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原著

전자빔 조사에 의한 오염토양중의 PAHs 및 PCBs의 분해

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Removal of PAHs and PCBs in artificially contaminated soils using electron beam irradiation

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요 약 문

난분해성 유기오염물로 오염된 토양 복원을 위한 전자빔 직접조사 공정의 적용가능성을 평가하기 위하여 PAHs 와 PCBs로 오염시킨 토양에 대한 전자빔 조사실험을 수행하였다. 전자빔 흡수선량 600kGy에서 PAHs의 제거율은 약 97% 이었고 PCBs는 800kGy에서 약 70%가 제거되었다. PAHs는 PCBs에 비해 낮은 흡수선량에서도 높은 제거율을 나타내었다. 오염물의 분해는 가속된 전자와 물의 반응으로 생성된 반응성 높은 중간생성물에 의한 산화/환원 반응보다는 고에너지 전자와 대상오염물의 직접적인 반응에 기인한다. 전자빔 조사에 의해 난분해성 오염물질로 오염된 토양을 효과적으로 제거할 수 있으나 이를 위해 높은 에너지를 요구하므로 비경제적인 공법이 될 수 있다. 따라서, 전자빔 직접조사 공정보다는 기존 토양복원 공법의 후처리 공정으로 개발하는 것이 경제적이고 실용화 가능할 것으로 판단된다.

주제어 : 전자빔, 오염토양, 복원, PAHs, PCBs

ABSTRACT

Direct electron beam irradiation experiments on artificially contaminated soil by polynuclear

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aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were performed to evaluate applicability of direct electron beam irradiation process for contaminated soil remediation. The removal efficiency of PAHs was about 97 % at 600 kGy and PCBs about 70 % at 800 kGy. PAHs were removed 27 % more, compared to PCBs although the absorbed dose was as low as 200 kGy. The contaminants decomposition was due predominantly to direct interaction of high-energy electrons and the target compounds rather than due to oxidation/reduction reaction by reactive intermediates. Radiolysis of electron beam may be able to decontaminate contaminated soil by toxic and recalcitrant organic compounds like as PAHs and PCBs effectively, but it may be economically uncompetitive. Thus, developments of post-treatment process of conventional site remediation technologies may be more practical and economical than direct radiolysis.

Key Words : Electron beam, contaminated soil, remediation, PAHs, PCBs

1. Introduction

Recently, in Korea, soil and groundwater contamination have been issued as a new indicator of environmental problem following the water and air pollution. Major soil contamination by military bases, waste disposal sites, gas stations and chemical process has been raised as a significant matter when these are closed or moved. Sixteen soil contaminants including petrochemicals, PCBs and heavy metals are controlled by Korea Soil Conservation Act. However, very few field applications of environmental site assessments and remediation technologies are known in Korea. PAHs are often found in petroleum contaminate sites. PAHs and PCBs are hazardous materials which are known to be toxic and carcinogenic compounds.

PAHs are components of coal tars, gasoline and jet fuel and leak to environmental through various sources. Because of their mutagenic and carcinogenic potential, sixteen PAHs such as naphthalene, fluoranthene, and pyrene are priority pollutants listed by the United States Environmental Protection Agency. The presence of these compounds in groundwater and soil constitutes a health hazard and their removal from contaminated sites is desirable. However, because their solubility and volatility are very low, they are resistant to typical *in-situ* remediation technologies including soil flushing, soil vapor extraction and soil venting. PAHs can be significantly removed by microbial actions, but this method is not time effective and cannot remove high molecular weight PAHs efficiently.

PCBs were first synthesized by Schmidt and Schulz in 1881 and then produced commercially under the name Arochlor (USA and UK, Monsanto), Clophene (German, Bayer), Fenchlor (Italy, Caffaro), Kanechlor (Japan, Kanegafuchi) and Phenoclor (France, Prodelec) since 1929.[1] PCBs, made from petroleum had been widely used as dielectric fluids in capacitors and transformers, special lubricants, additives in paints and pesticides. But in 1979, the harmful effects of PCBs were revealed and the use of PCBs was prohibited

in America. The total amount of PCBs production was up to 1,200,000 tons before the prohibition[2]. Since they are very stable thermally and chemically, the residual PCBs still exist in the sediments of rivers and harbors[3]. Because they are stable lipophilic compound and able to accumulate in the living organism through the food chain, adverse effects are expected in the human body[4]. PCBs are also considered to be endocrine distrupters. Incineration is the most common technology for destructing PCBs. However, it often leads to the formation of more toxic oxygenated derivatives(*e.g.*, polychlorinated benzofurans and dioxins), if not carefully controlled incineration temperature.

Various innovative technologies have been developed and applied for the remediation of soils contaminated by hazardous and recalcitrant compounds worldwide. Among these, ionizing radiation which is applied in many environmental fields such as wastewater treatment, gas treatment, and sludge disinfection is also a potential soil remediation technology to destroy hazardous and recalcitrant organic compounds[5),6),7)]. In a variety of ionizing radiation sources, high-energy electrons from electron accelerator and γ-ray from ^{60}Co have been considered as alternative treatment technologies. γ-ray has the attraction property of treating solid substances because of providing deep penetration into dense material. But γ-ray is more economical for relatively low throughput of low dose processes with low power requirements, while high-energy electron processing (≥10MeV) will be advantageous for high throughout or high dose processes requiring high power sources[7),8)].

There are two possible methods of electron beam accelerator applications for contaminated site remediation. One is direct irradiation of electrons from high-energy electron beam accelerator (≥10MeV) on the contaminated soil which is excavated from contaminated sites[7]. The other is post-treatment processes using medium- energy electron beam accelerator (0.5 ~ 5.0MeV) of conventional remediation technologies such as soil washing, pump and treat, soil vapor extraction, and thermal desorption. Unlike post-treatment processes, the direct electron beam irradiation process offers the possibility of soil treatment without phase separation. The objectives of this study are to evaluate applicability of direct electron beam irradiation process for contaminated soil remediation through removal experiments of PAHs and PCBs in artificially contaminated soil.

2. Materials and methods

2.1 Soil

The soil used in this research was collected from a depth of 30~40cm beneath the ground surface in the yard of Korea Institute of Construction Technology which is located in the middle western part of Korea. The collected soil was air-dried and passed through a 2 mm sieve. Physicochemical properties of the soil sample are listed in Table 1. The particle size and density were analyzed according to Korea Industrial Standard (KS) F 2302 and F 2308, respectively. The pH of soil was measured in accordance with EPA SW-846 method 9045C. The organic content was

Table 1. Physicochemical Properties of the Soil Sample

Soil characteristics	Measured values	Soil composition	Weight percent(%)
		SiO_2	61.97
soil component(wt%)		Al_2O_3	18.01
sand($\geq$ 50㎛)	78	Fe_2O_3	7.52
silt(50 ~ 2㎛)	15.5	CaO	0.58
clay($\leq$ 2㎛)	6.5	MgO	1.56
soil type	loamy sand	K_2O	3.45
		Na_2O	0.36
pH	7.3	TiO_2	0.77
organic content(%)	1.19	MnO	0.11
density(g/㎤)	2.65	P_2O_5	0.09
		ignition loss	5.44

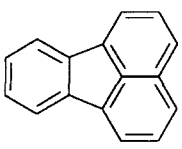
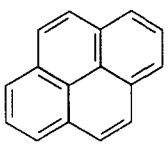
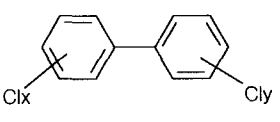
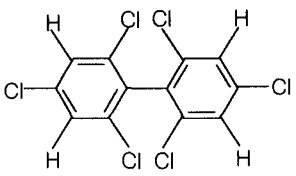
measured by the weight difference before and after the ignition of water-free soil sample at 550℃ for 30 minutes. Chemical composition of the soil sample was measured by X-ray fluorescence (XRF).

2.2 Contaminants

In this study, Fluoranthene and Pyrene (Aldrich, 98% purity) were chosen as model contaminants among PAHs. Arochlor 1260 (Chem Service, Inc., mix of isomers, 60% chlorine) and 2,2′,4,4′,6,6′-hexachlorobiphenyl (HCB, Chem Service, Inc., 99.2% purity) were selected among PCBs. Physicochemical properties of model contaminants were listed in Table 2.

In order to make a homogeneously contaminated soil, PAHs were dissolved in methylene chloride and PCBs in hexane and the solutions were slowly poured onto the soil, respectively. Then the slurry was continuously stirred until all the solvent evaporated. Moisture content of the spiked soils was adjusted to 25% by spraying distilled water

Table 2. Physicochemical Properties of Model Contaminants

Contaminants	Molecular formula	Boiling point (℃)	Vapor pressure (mmHg)
Fluoranthene[9]	$C_{16}H_{10}$	250	6×10^{-7}(@25℃)
Pyrene[9]	$C_{16}H_{10}$	360	6.85×10^{-7}(@25℃)
Arochlor 1260[10]	Mixture(60% chlorine)	385~420	< 0.1(@38℃)
HCB[10]	$C_{12}H_4Cl_6$	200	< 0.1(@38℃)
			
Fluoranthene	Pyrene	PCBs	HCB

(HPLC grade). These soil samples were stored in glass bottle with teflon cap and kept at 0 ~ 4℃.

2.3 Electron beam irradiation experiment

Electron beam accelerator is a machine which generates high energy electrons. Electrons from a cathode are accelerated to the speed of light within a vacuum enclosure by a high voltage. When the high energy electrons are irradiated on a material, a molecule of the material absorbs the energy and produce an electronically excited state and primary ionization products. These reactive intermediates react with organic and inorganic compounds and lead to the oxidation or reduction of the compounds to CO_2, H_2O and inorganic salts. The reactions induced by electron beam irradiation are given in Equation (1) ~ (4) as follows[11]:

$$AB + e^- \rightarrow AB^* + AB^+ + e^- \quad \text{electronic excitation and ionization} \quad (1)$$

$$AB^+ + e^- \rightarrow AB^* \quad \text{recombination} \quad (2)$$

$$AB^* \rightarrow A\cdot + B\cdot \quad \text{fragmentation} \quad (3)$$

$$AB^+ \rightarrow A^+ + B\cdot \quad \text{fragmentation} \quad (4)$$

High-energy electron irradiation of pure water results in the formation of electronically excited states and free radicals along the path of the electron. 10^{-7} sec after the electron has passed through a solution the products that are present are shown in Equation (5)

$$H_2O \rightarrow [2.7]OH\cdot + [2.6]e^-_{aq} + [0.6]H\cdot + [0.7]H_2O_2 + [2.6]H_3O^+ + [0.45]H_2 \quad (5)$$

The efficiency of conversion of a high energy electron to a chemical process is defined as G-value. In Equation (5), the numbers in brackets, the G-values, represent radiation-chemical yield expressions, and are defined as the number of radicals, excited states or other products, formed or destroyed per 100 eV of radiation energy absorbed. Of the products formed in Equation (5), the most reactive are the oxidizing, hydroxyl radical ($OH\cdot$) and the reducing, aqueous electron (e^-_{aq}) and hydrogen radical ($H\cdot$). These reactive species could result in the complete decomposition of organic and inorganic pollutants. These reactions have been well documented in many researches[12].

When high energy electrons are irradiated on contaminated soils with moisture, decomposition of contaminants occurs by direct and indirect interaction[8]. Direct reactions result from the direct radiation "hit" of high energy electrons which are accelerated by the speed of light on target contaminants. Indirect effects involve the absorption of ionizing radiation by the environment (*e.g.*, the solvent or water), generating reactive intermediates which are shown in equation (5) and may destroy the target molecule.

Electron irradiation experiments were conducted with medium-energy electron accelerator (1MeV, 40kW) at the EB-TECH. Co., Ltd. in Korea. After spreading soil samples on stainless reactor, we irradiated electron beam on the reactor directly. The reactor, illustrated in Fig. 1, was made of stainless and designed to circulate cooling water to reduce temperature rise. In these experiments we didn't seal up the reactor by titanium foil. We measured the temperature using surface temperature indicating strips

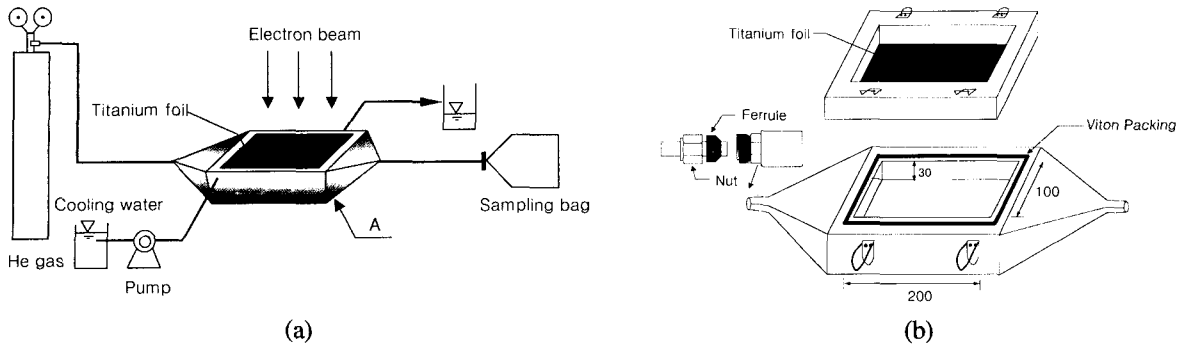


Fig. 1. Schematic diagram of the experiment apparatus(a); (b) reactor(part A in (a))

(Thermax, Thermographic Measurement Co. Ltd., ±1% accuracy) after electron beam irradiation. Change in the strip color from silver white to black indicates that the rating has been reached. The thermometer attached on the reactor and soil sample was spread out about 5 mm thickness before electron beam irradiation.

2.4 Analytical method

Model contaminants were analyzed using U.S. EPA SW-846 Method by a HP 5890

Table 3. Operational Conditions for Gas Chromatographic Contaminant Analysis

1. PAHs(Fluoranthene, Pyrene)	
Gas chromatographic method	EPA 8100
Extraction method	EPA 3550B(ultrasonic extraction)
Detector type	Flame ionization detector(FID)
temp.	300℃
Injector temp.	280℃
Oven temperature program	200℃ hold 2min, 300℃ @ 15℃/min
2. PCBs	
Gas chromatographic method	EPA 8082
Extraction method	EPA 3550B(ultrasonic extraction)
Detector type	Electron capture detector(ECD)
temp.	300℃
Injector temp.	300℃
Oven temperature program	150℃ hold 2min, 300℃ @ 8℃/min, 320℃@ 5℃/min, hold 5min
3. HCB	
Gas chromatographic method	EPA 8082
Extraction method	EPA 3550B(ultrasonic extraction)
Detector type	Electron capture detector(ECD)
temp.	300℃
Injector temp.	300℃
Oven temperature program	150℃ hold 3min, 250℃ @ 15℃/min, hold 1min

Series II gas chromatography equipped with a 30m×0.25mm×0.25㎛ DB-5 capillary column (J&W Scientific Inc.). The gas chromatographic operation conditions and detectors were listed in Table 3.

Concentrations of chloride ion were measured using ion chromatography (DX-500, Dionex, USA).

3. Results and Discussion

3.1 Removal of PAHs

Direct electron beam irradiation experiments on the contaminated soil which was spiked with fluoranthene and pyrene homogeneously were conducted. The initial concentrations of the PAHs were 150 and 300 mg/kg-soil, respectively. Fig. 2 compares the removal efficiency of the model contaminants. More than 97 % removal was achieved at 600 kGy. The SI unit for absorbed dose is kilojoule per kilogram (kJ/kg), which is given the special name kilogray (symbol kGy). Pyrene is more stable than fluoranthene structurally as shown in Table 3. Therefore, removal efficiency of pyrene is lower than that of fluoranthene at 200 kGy, but there is not a large difference in the removal efficiency between fluoranthene and pyrene over 400 kGy.

Water added in the soil samples was evaporated and nearly dried out after electron beam irradiation with 600 kGy. When moisture content of the contaminated soil was 15 %, the removal rate was higher about 5 % than that of soil sample with water content of about 25 % at 200 kGy. However, the moisture content did not affect removal efficiency at more than 400 kGy.

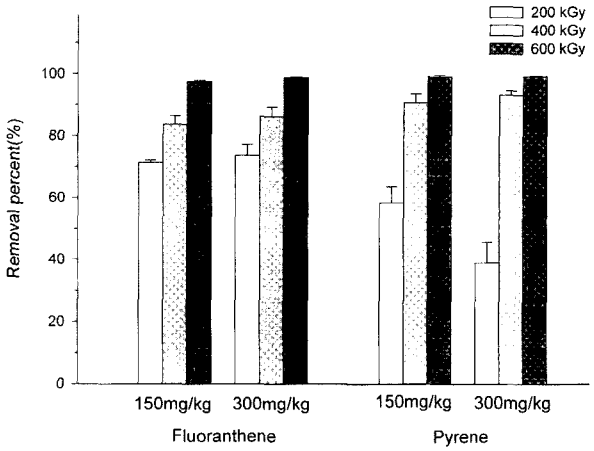


Fig. 2. Removal efficiency of Fluoranthene and Pyrene.

Direct and indirect radiation reactions occur simultaneously in a system. Because the reactive intermediates, hydroxyl radical and aqueous electron, are not able to move easily in soil matrix, the decomposition of contaminants was due predominantly to direct interaction of high energy electrons and the target compounds. Hydrophobic organic contaminants like PAHs and PCBs used in this study are adsorbed on soil surface and the surface is enclosed by water. Electrons react with water before destructing target contaminants. As a results, removal efficiency of soil sample whose water content was adjusted to 15 % was better at low absorbed dose. In order to detect reaction by-products and determine decomposition pathway, we modified the analytical condition of GC in a various way. However, we have been unable to detect measurable quantities of by-products.

3.2 Removal of PCBs

The removal efficiency of PCBs increased

with absorbed dose as shown in Fig. 3. Initial concentrations of Arochlor 1260 and HCB were about 35 and 250 mg/ kg-soil, respectively. Arochlor 1260 was removed much higher than HCB. This is thought to be due to the fact that the initial concentration was very low compared to initial concentration of HCB. Arochlor 1260 consists of chlorinated biphenyl mixtures that contain various amounts of chlorine such as mono-, di- and hexachlorinated biphenyl. Chlorinated biphenyls whose molecular weight is low may be removed easily and overall removal efficiency is high at low absorbed dose. Although fluoranthene and pyrene were removed more than 97 % at 600 kGy, PCBs decomposition was relatively lower than PAHs and it may be necessary to radiate more than 1,000 kGy to obtain removal efficiency over 90 %.

Gray and Hilarides[8] have demonstrated that 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) can be converted to products of negligible toxicity by radiolysis with γ-rays from ^{60}Co. Decomposition occurs via stepwise reductive dechlorination producing lesser chlorinated dioxins and a final product of dibenzo-p-dioxin. We expected similar results with electron beam irradiation and conducted direct electron beam experiments for HCB contaminated soil. As the absorbed dose increased, concentration of chloride ion went up, and concentration of the HCB decreased. This result is shown in Fig. 4. However, biphenyl, a final by-product of dechlorination, was not been detected in our experiments. GC/MS(HP5890/HP5973) analysis was preformed for identification of by-products and we detected about 10 mg/kg-soil of 2,2′,4,6,6′-pentachlorobiphenyl and 2,2′,4,4′,6-pentachlorobiphenyl, respectively. We could not complete mass balance on organic species and chloride ion due to an inability to detect biphenyl, chlorinated by-products, and ring cleavage products.

The changes of HCB concentration and temperature with absorbed dose are shown in Fig. 5. The soil temperature was about 87℃ at absorbed dose of 800 kGy. Most thermal desorbers operate at temperatures between 150~550 ℃. More volatile products (*e.g.*, gasoline) can be desorbed at the lower

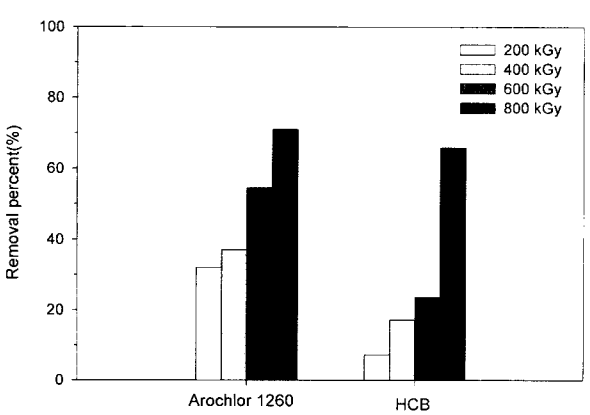


Fig. 3. Removal efficiency of Arochlor 1260 and HCB.

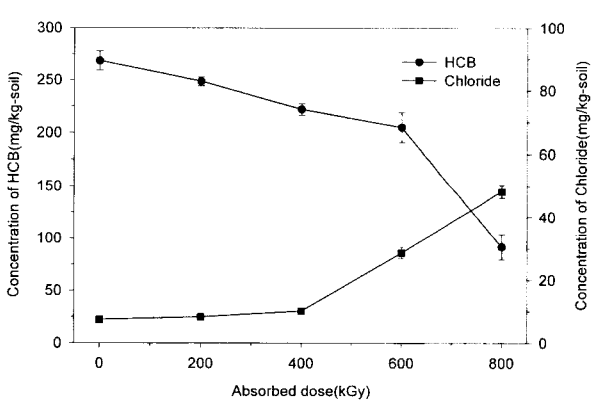


Fig. 4. Concentrations of HCB and chloride on soil with absorbed dose.

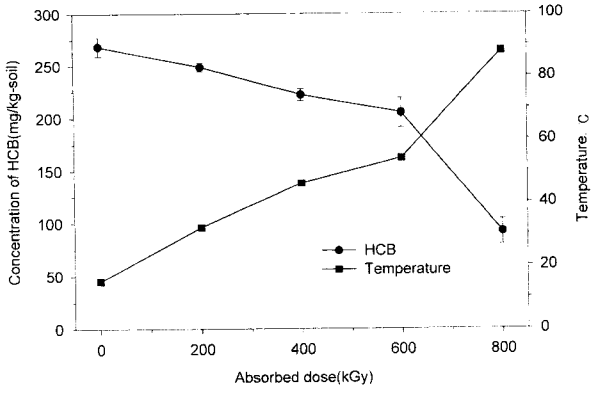


Fig. 5. Change of HCB concentration and temperature with various absorbed dose.

operating range, while semivolatile products (*e.g.*, kerosene, diesel fuel) generally require temperatures in excess of 400 ℃[13]. Along with boiling point, vapor pressure is used to measure a compounds volatility. Boiling point and vapor pressure were listed in Table 2 and model contaminants were semivolatile. Based upon the comparison, we can not exclude the possibility of transformation of target contaminants to air. More research is required to determine the mass balance on organic species and chloride ion and then evaluate the possibility of conversion to air. Presently, we are progressing with research to collect gas and analyze its composition using the reactor sealed by titanium foil. Schematic diagram of the reactor and gas sampling method are shown in Fig. 1.

4. Conclusions

Direct irradiation experiments were performed to evaluate applicability of electron beam process for remediation of contaminated sites polluted by toxic and recalcitrant organic compounds like PAHs and PCBs. The removal efficiency of PAHs was about 97 % at 600 kGy and PCBs about 70 % at 800 kGy. PAHs were removed 27 % more, compared to PCBs although absorbed dose was low as 200 kGy. The decomposition of the contaminants was due predominantly to direct interaction of high energy electrons and the target compounds rather than oxidation/reduction reaction of reactive intermediates. We could neither complete mass balance nor identify decomposition pathway of target contaminants due to an inability to detect biphenyl, chlorinated by-products, and ring cleavage products. However, the removal may be break down of the contaminants rather than volatilization by the direct irradiation hit of high energy electrons.

Radiolysis of electron beam may be able to decontaminate PAH contaminated soil effectively, but it may be economically uncompetitive. Therefore this technology should be developed as an alternative technology to clean-up PCBs or dioxin contaminated sites of which remediation cost is very high. Considering the cost of electron accelerator and characteristics of contaminated sites scattered all over the country, a mobile type electron beam process should be developed. Unlike other methods of soil remediation, the advantage of direct electron beam irradiation is obviating the need to extract the pollutant from the solid surface of the contaminated material. However, it is difficult to control heterogeneous soil continuously and the process requires high absorbed dose unlike water and air treatment. Thus, developments of post-treatment process

of conventional site remediation technologies may be more practical and economical than direct radiolysis.

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