiolysis products are clustered in spurs and proceed to diffuse out of the spur volume. During this process recombination reactions take place, leading to the formation of molecular secondary radical

products. The spur expansion is complete within 10^{-7} s. The G-values for products of electron water radiolysis are given in Table 4. Highly reactive radicals oxidizing OH and reducing H and e^-_{aq} are formed.

The radiation can have a direct effect on cell molecules by producing lesions in them or an indirect action due to the interaction between the solute molecules and the products of radiolysis.

The direct effect occurs through excitation or ionization of the molecule. These ionized or excited molecules have an excess of energy which can be dissipated either by emission of photons (fluorescence) with return to the initial state or by rupture of a covalent bond and scission of the molecule into two radicals. Scission is more probable after ionization than after excitation because the amount of energy received is greater in the first case. The breakage of a bond does not require the initial physical event to take place on the electron of this bond. The energy absorbed can migrate within the molecule (intramolecular migration) and the breakage often occurs at the site of the weakest bond. The energy absorbed by a molecule can also be transferred to another molecule (intermolecular migration) which thereby suffers the consequence of the attack on the first as though it had itself been directly attacked by radiation.

The indirect effect results from the interaction between the products of radiolysis of water and the molecules contained in the aqueous solutions. The radicals diffuse in the solution and react with the solute molecules producing chemical modifications. For example, for an organic molecule R : H, the following reactions may occur:

a) dehydrogenation followed by hydroxylation by OH radical

$$R : H + OH \rightarrow R + H_2O \quad (2)$$

$$R + OH \rightarrow R : OH \quad (3)$$

b) dehydrogenation by H radicals and formation of new compounds by addition

$$R : H + H \rightarrow R + H_2 \quad (4)$$

$$R + R' \rightarrow R : R' \quad (5)$$

c) opening of double bonds by aqueous electrons followed by the formation of new compounds by addition [7].

The scheme of the radiation effect caused by electrons for a DNA molecule is given in Fig.6. Biologically - induced effects from radiation have been used commercially for sterilization since the late 1950s.

The influence on microorganism content reduction can be presented by the equation:

$$\log\frac{N}{N_0} = -\frac{D}{D_{10}} \tag{6}$$

where: N - number of microorganisms after sterilization, N_0 - initial number, D - dose, D_{10} - dose necessary to reduce the number of microorganisms by a factor of 10.

Radiation sensitivity of some bacteria species is given in Table 3. Aerobic bacteria and some viruses are characterized by high resistance to radiation. In most countries a dose of 25 kGy is the standard for sterilization.

2.2. Polymer degradation

Electron beams are widely used for polymer processing, polymerization, grafting, crosslinking, and degradation. Fig.7 represents doses used for polymer processing. The most important reactions are given in Table 2. As it can be noted from this figure, crosslinking and polymerization are concurrent processes. Crosslinking is dominating over degradation in polyethylene and natural rubber. Degradation is dominating in PFTE, plexiglas and cellulose. Therefore the process can be applied to cellulose waste pretreatment [8].

3. SOLID MATERIALS PROCESSING

The interaction of high energy electron with condensed matter depends on both kinetic energy of the electrons and the atomic composition of processed material. The intensity of absorbed dose first increases and then decreases (Fig.8). The useful "penetration depth" is that at which the dose is equal to that at the surface (Fig.8), which, for electron energies in the range 1-10 MeV, is given by:

$$d \approx \frac{0.4E - 1}{\rho} \tag{7}$$

Where E is the electron energy in MeV, and ρ bulk density in g/cm^3. The thickness of material treated with optimum dose can be enlarged by two-sided irradiation (Fig.9).

The practical thickness of irradiated material, depending on electron energy, for one- and two-sided irradiation is presented in Fig.10 [9].

Mostly, treatment of solid bulk material is performed on the conveyor, however, treatment in pneumatic transport of granulated or grain material has been proposed. This solution enables the application of accelerators with lower electron energy.

In the case of high density materials or required higher depth of penetration, e^-/X conversion can be applied. The structure of the convertor is given in Fig.11 [10].
The conversion factor achieved in the reported case does not exceed 6.1%, however, the penetration range is quite long (Table 4). Application of high power accelerators (150-200 kW) makes this process feasible [11].

4. MUNICIPAL SLUDGES TREATMENT

Sludges from municipal sewage treatment plants contain components usable as soil fertilizer, so if desinfected they can be beneficially recycled in agriculture instead of being discarded as waste.

Municipal sludge contains useful amounts of nitrogen and phosphorus which are usually applied in fertilizers. Additionally, it is a source of organic colloids which contribute to soil aggregate stability and soil structure. Maximum allowable concentration of metals in soils amended with sewage sludge is given in Table 5.

Even if content of heavy metals is low, most of them are contaminated with bacteria, viruses, fungi and parasite eggs. Composting, thermal drying, pasteurization, chlorine desinfection or lime addition are used for the sludge hygenization. Sludge for agricultural use should contain Coli counts $\leq 10^{-2}$, clostridium $\leq 10^{-3}$, salmonella sp. - not observed, ascaris eggs - no organisms capable of breeding. Irradiation with a suitable dose makes the sludge sanitary and usable as a soil fertilizer immediately after treatment.

However, it is the pollutants in sludge which limit its usefulness. Heavy metals are a particular problem because they may be concentrated in sludge and will accumulate in the soil with continued applications. Median metal concentration in sewage of selected countries is given in Table 6.

4.1. Disinfection process

The effect of radiation on bacteria, viruses, parasites and other microorganisms is well known and has been used for for years medical products sterilization [12]. Another well established application of radiation is for food preservation and hygenization [13].

Pilot plant tests for samples of sludges were performed; sludges 1 kg weight 2-3 cm thick and double bagged were irradiated with doses of 5-7 kGy, by electrons with energy 10 MeV using LAE 13/9 accelerator [14]. Total bacteria content, spore forming bacteria content, Coliform counts and *Clostridium perfringens* counts, and the number of parasites and their eggs were determined. Results of the experiments are presented in Tables 7 and 8 [14]. A dose of 6 kGy kills all parasite eggs and decreases total bacteria content by 3 logs, spore forming bacteria and Coliform counts by 2 logs and *Clostridium perfringens* counts by 1 log. It should be noted that all adult parasites were killed too, as they are much more radiosensitive than their eggs. Other work has shown that 2 kGy dose is enough to kill coliforms in sludge [15].

The depth of electron beam penetration depends on electron energy and should be considered during facility design. In the case of a beam energy equal to 2 MeV the thickness of sludges should not exceed 6 mm (Fig.12) [16]. In this case tit was decided that the surface dose 5 kGy.

5. TECHNICAL PROCESS REALIZATION

5.1. Dewatered sludge disinfection

A flowsheet of the proposed process is presented in Fig.13 [17]. The fermented sludge is dewatered on centrifuge and then the layer is formed on the conveyor which transports it under the beam. The installation equipped with a 10 kW power accelerator and 10 MeV beam energy, may treat (with the required dose of 5 kGy) 70 tons of sludge (dewatered) per day.

This amount of sludge orginates from treating the plant with the flow of waste water of 48,000 m^3 per day. The irradiation unit is presented in Fig.14. The main parameters of the installations are:

- constructions area 750 m^2,
- usable area 1150 m^2,
- power installed 300 kW,
- water consumption 0.3 m^3/day,

- manpower 12 persons,
- capital cost, U.S. $ 4 million (1995) [18].

A similar concept is proposed in [19]. The 50 kW power accelerator with electron beam energy 10 MeV can treat sludge after drying to the 65% solids concentration. Mass throughput is 97 tons per day (63 tons dry mass per day) at the dose 5 kGy. A flowsheet for installation is presented in Fig.15. Sludge is dewatered using belt filter press after chemical conditioning (polymer addition). A solids concentration of 20 to 25% can be achieved in this way.

The dewatered sludge cake is conveyed to a mixing building where it is continuously mixed with woodchips at a 1:1 ratio. The woodchips improve porosity for better handling and drying of the sludge. The mixed product is spread for drying and routinely turned to enhance drying. After drying (which depends on weather conditions) the mixture is transferred to a screening pit where woodchips are removed for recycling. The screened product is conveyed to a sterilization facility and eventually bagged for various fertilizer applications.

The design concept is presented in Fig.16. In this case a dried product is fed to the hopper and by airstream conveyor (about 25% of solids by volume) is transported to the process channel in front of the accelerator. The process channel is approximately 5 cm high and 20 cm wide. The product is collected in a second hopper for shipping.

The plant provides employment for 19 people. The capital cost of the sterilization component is about 37% of the total cost of sludge treatment plant. The dewatering system is dominant in the total capital cost.

It should be noted that raw sludge electron treatment improve sludge dewatering [20]. The settled volume is about 50% smaller when treated with the dose 20 kGy (Fig.17).

A continuous flow test facility was operated at Deer Island wastewater treatment plant. The installation was equipped with an ICT type accelerator, 50 kW power and 750 kV electron energy. An irradiation dose of 4 kGy was applied. The scheme of the irradiation unit is presented in Fig.18. The size of an irradiation chamber was 2.4x2.4x3.6 m and concrete shielding was 1.8 m thick. Sludge is transported through disintegrators and vessels in which air oxygen is introduced, then a thin sludge layer (1.8 m wide and 2 mm thick) is irradiated. The velocity under the beam is equal to 2 m/s. The throughput was equal to 380 m^3 per day of sludge, containing 12% dry mass. The irradiation process improves sedimentation and sludge was separated from water in a separator. The cost of treatment was estimated by HVEC as equal to $ 1.5/ton (1980).

Another study has been performed in Germany by AEG-Telefunken. The scheme of the system is presented in Fig.19. The accelerator 1-1.5 MeV was proposed and thickness of the treated layer 3-5 mm. According to the test results, a dose of 2 kGy is equivalent to heat sludge treatment for 30 min at 70^0C. For an accelerator with power 30-150 kW, 300-1500 m^3 sludge per day at 4 kGy may be treated.

The test results have shown a deactivation factor for aerobic bacteria equal to 10^{-4}-10^{-5}. Another advantage of this process is improvement of sedimentation velocity (by a factor of ten).

5.2. Disinfection and composting

In conventional composting, sludge is disinfected by heat which is generated during composting. Composting is induced by microorganisms, however, the high temperatures necessary to kill pathogenic bacteria cause damage to composting bacteria, resulting in longer times to complete composting. Generally, recommended composting time is 10 to 14 days.

In the proposed process [15] pathogenic microorganisms are killed by electron beam, then composting is done in optimum conditions for 2 or 3 days only. The optimum temperature range is 40-50^0C and optimum pH 7-8. It is also necessary to supply oxygen for aerobic fermentation. It has been proposed that the optimum size of granulated sludge is 5 mm. A flow sheet on this proposed process is presented in Fig.20 [16]. The reported test was performed for a pilot plant with a yield of 500 kg/batch. Its composition is given in Table 9. The granulation increased the carbon conversion efficiency and reduced the compositing time (Fig.21) [15].

The compost made from irradiation sludge did not contain coliforms, while in the case of conventional composts, concentrations between 10^2 to 10^4 counts per gram have been reported.

5.3. Agricultural tests

We found that disinfected sludges can be safely used as good soil fertilizer and conditioner. The results of our tests are presented in Table 10. It appears that the yield of tested vegetables enriched with sludges was 50 to 100% higher compared to the yield untreated soil [17]. Similar results were obtained for rice, vegetables, mulberry and flower using compost from irradiated sludge. The flowers (aster) produced larger plants with longer stems [15].

6. CELLULOSE MATERIALS TREATMENT

A large amount of cellulose agricultural wastes or byproducts like sugar cane bagasse, rice straw and palm oil empty fruit bunch are discarded or burned, practice which add to existing serious environmental problems for examples about 3 million tons (dry weight basis) of palm oil empty fruit bunches after fruit stripping are produced in Malaysia per year [20]. Upgrading these wastes into more useful end-products may be a potential solution to increasing demands of food, feed and fuel. Research efforts have been directed to the enzymatic conversion of cellulose to glucose and subsequent fermentation to ethanol. However, the enzymatic hydrolysis of lignocellulosic materials is very slow, mainly due to compositional heterogeneity and structural complexity. The forest biomass contains 40-60% cellulose, 10- 25% hemicellulose, and 13-18% lignin; agricultural wastes contain 30-45% cellulose, 16-29% hemicellulose, and 3-13% lignin [21].

6.1. Radiation treatment of cellulosic agricultural wastes

Gamma irradiation for pasteurization of sugar cane bagasse and rice straw and fermentation were also studied. The initial contamination by fungi and aerobic bacteria was high both in bagasse and straw. Doses of 30 kGy for sterilization and 8 kGy for elimination of fungi were required [22]. In the case of oil palm wastes, doses of 25 kGy and 10 kGy were necessary. The suitable microorganisms used for fermentation increased protein content to 13% and decreased crude fiber content by 20% after 30 days of treatment at 30^0C. The end product was suitable for mushroom cultivation. The scheme for this process is presented in Fig.22 [23]. In all of the above reported tests gamma sources were used for irradiation, however, powerful accelerators may be used to treat properly prepared materials this procedure is reported in the next section.

The combination pretreatment of cellulosic wastes such as corn stalk, cassava bark and peanut husk were studied using chemical methods and irradiation by electron beam [24]; their evaluated the effect of 20% NaOH and irradiation at doses of 100, 300 and 500 kGy on the cellulosic waste by measurement of the glucose yield in enzymatic hydrolysis. Irradiation was carried out with an electron beam machine with beam current 50 mA and electron energy 300 keV. The glucose yield was higher by increasing the irradiation dose and treatment with 2% NaOH, especially in corn stalk; the glucose yield of corn stalk was 20% in untreated samples and increased to 43% after irradiation with electron beam at a dose of 500 kGy and treatment

with 2% NaOH solution. Cassava bark and peanut husk produced glucose yields of only 3.5 and 2.5%, respectively.

It should be noted that electron beam energy applied in this case seems to be too low for solids treatment. This treatment could be considered effective only in the case of enzymatic hydrolysis of corn stalk [24].

6.2. Cellulose wood pulp treatment

Cellulose is a linear polymer consisting of a chain of molecules (Fig.23). The cellulose polymer chain resembles a flat ribbon with hydroxyl groups protruding laterally from its edges and hydrogen atoms oriented above and below. The hydroxyl groups and pyranose ring oxygen can participate in extensive intra-and intermolecular hydrogen bonding. Several layers of these planes of ribbons can stack one upon the other, held in place by Van der Waals forces and hydrogen bonding, forming a highly ordered three-dimensional system with crystal-like properties.

The supramolecular structure of cellulose contains chains packed in both regular or crystalline arrays, as well as in a irregular or amorphous manner (Fig.24). The amount of crystallinity varies depending on the origin, and is in the order of 60 to 70% for wood pulp [25].

The amorphous regions are fully accessible to water and reagents, but the packing of the chains in the crystalline regions is very dense, with no hydroxyl groups accessible. Consequently, these regions are fully unreactive, and therefore drastic conditions and high reagent concentrations are usually required for homogeneous processing of cellulose.

The viscose (rayon) industry uses a process developed at the beginning of this century, to convert cellulose from wood pulp and cotton lint into filament, fiber, cord, casing, and film.

In the viscose process (Fig.25), cellulose wood pulp, usually in the form of thin sheets, is converted into a metastable viscous liquid ("viscose") by reaction with carbon disulfide (CS_2). Cellulose in the viscose is then regenerated in solid form as fiber, filament, cord, casing, or film, through a spinning process.

The main steps of this process are:

- Alkalization-pulp is treated with NaOH [(18-20%) of cellulose weight to form alkali cellulose ($R - OH + NaOH \rightarrow R - O^- Na^+ + H_2O$). This reaction causes the to swell cellulose exposing additional reactive surfaces and changing crystalline lattice structures, making them more reactive; this ensures oxygen solubility which enhances oxygen-caused degradation

and aging. Formed cake is then pressed to remove excess alkali. The pressed cake, which contains about 30 to 35% cellulose and 14 to 16% alkali by weight, is then shredded to maximize its surface area.

- Aging-alkali cellulose is incubated for several hours at temperatures between 40 and 60°C to reduce the degree of polymerization (DP) from 700 to 1200 (this exists in raw cellulose from 250 to 300). The process is caused by oxygen and catalyzed by heavy metal ions. The peroxide intermediates occur in the chain reaction.
- Xanthation-oxygen is removed by evacuation of air or nitrogen flushing and carbon disulfide (28 to 38%) is added to the mixture.
- Esterification occurs ($R - Na^+ + CS_2 \rightarrow R - O - C (=S) - S^- Na^+$). The hydrogen bonding network is destroyed and a fiber-free solution in diluted alkali may be produced.
- Ripening-xanthate is dissolved in diluted alkali to achieve a viscose solution containing 6 to 10% cellulose and 5 to 8% alkali. More homogeneous distribution of xanthate groups along the cellulose chain occurswhich results in decreased viscosity of the mixture.
- Spinning - after filtration the viscose is spun in an acidic bath containing high concentrations of sulfuric acid, sodium sulfate, and zinc sulfate. Cellulose and CS_2 are regenerated. As an effect of this neutralization reaction and some amount of side byproduct H_2S is emitted. Sodium sulfate promotes coagulation of the cellulose by acting as a dehydrating agent, and the removal of water allows the reformation of hydrogen bonds between cellulose chains. Zinc cations help to regulate the rate of coagulation, ensuring sufficient stretchability and proper alignment of the chains.

The end product is used for manufacturing various materials.

It should be mentioned that CS_2 and H_2S, released during spinning, are often emitted in to the atmosphere, which is a tremendous problem due to the high toxicity of CS_2. Several plants have been shut down because they could not solve this emission problem.

New technology utilizing cellulose irradiation has been proposed [26, 27], however. Irradiation of cellulose results in the formation of several different radical species which, through different reaction pathways, lead to disproportionation, hydrogen-abstraction, etc. Reactions may lead to the opening of the glucopyranose ring the production of aldehyde, keto or acid groups, formation of smaller chain sugars, chain cleavage, and the elimination of water, carbon monoxide and hydrogen. The DP of cellulose is reduced and its reactivity increases due to the effects of the radiolytic products. The crystalline lattice is partly destructed, making it more accessible to chemical reagents.

Irradiation by electron beam leads to DP reduction. The degree of DP reduction depends on the dose (Fig.26) [27]. Such treatment can replace the aging step necessary in conventional technology. Increased cellulose reactivity resulting from irradiation reduces the demand for alkali (by approx. 16%) and for CS_2 (by 25 to 50%). Filtration parameters are improved as well (Fig.27) [27]. This modified process for viscose production is presented in Fig.28.

Big savings in chemicals used can be achieved and apart from this, the process is beneficial for the environment. CS_2 and H_2S emission (or cost of pollution control) are reduced remarkably.

7. SANITARY WASTE TREATMENT

Hospital waste disposal is becoming a problem of increasing importance in many countries. In Italy the yearly hospital waste production is about 250,000 tons and only 60,000 tons are treated by incineration at present [28]. The remaining wastes could be landfilled as municipal refuse if first submitted to suitable sterilization. The production rate of HW (hospital waste) is estimated as ranging from 0.5 to 3.0 kg/day/bed. The fraction attributate to solid municipal refuse is around 50-60% of the total amount. HW requires sterilization treatment instead of a disinfection or sanitation treatment.

Sterilization can be achieved by thermal (incineration, autoclave, steam/microwaves) or physicochemical (chemical agents, irradiation) processes. Incineration processes inside the hospital is being licensed if the minimum throughput is 100 t/day (Italy). In the case of eb process dose 25 to 35 kGy is needed for sterilization and 10 kGy for sanitation.

In the reported work [28] the eb treatment has been compared with mw (microwaves) treatment. The eb is economically advantageous if throughput is bigger then 0.25 ton/h.

A incinerator for biological waste based on the electron accelerator is proposed in [19]. The block scheme is given in Fig.29 and arrangement of the incinerator chamber in Fig.30. An accelerator with electron beam current 70 mA and energy 800 keV was used in these experiments. A utilization time reduction and better energy efficiency were demonstrated in this system in comparison to standard small incinerators (gas or oil fired) [29].

8. CONCLUSION

The growing need for waste recycling has opened new opportunities for electron beam technologies. Already investigated technologies have proven such opportunities (e.g. sludge hygenization, cellulose waste treatment, hospital waste treatment), however, there are other possible areas of application. Due to the high density of materials, treatment accelerators with high energy or new methods of processing (pneumatic transport flow, fluidized bed) need to be investigated. Conversion e^-/X opens new opportunites as well, however, high power accelerators should be used for such purposes due to the low conversion factor.

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Table 1. Interaction between radiation and matter with time.

-log t (sec)	Phenomena	Process
18	A high-energy electron passes through a molecule	
17	Transfer of energy from high-energy secondary electron	
16	Energy transfer through electronic excitation (vibration held)	
14	Fast reaction of ion and molecule including the transfer of atom H, molecular vibration, fast dissociation	
12	Thermalization of electron, time scale of self-diffusion in low molecular liquid	
11	Dielectric relaxation of water, neutralization in polar medium	
10	Production of spur	
9	Reaction within spur	
8	Reaction within track	
7	Neutralization time in liquid of low viscosity and high dielectric constant	
6		
4		
3	Decay time of solvated electron in a system of low viscosity and high dielectric constant	
0	Life of triplet state	
-2	Neutralization time in medium of high viscosity and low dielectric constant	
-4		

Table 2. Chemical reactions induced by ionizing radiations [5, 6].

Primary Reactions
The symbol AB* denotes an excited molecule, AB+ is a positive ion and e^- is a free secondary electron

$$AB \xrightarrow{rad} AB^*$$
Molecular Excitation by Energy Absorption

$$AB \xrightarrow{rad} AB^+ + e^-$$
Molecular Ionization by Energy Absorption

Secondary Reactions
The symbols A• and B• denote free radicals while C and D are stable molecules

$$AB^+ + e^- \longrightarrow AB^*$$
Molecular Excitation by Ion-Electron Recombination

$$AB^* \longrightarrow A\bullet + B\bullet$$
$$AB^+ \longrightarrow A^+\bullet + B\bullet$$
Free Radical Formation by Molecular Dissociation

$$A\bullet + BR \longrightarrow AR + B\bullet$$
Free Radical Abstraction

$$A\bullet + C \longrightarrow AC\bullet$$
$$AC\bullet + C \longrightarrow ACC\bullet$$
Free Radical Propagation by Addition

$$A\bullet + B\bullet \longrightarrow AB$$
Stable Product Formation by Recombination of Radicals

$$CH\bullet + DH\bullet \longrightarrow CH_2 + D$$
Stable Product Formation by Hydrogen Transfer

$$AB^* \longrightarrow C + D$$
$$AB^+ \longrightarrow C^+ + D$$
Stable Product Formation by Molecular Dissociation

$$Solvent + e^- \longrightarrow e^-_{sol}$$
Formation of Solvated Electrons in Liquid Media

$$AB + e^- \longrightarrow AB^-$$
Negative Ion Formation by Electron Attachment

$$C^+ + D^- \longrightarrow C + D$$
Stable Product Formation by Ion-Ion Neutralization

Table 3. Radiosensitivity of bacterias.

Microorganisms	Dose D_{10} [krad]
Bacteria	
Pseudomonas aeruginosa	2.9
Escherichia coli	8.5
Aerobacter aerogenes	5.6
Klebsiella pneumoniae	24.0
Salmonella paratyphi B*	19.0
Bacteria	
Micrococcus pyogenes var. aureus	18.0
Sarcina lutea	89.0
Diploccus pneumoniae	52.0
Dtreptococcus pyogenes	32.0
Corynebacterium acnes	29.0
Aerobic bacteria (spore)	
Bacillus globigii	120.0
B. subtillis	170-250
B. pumilus	170-330
B. stearothermophilus	210.0
Anaerobic bacteria (spores)	
Clostridium novyi	220.0
Cl. Welchii	270.0
Cl. botulinum*	130-340

irradiated medium * - phosphate buffer, others - paper tape.

Table 4. Penetration ranges of accelerated electrons and X-rays in products of different density.

Product density (g/cc)	Electron beam 10 MeV (cm)		X-rays 5 MeV (cm)	
	one-side	two-side	one-side	two-side
1.00	3.8	8.0	11.3	30.0
0.73	4.9	10.9	15.1	41.0
0.40	8.8	20.0	28.3	75.0
0.25	14.0	32.0	45.2	120.0
0.15	23.3	53.3	75.3	200.0

Table 5. Maximum allowable concentrations of heavy metals in soils for the EU, the US and Poland.

Element	Maximum allowable concentration in soil (mg/kg)		
	EU	USA	Poland
Cd	1-3	20	5
Cu	50-140	750	100
Cr	100-150	1500	100
Hg	1-1.5	8	-
Ni	30-75	210	100
Pb	50-300	150	100
Zn	150-300	1400	300

Table 6. Median metal concentration in sewage in some countries.

Element	Median (50%) metal concentration (mg/kg DM)	
	GB	Poland
Cd	3.2	20
Cu	473	370
Cr	86	730
Pb	217	370
Hg	3.2	-
Ni	37	120
Zn	889	3500

Table 7. Bacteria content in dewatered sludges (35% of dry matter).

Bacteria	Dose (kGy)[1)]			
	0	5.0	6.0	7.0
Total bacteria content (in 1 ml)	1.1×10^9	2.7×10^7	6.5×10^6	1.1×10^5
Spore-forming bacteria (in 1 ml)	4.1×10^6	1.4×10^5	9.3×10^4	-
Coliform counts	10^{-5}	10^{-5}	10^{-3}	10^{-2}
Clostridum perfringens counts	10^{-4}	10^{-4}	10^{-3}	10^{-2}

[1)] 1 kGy = 1 kJ/kg.

Table 8. Parasite eggs content in dewatered sludges (35% of dry matter).

Dose (kGy)	Living eggs (number/kg dry matter)			
	Ascaris sp. (A)	Trichuris sp. (T)	Toxacara sp. (T)	Total (ATT)
0	90	90	60	240
5.0	30	0	0	30
6.0	0	0	0	0
7.0	0	0	0	0

Table 9. Sludge cake composition.

	Mean value	Range
Moisture content	75.2%	68.3-78.3%
VTS	75.7%	57.6-81.8%
T-C	38.8%	31.0-44.0%
T-N	4.14%	2.52-4.95%
BOD	250 mg/g	204-303 mg/g
pH	6.10	5.40-8.00
Conductivity	1240 s/cm	540-1950 s/cm
NH_4-N	1.56%	0.36-3.02%
$N0_3$-N	0	0
$N0_2$-N	0.36%	0-0.80%
P	1.75%	0.61-3.13%
K	0.33%	0.16-0.58%
Ca	1.07%	0.20-1.83%
Calorific value	3.930 kcal/kg	2.980-4.330 kcal/kg

Table 10. The influence of sludge addition on the yield of vegetables in pot tests.

Medium	Yield (g)[1)]		
	Radish	Lecttuce	Dill
Soil only	61	121	44
Soil + unirradiated sludge [2)]	107	189	108
Soil + irradiated (6 kGy) sludges [2)]	96	172	95

[1)] weight of vegetables grown from the same number of seeds sown in each medium.
[2)] 10 tons of sludges (as dry matter) per acre.

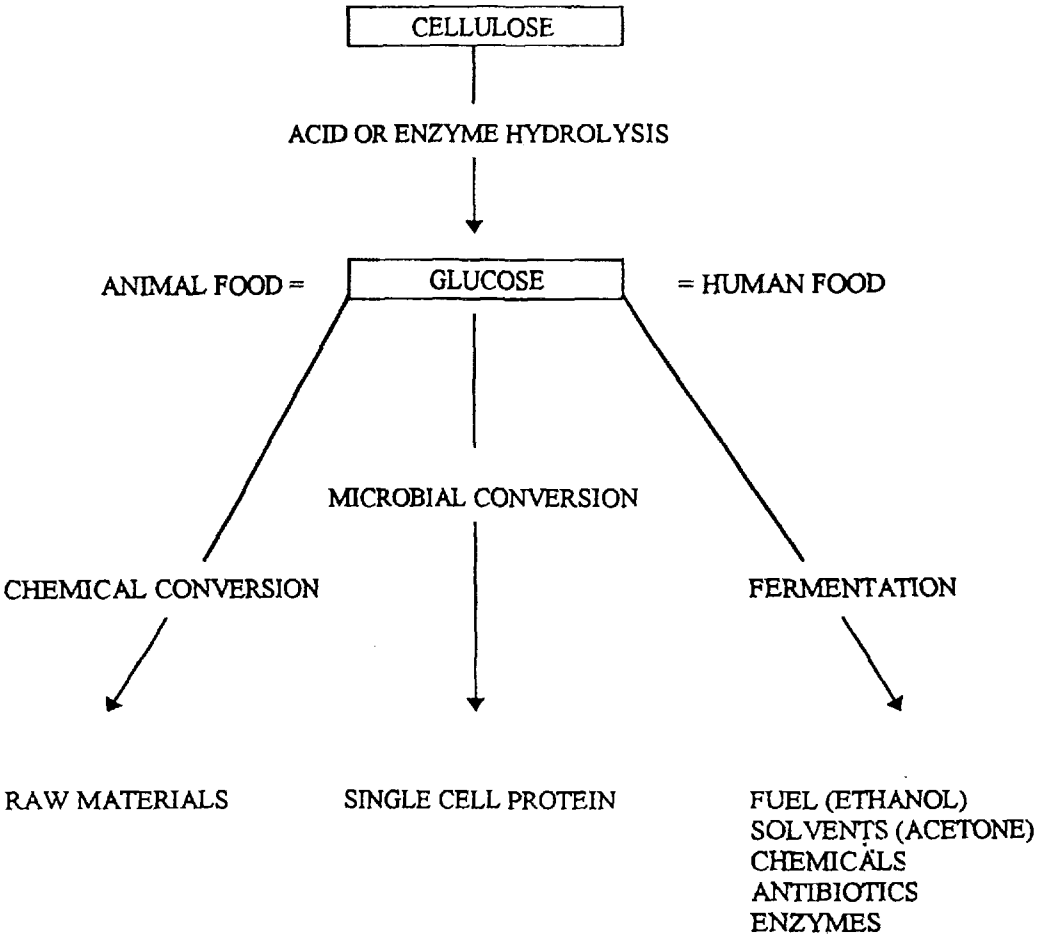

Fig. 1. Waste cellulose utilization routes [3].
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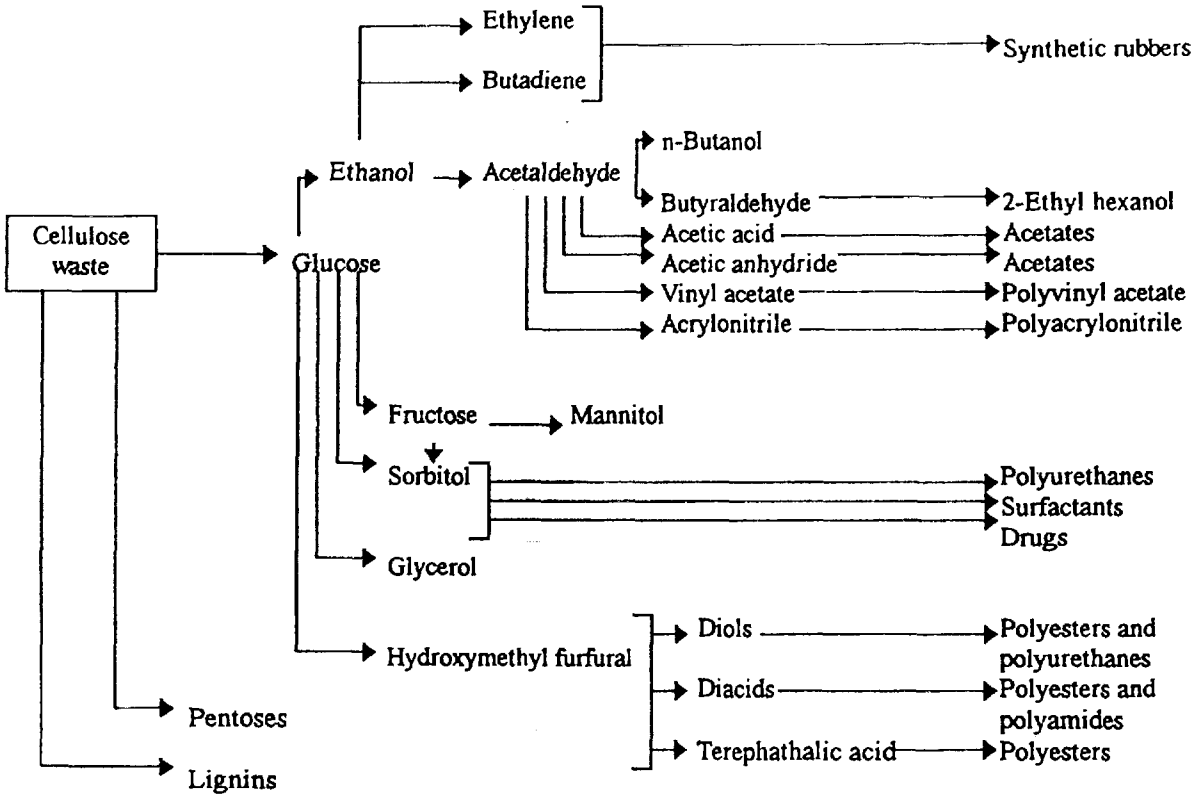

Fig.2. Possible routes to petrochemicals from cellulosic wastes [3].
(Source as Fig.1)

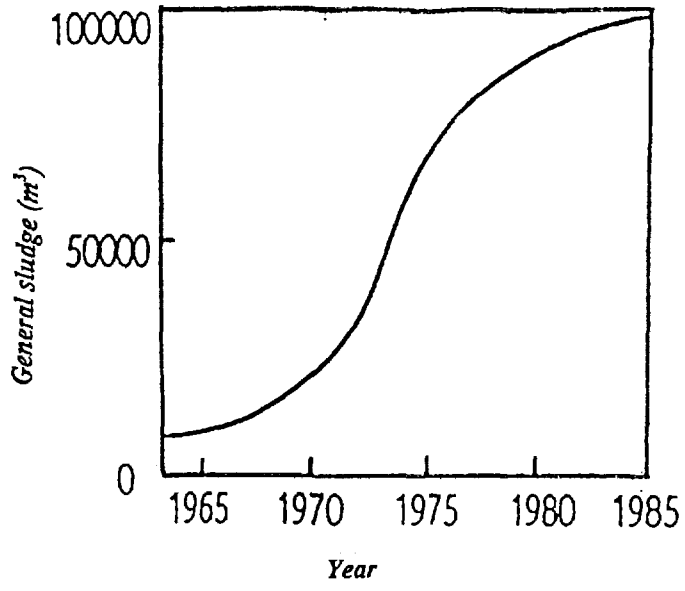

Fig.3. Amount of sludge generated in Tokyo [4].
(Reprinted from Radiation Physics and Chemistry, Vol.35(1-3), T. Sawai et al, Improvement of sedimentation and dewatering of municipal sludge by irradiation, 465-468, Copyright 1990, with kind permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington OX5 1GB, UK).

Fig.4. Track of the fast electron.

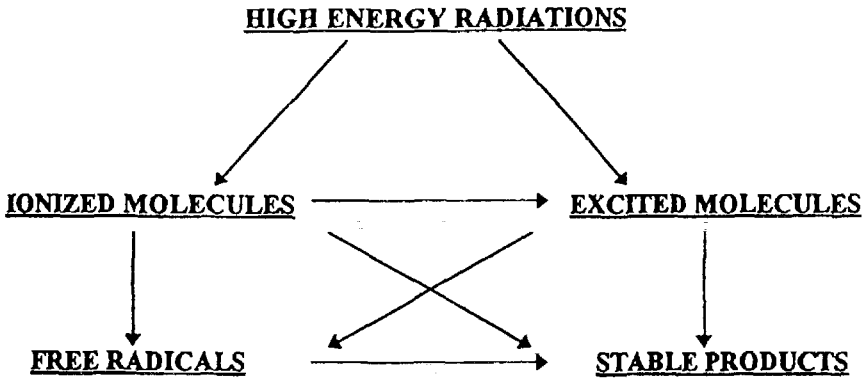

Fig.5. Radiation induced processes [6].

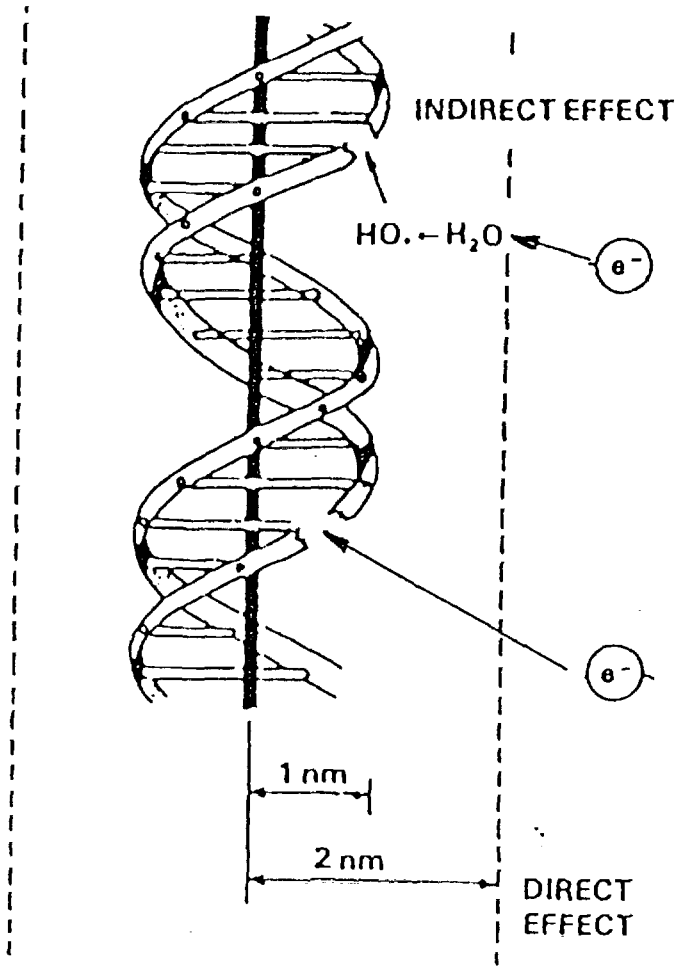

Fig.6. Radiation effects caused by electrons to DNA molecule.

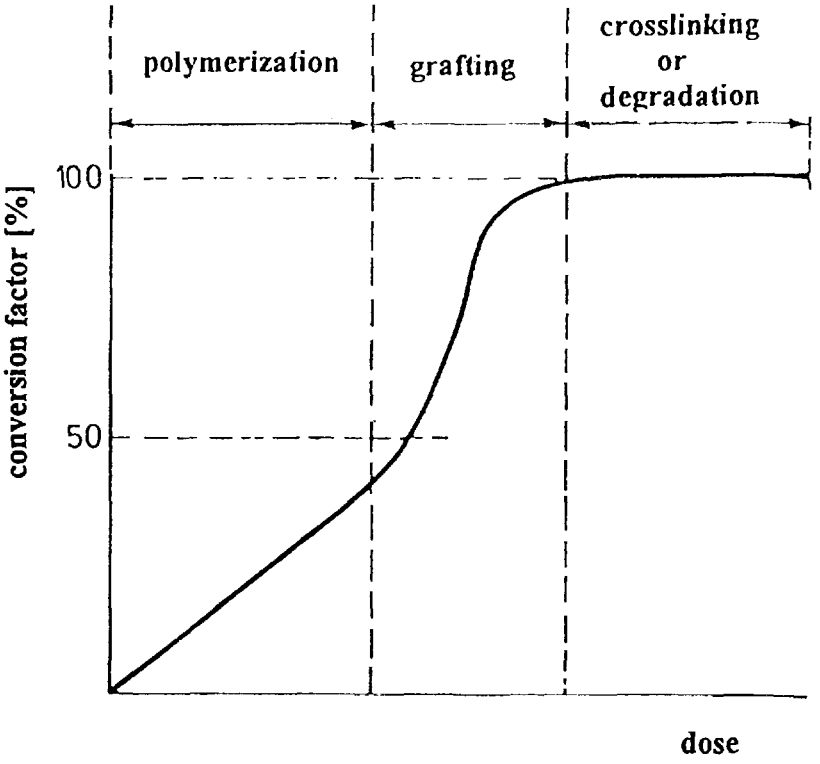

Fig.7. Dose ranges for polymer processing.

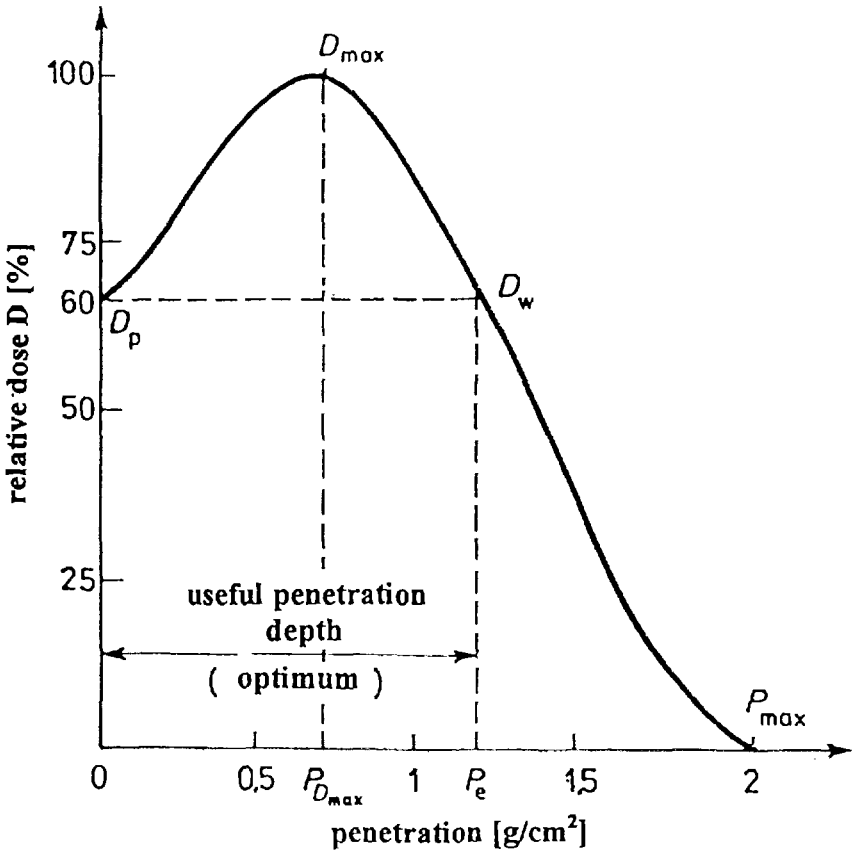

Fig.8. Absorbed dose vs. material thickness.

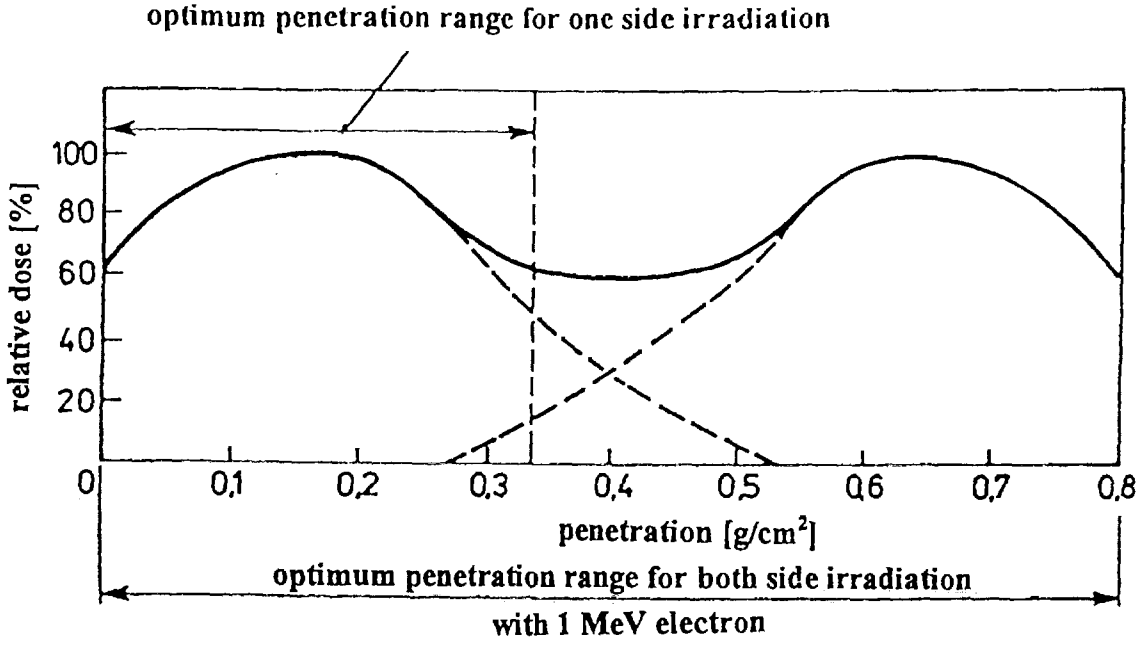

Fig.9. Two side material irradiation.

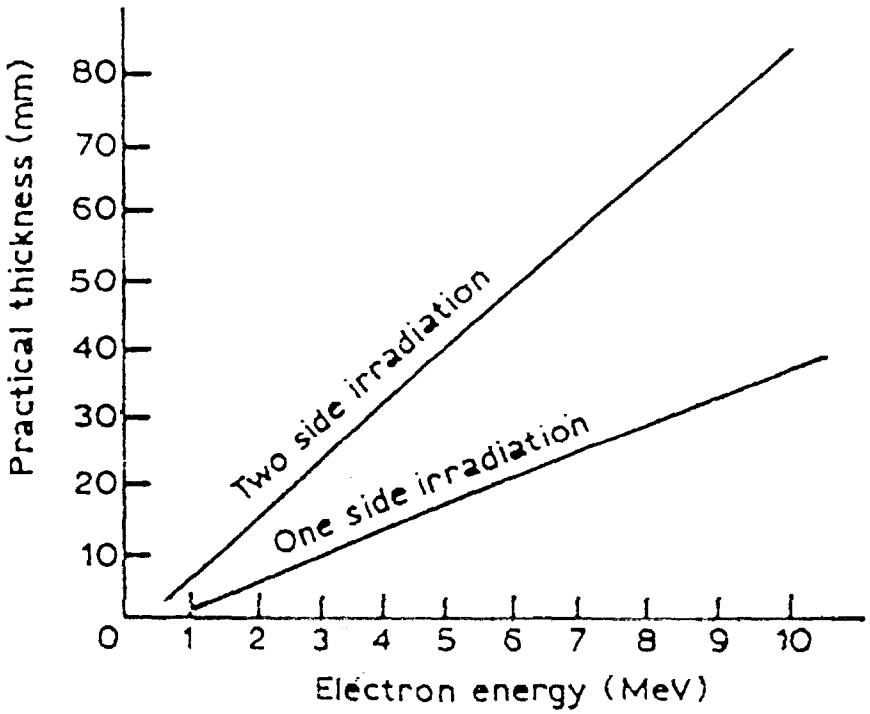

Fig.10. Practical thickness vs. electron energy. (Bulk density = 1).

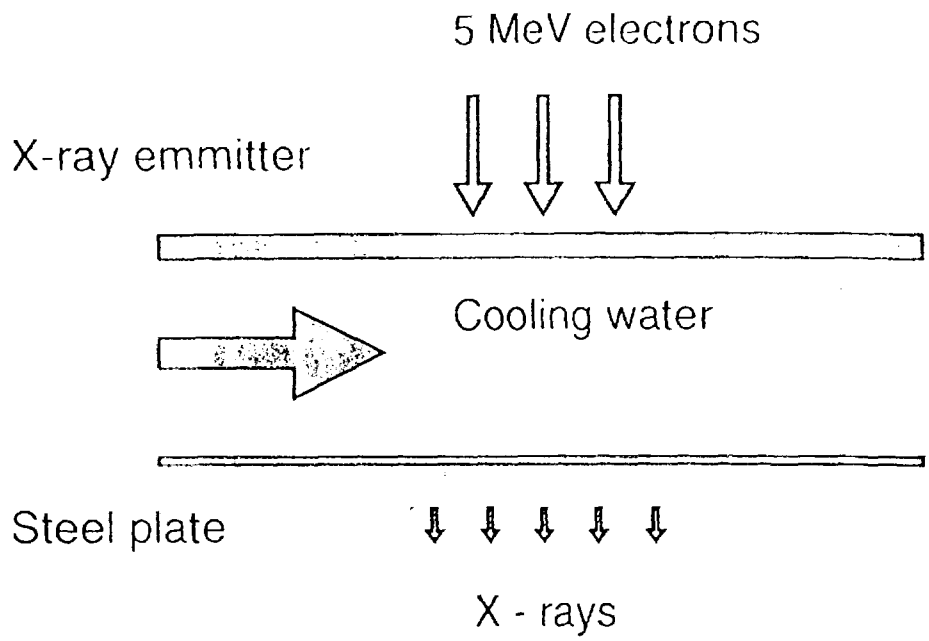

Fig. 11. Structure of e⁻/X converter.

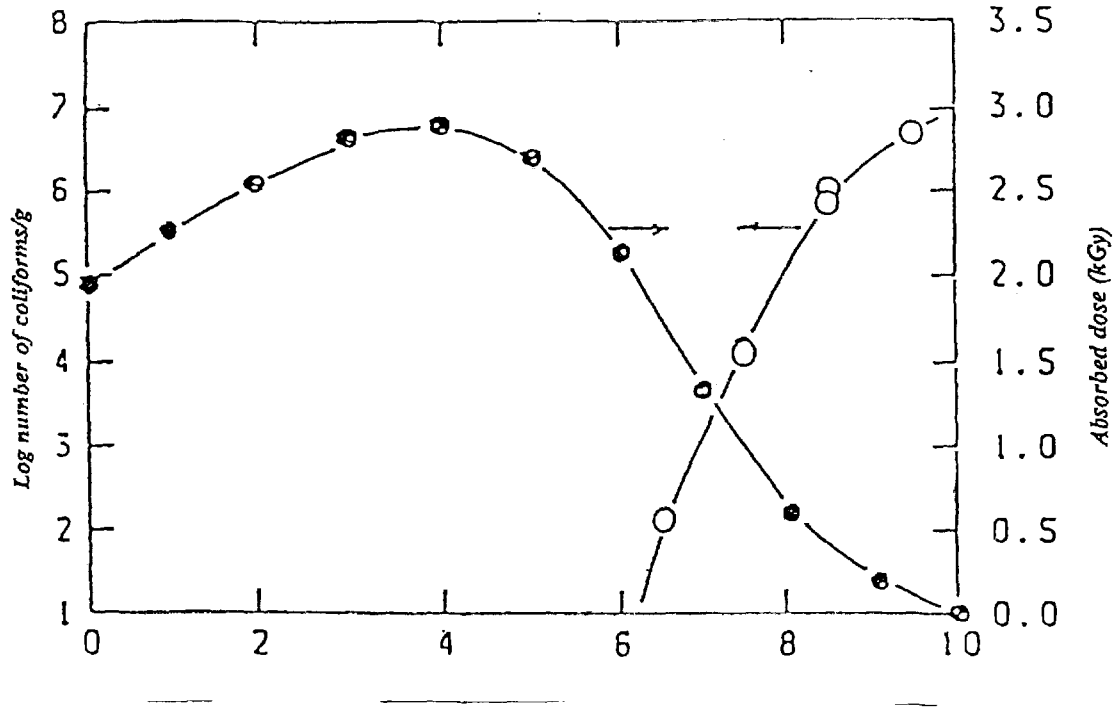

Fig. 12. Distribution of absorbed dose and coliforms in the irradiated cake [16].

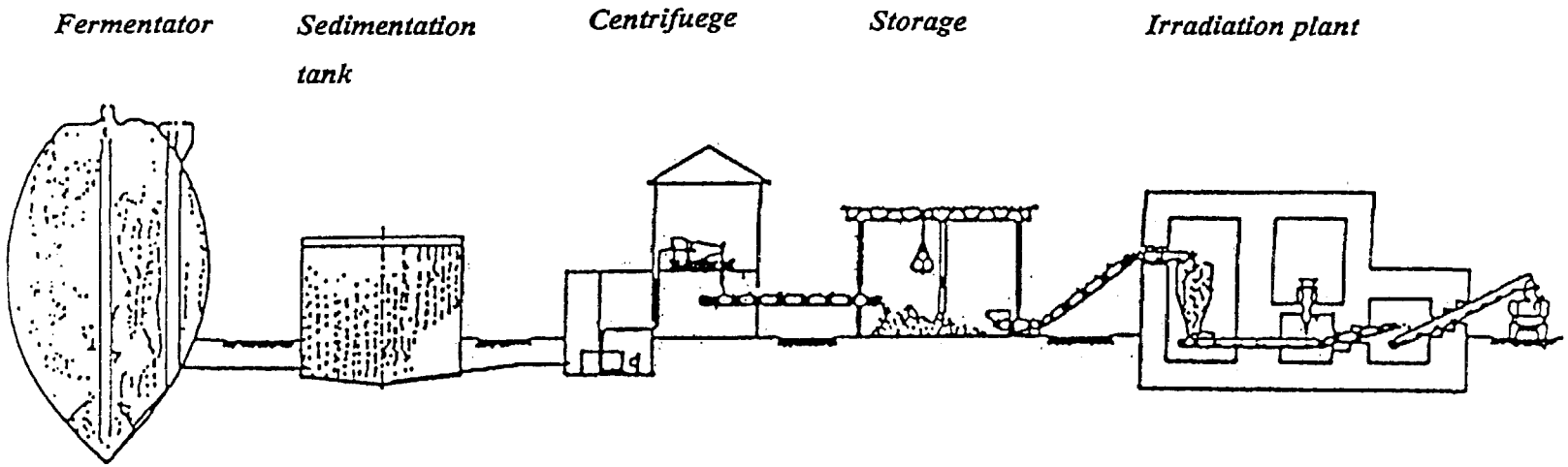

Fig. 13. Flowsheet of sludge disinfection plant [17].

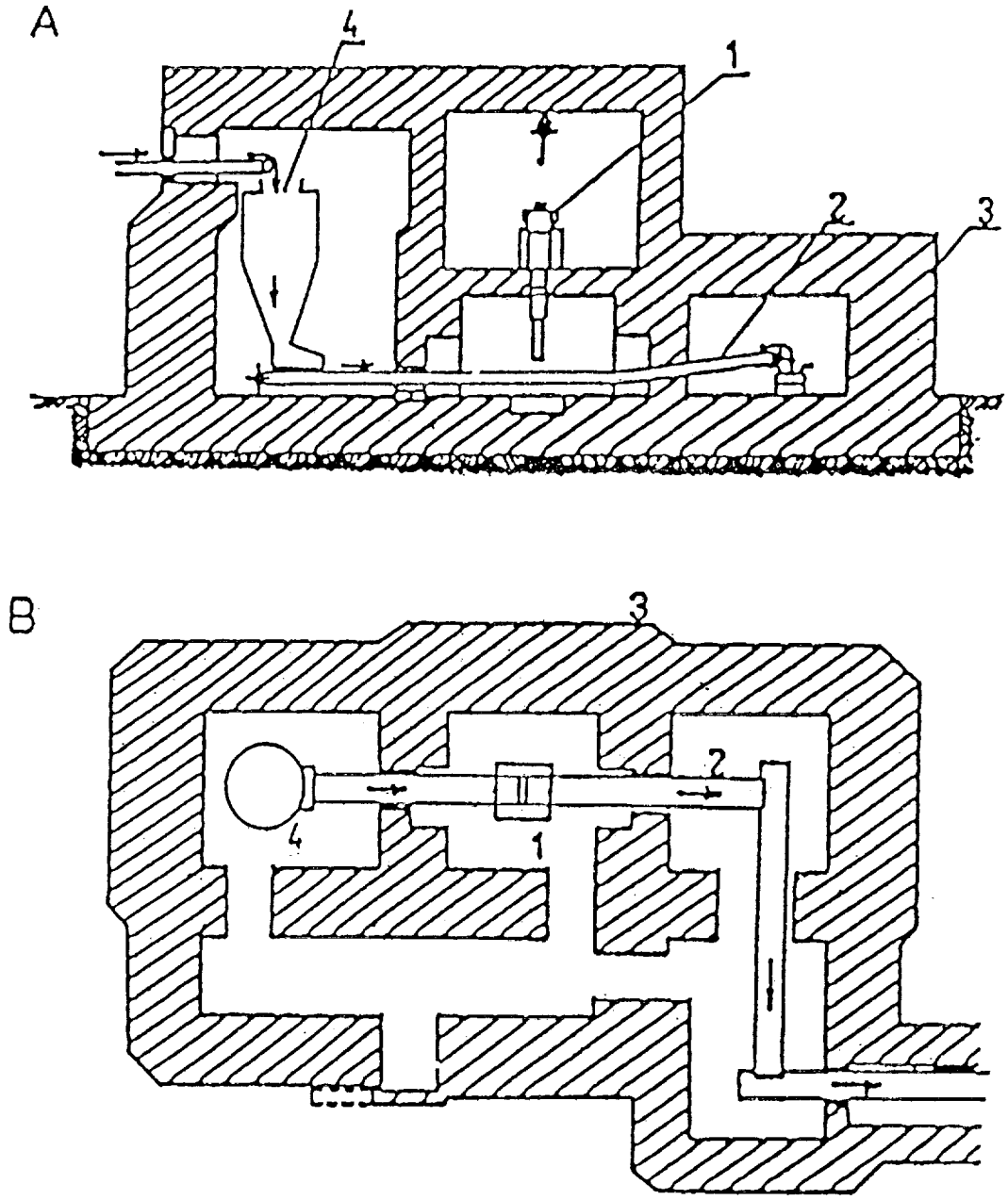

Fig. 14. Sludge irradiation facility [18]: 1 - accelerator, 2 - conveyer, 3 - shielding, 4 - tank.

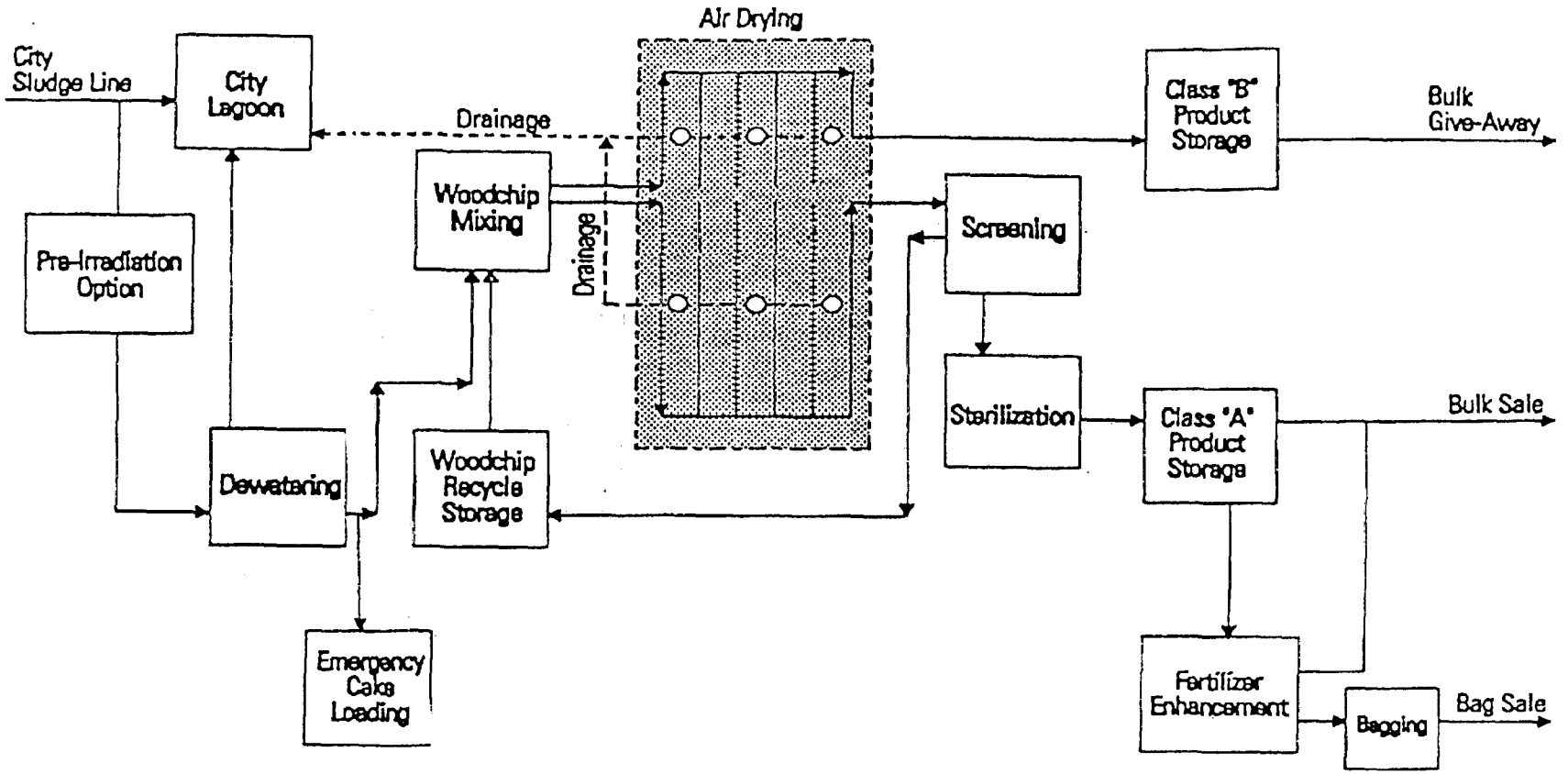

Fig. 15. Flowsheet of sludge treatment facility [19].

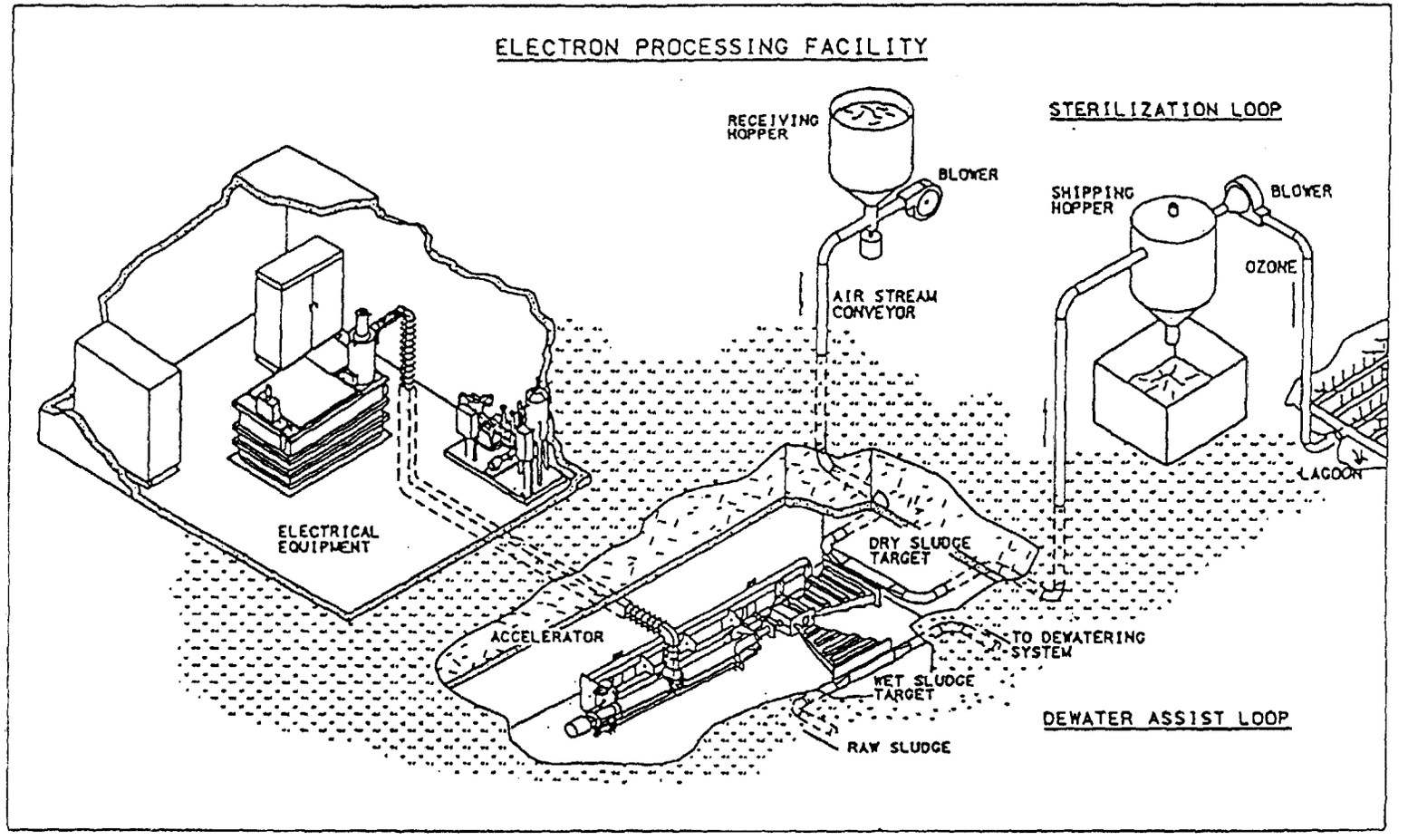

Fig. 16. Design concept of electron beam plant [19].
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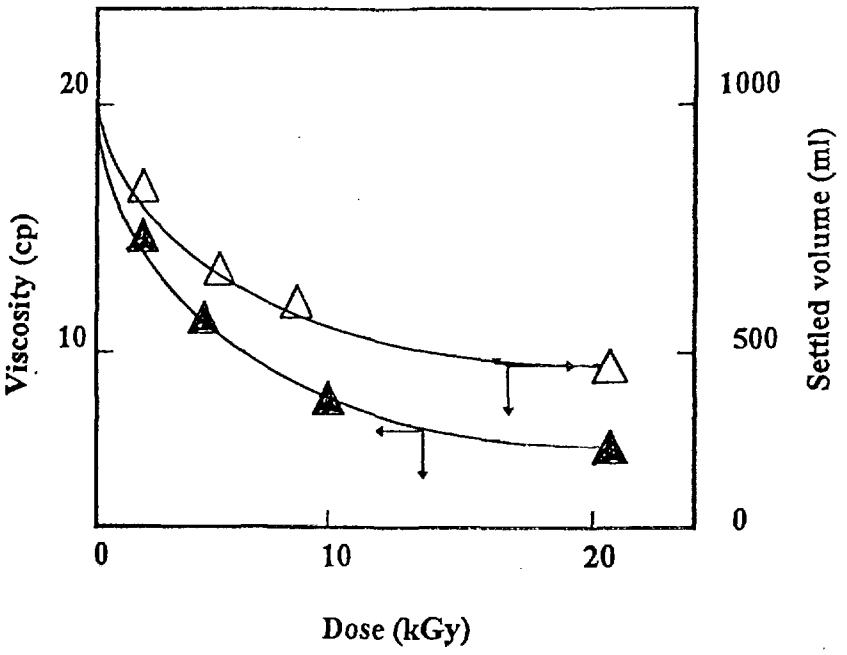

Fig.17. Sludge settling parameters after irradiation [20].
(Source as in Fig.3)

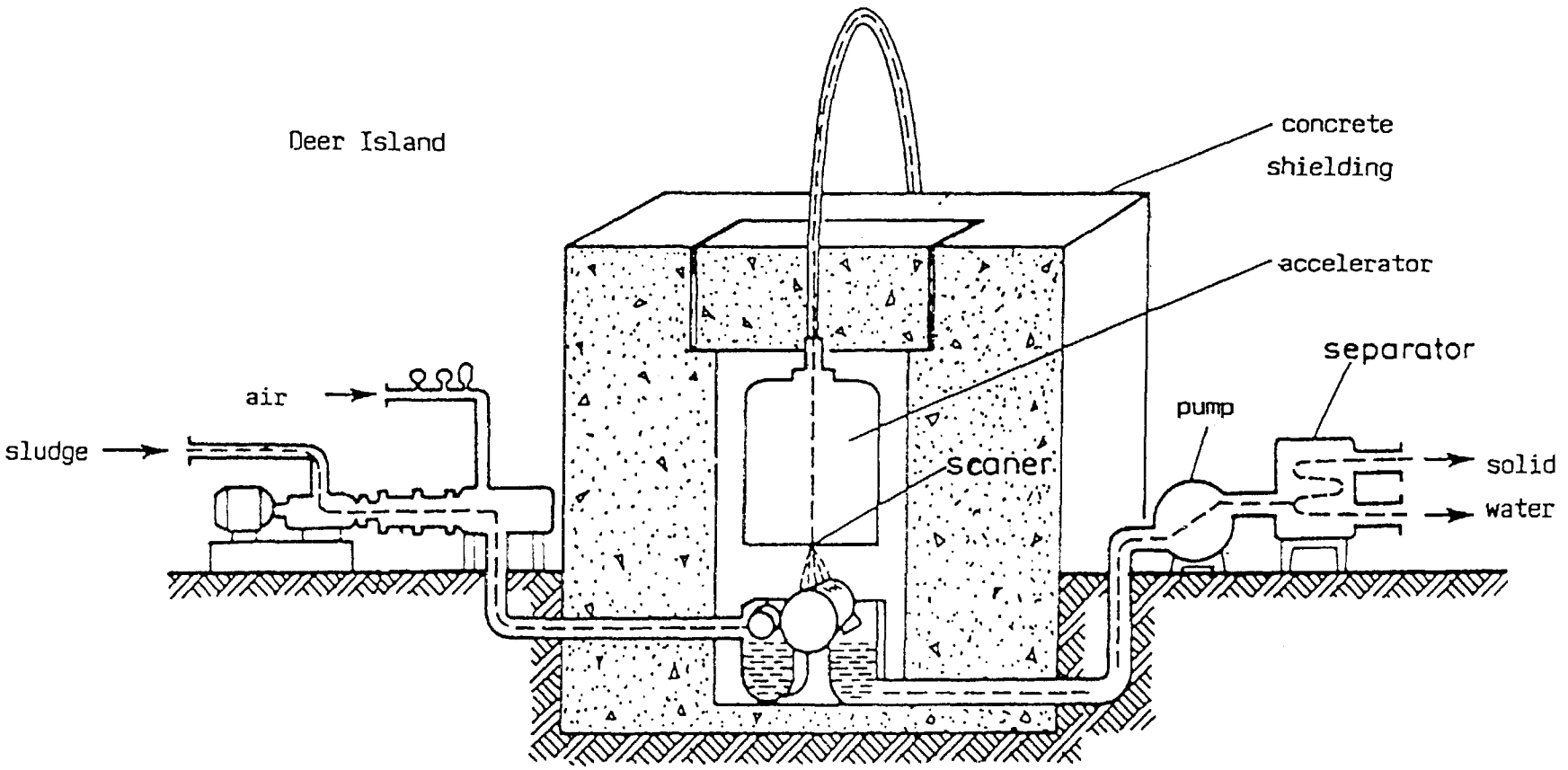

Fig. 18. Sludge irradiation facility at Deer Island wastewater treatment plant.

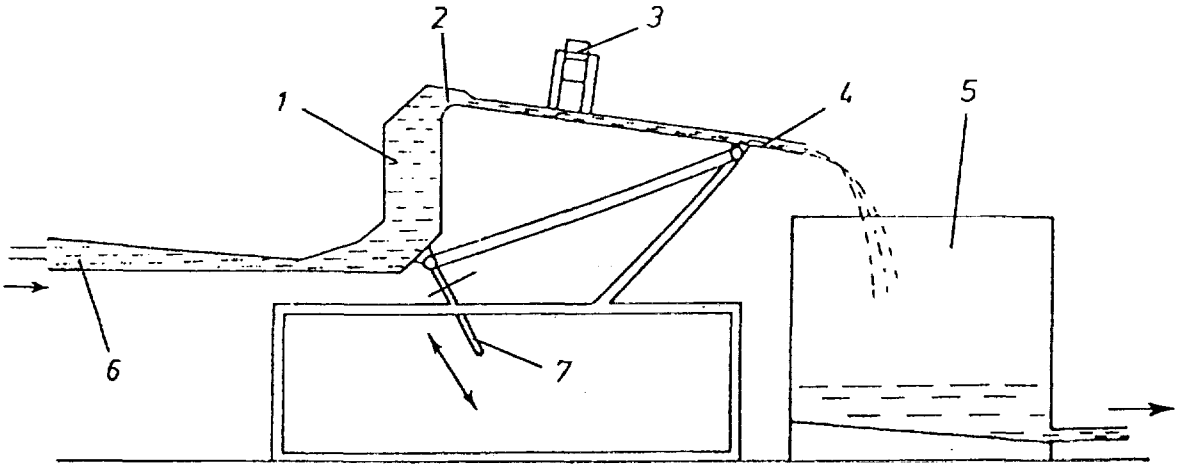

Fig. 19. Sludge irradiation system.

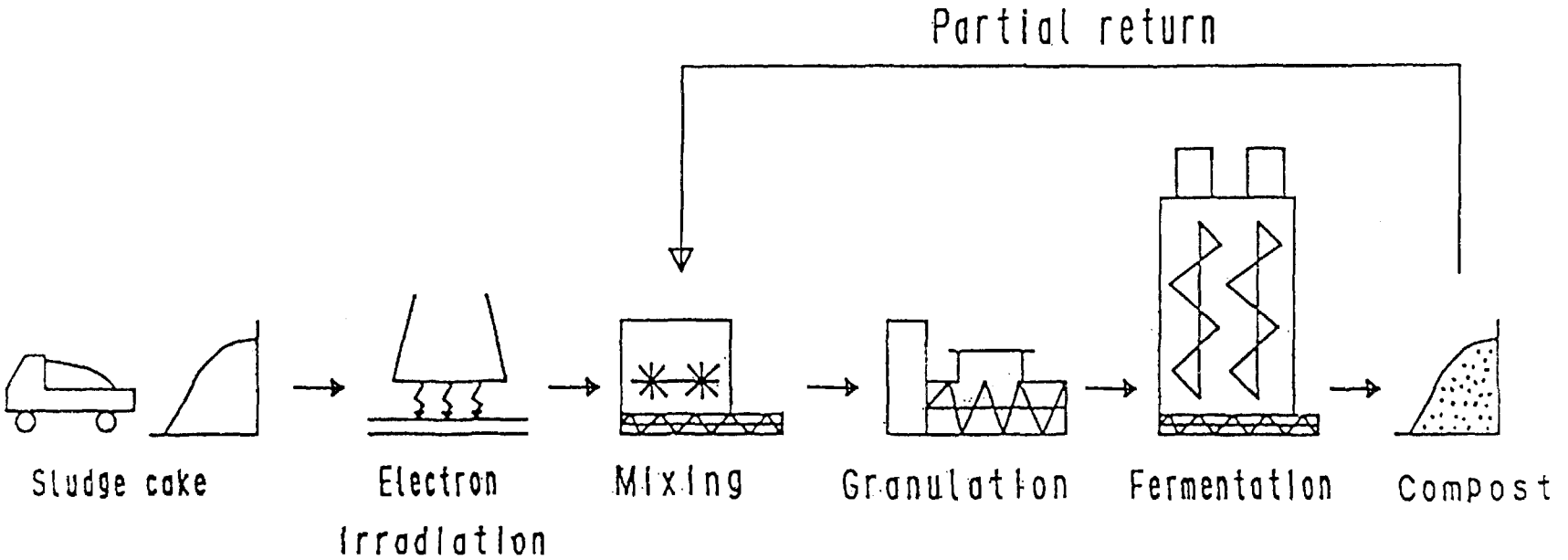

Fig.20. Flowsheet of sludge irradiation and composting [15].

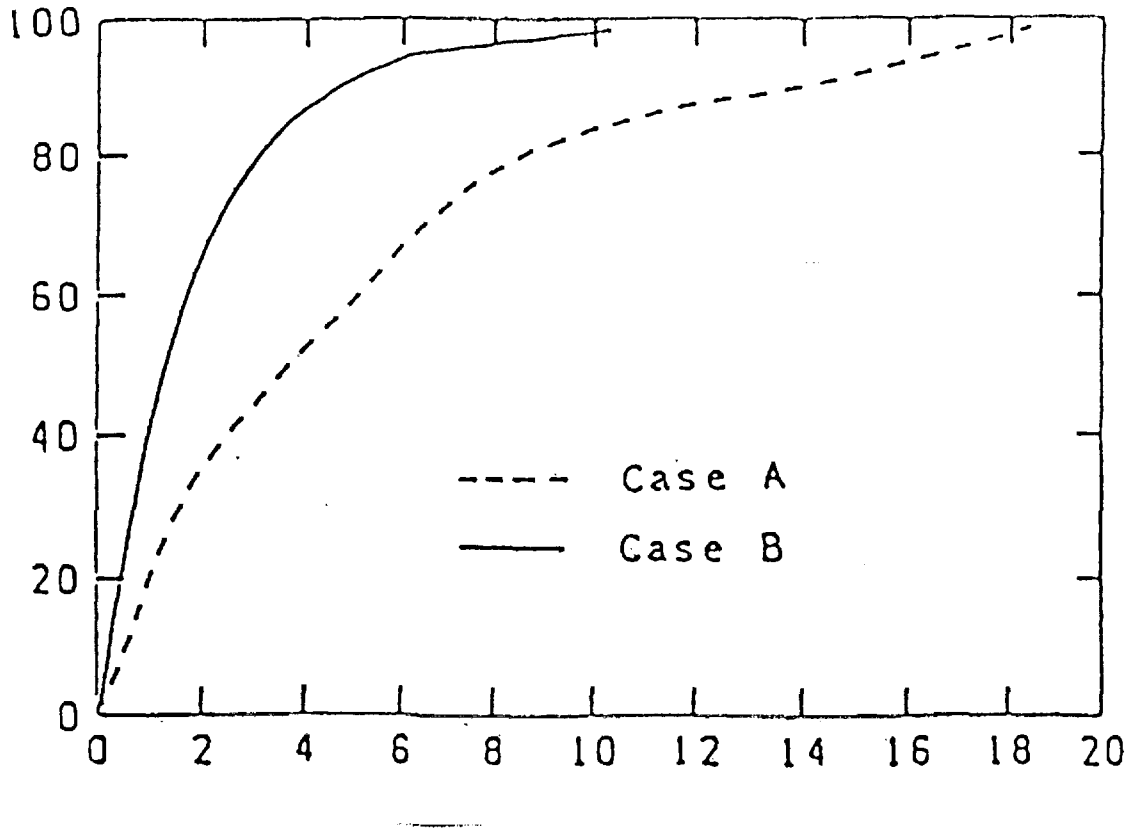

Fig.21. Relative carbon conversion [15]:
A - unirradiated (fermented for 2 days at 65°C),
B - irradiated (granulated 7 mm, fermentation 40-50°C).

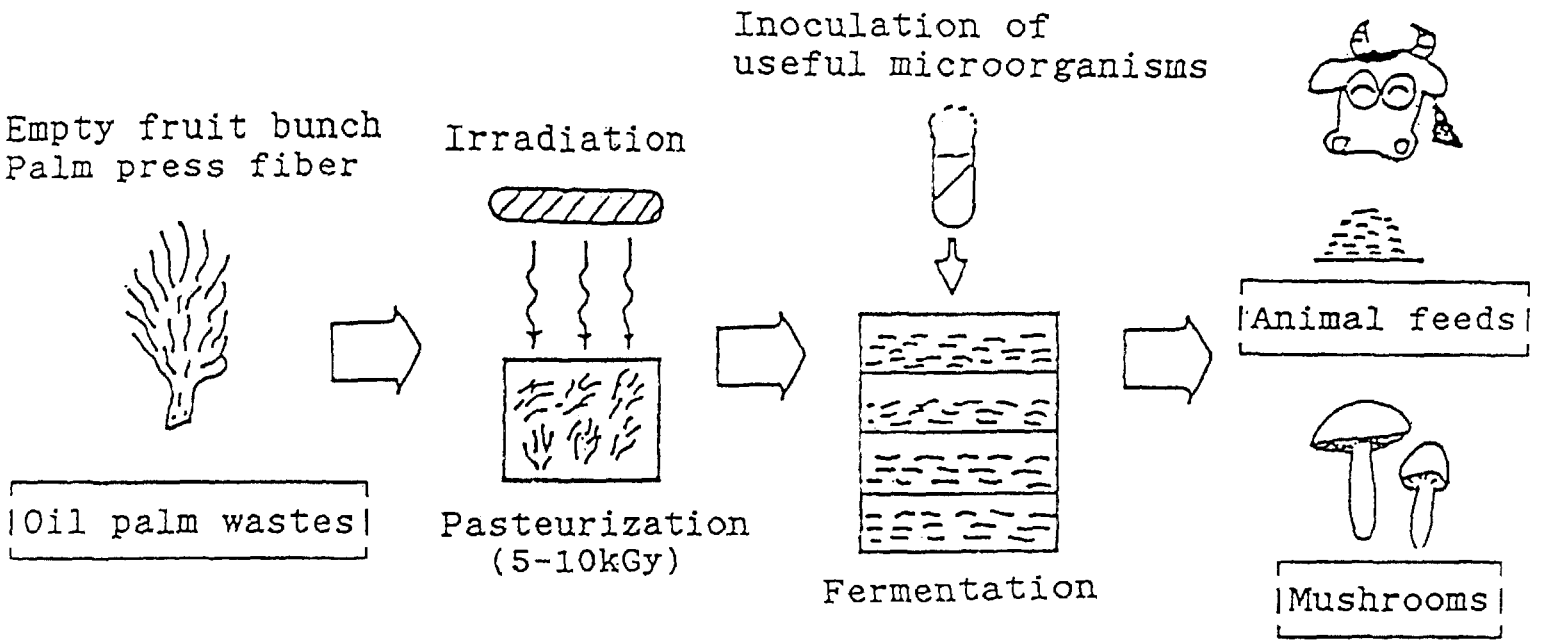

Fig.22. Upgranding of oil palm wastes by irradiation [23].

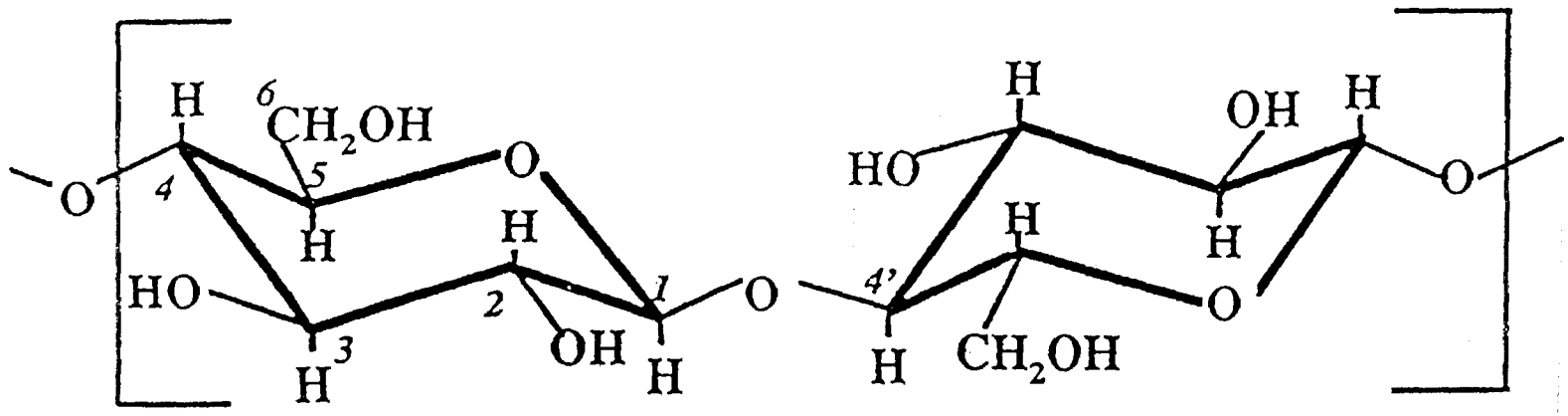

Fig.23. Cellulose chain.

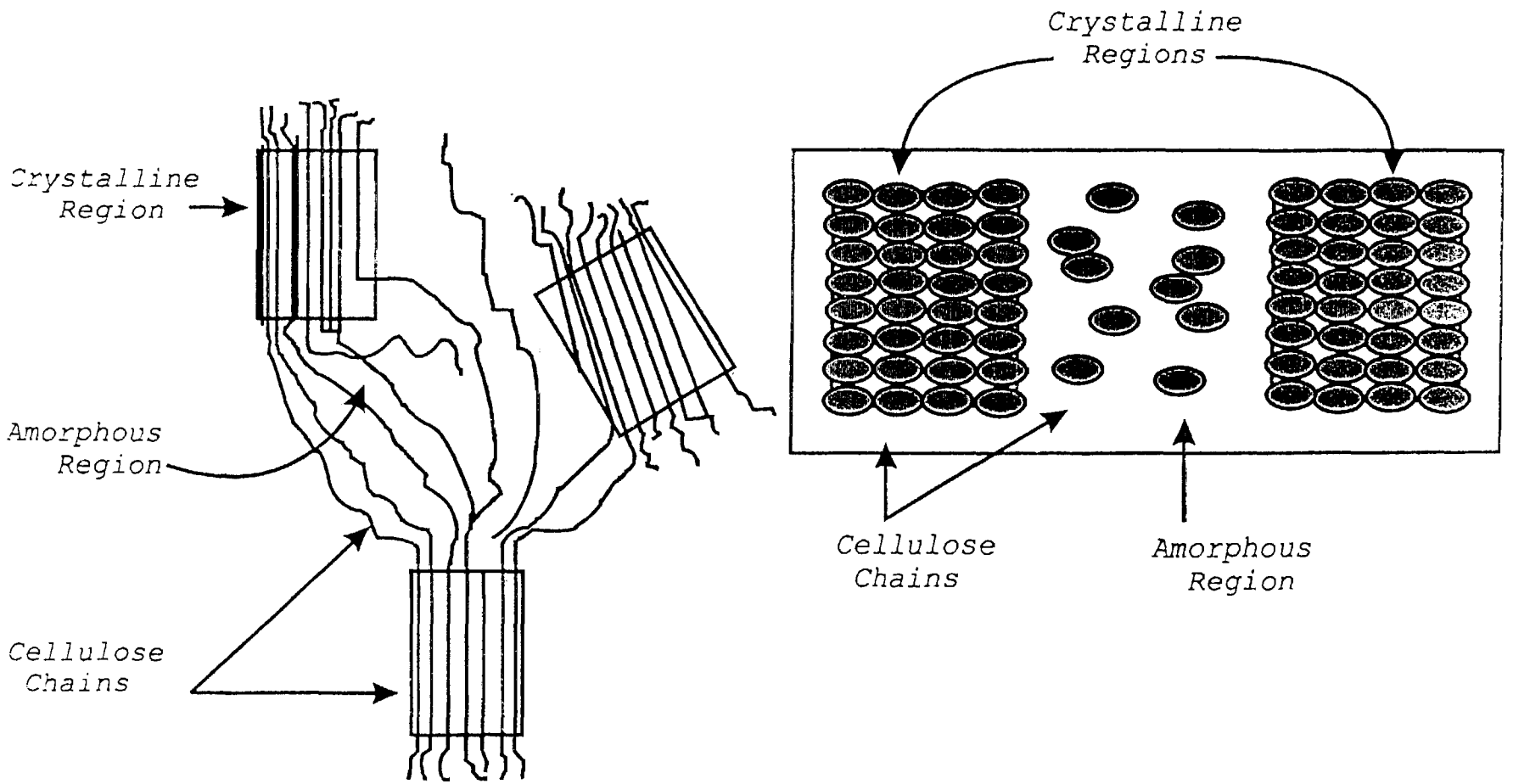

Fig.24. Cellulose structure [25].

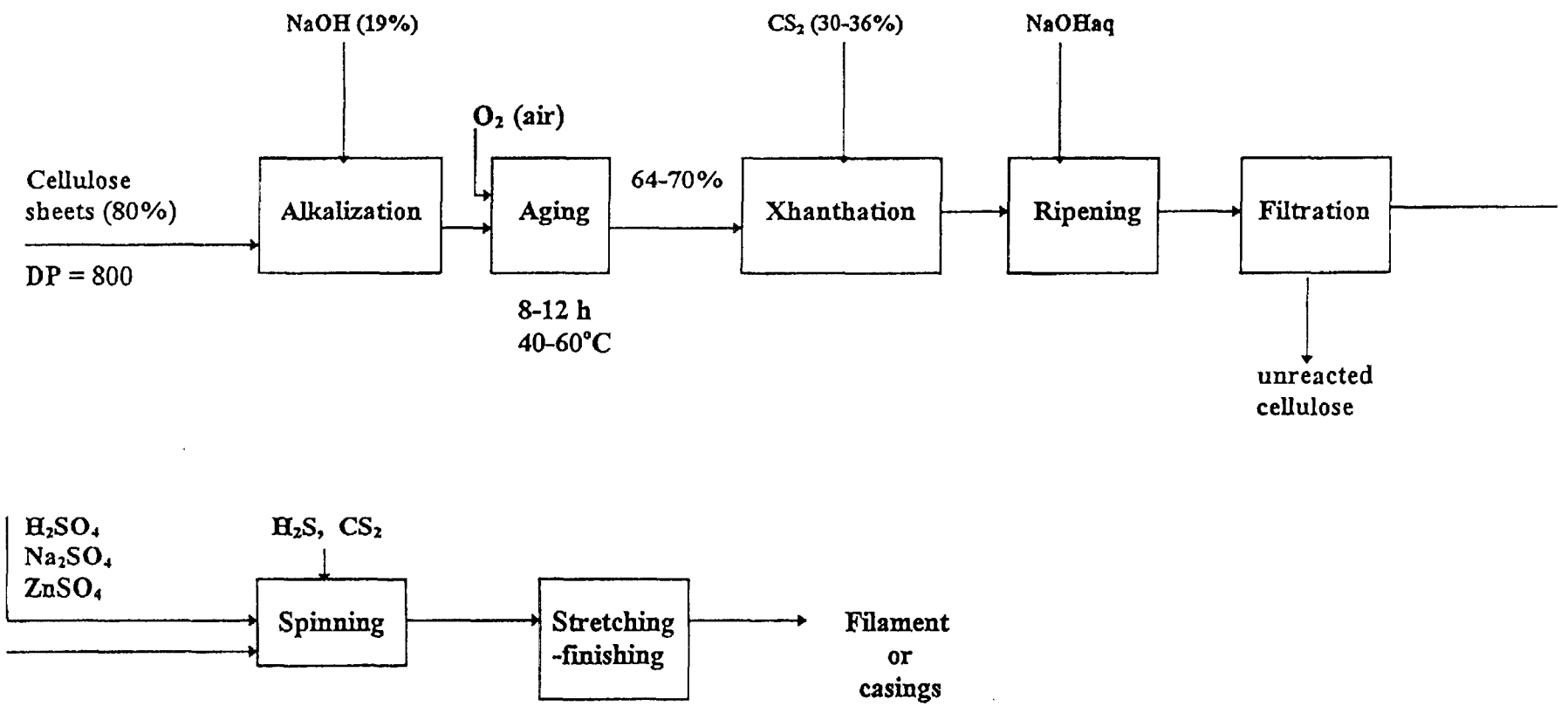

Fig.25. Viscose manufacturing process - conventional.

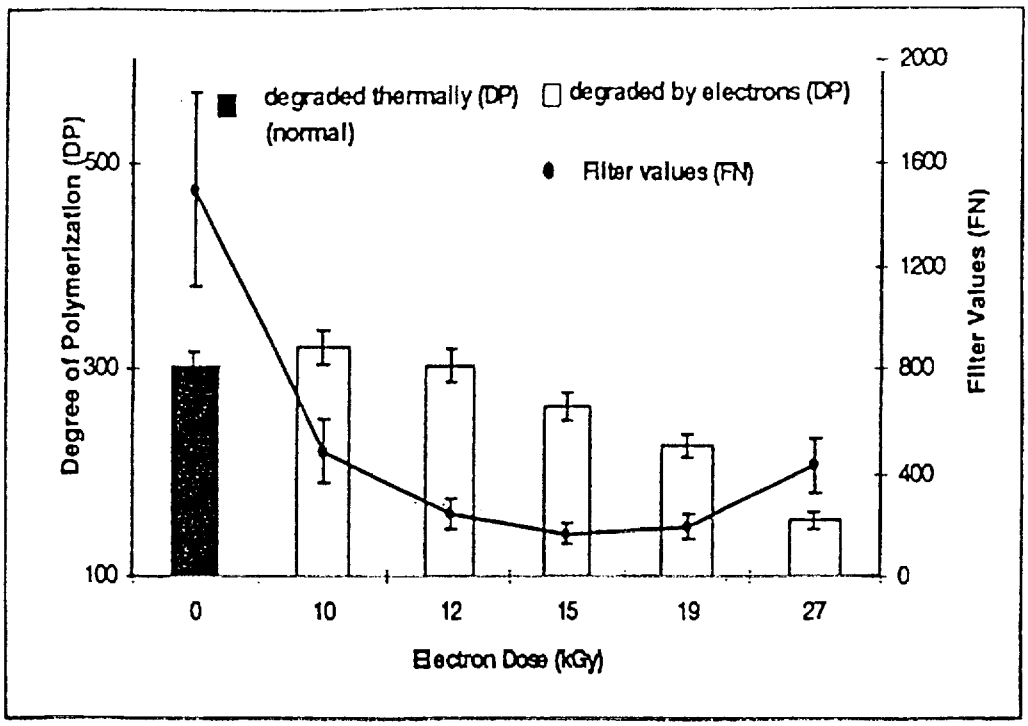

Fig.26. Dependence of cellulose degradation on dose [27].
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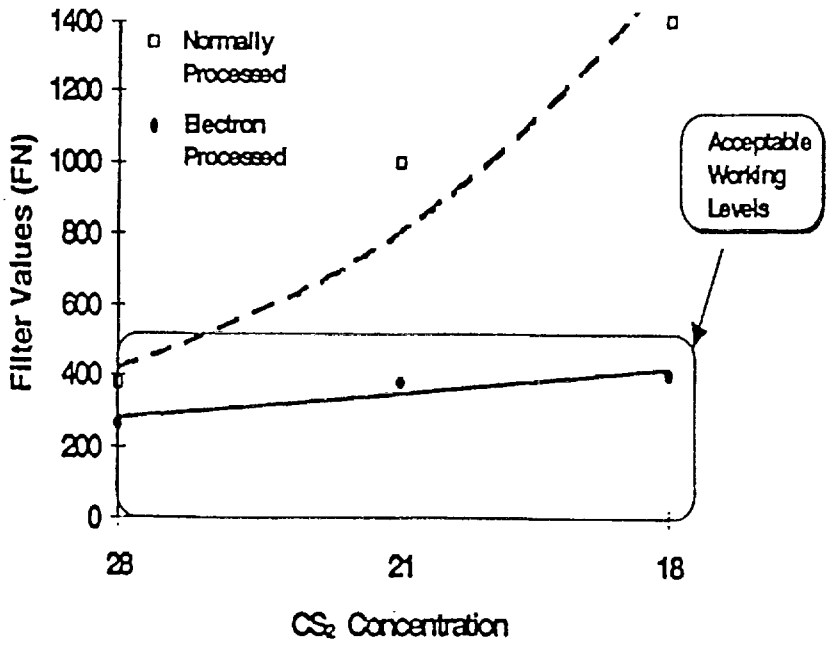

Fig.27. Filtration parameters after irradiation [27].
(Source as Fig.26)

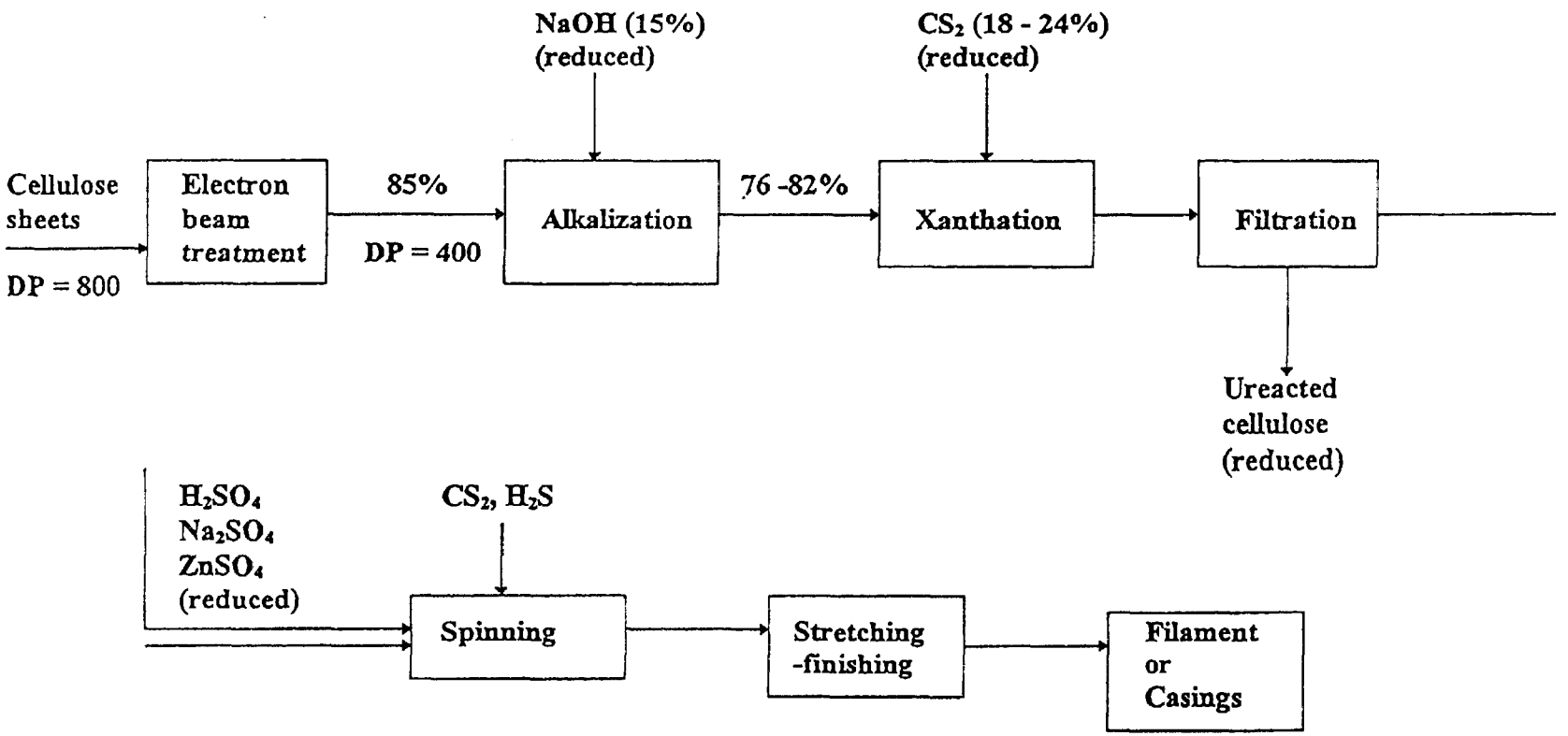

Fig.28. Viscose production process-electron beam cellulose pulp treatment (note that aging stage is avoided).

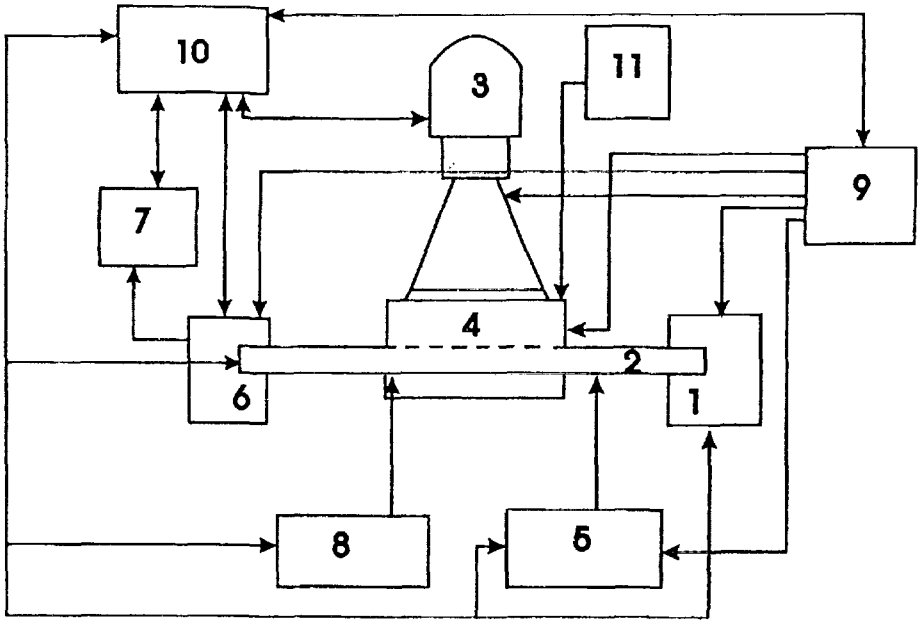

Fig.29. Block-scheme of the utilization device [29]:

1 - object charging block,
2 - object motion system during the utilization cycle,
3 - accelerator of electrons with an outlet beam device for transfering,
4 - reaction chamber,
5 - system of providing reaction chamber with a gas-medium,
6 - discharging and packing block,
7 - system of ventilation, gas filtration and fertilizer production,
8 - system of compressed air supply,
9 - system of water supply,
10 - system of electric power supply and automatic equipment gerating system.

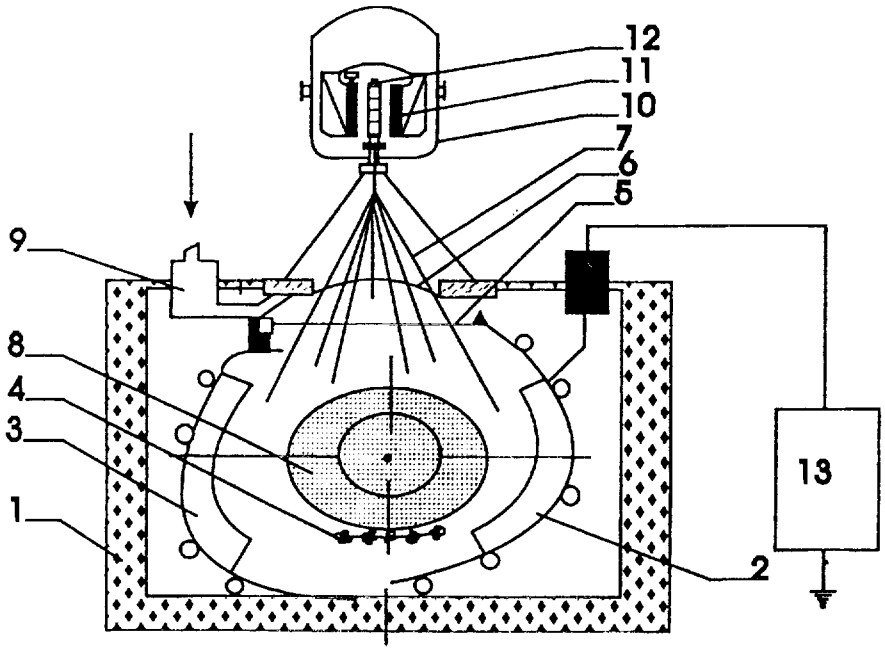

Fig.30. An arrangement of reactionary chamber [29]:
1 - radiation shielding,
2, 3 - flue gas discharge system,
4 - object rotating system,
5 - protection foil,
6 - foil window,
7 - accelerator sweep chamber,
8 - object to be cremated,
9 - compressed air,
10, 11, 12 - high-voltage generator,
13 - cascade generator.

UKD: 621.039.9:628.477
INIS: C52.00
KEY WORDS: ELECTRON BEAM, SOLID WASTE, MUNICIPAL WASTE, BIOLOGICAL SLUDGE, CELLULOSE DEGRADATION