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CASE STUDIES OF THE HIGH VOLTAGE ELECTRON BEAM TECHNOLOGY FOR WASTEWATER TREATMENT

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INTRODUCTION

The development of innovative technologies for the remediation of contaminated sites is continually being considered as a treatment option for several reasons. From an economic standpoint, the treatment costs of conventional technologies continues to increase and from an environmental impact view, treatment technologies are sought that destroy contaminants without creating additional disposal problems.

The high energy electron beam process has been shown to be effective in destroying many organic compounds associated with contaminated sites[1-3]. The experiments to date have been conducted at both bench and full scale. Bench scale studies are performed using a 5000 Curie ^{60}Co-γ source whereas full scale studies have been completed at a pilot facility that has a daily capacity of 170,000 gallons (120 gallons per minute, gpm). The application of this technology to problems that face EPA could result in cost effective treatment of contaminated groundwater, soils, sediments and sludges, as well as demilitarization (chemical weapons), and as an industrial treatment unit process.

To provide "on-site" treatability/feasibility studies as well as small scale clean-ups we have now developed a mobile system. This system is capable of treating up to 50 gpm, employing a 500 kV, 40 mA accelerator. The system is self contained and can be used in remote locations if necessary.

We have received an US Environmental Protection Agency, SITE Emerging Technology project which has as its focus the application of this process to complex mixtures of contaminants in groundwater, wastewater, soils, sediments, and sludges. This paper will discuss the details of several case studies conducted at full scale using the mobile treatment process and review data obtained from on-going studies that have direct benefit to EPA and may assist groups within the environmental clean-up field to more effectively accomplish their mission.

METHODOLOGY

Aqueous Chemistry of High-Energy Electrons. The scientific foundation for the use of high energy electron beam in water treatment is based in the field of radiation chemistry[4]. The purpose of this section is to provide a brief overview of aqueous-based radiation chemistry which is intended to familiarize the reader with the chemistry and show its applicability to achieving the goals and objectives of this project.

Irradiation of pure water results in the formation of electronically excited states and/or 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 1:[4,5]

$$H_2O \text{ -\/\/\/\-> } [2.7]\ OH\cdot + [2.6]\ e^-_{aq} + [0.6]\ H\cdot + [0.7]\ H_2O_2 + [2.6]\ H_3O^+ + [0.45]\ H_2 \quad [1]$$

Unlike photochemical reactions where one photon of light initiates one (molecular) reaction, a high energy electron is capable of initiating several thousand reactions as it dissipates its energy. The efficiency of conversion of high energy electron radiation to a chemical process is defined as G (shown in brackets in Equation 1). G is the number of radicals, excited states or other products, formed or lost in a system absorbing 100 eV of energy. Of the products formed in Equation 1, the most reactive species are the oxidizing, hydroxyl radical (OH·), and the reducing, aqueous electron (e^-_{aq}) and hydrogen atom (H·). Thus, the chemistry of primary interest in the high energy electron irradiation process is that of these three species. The concentrations of these reactive species, at several radiation doses, are summarized in Table 1.

TABLE 1. ESTIMATED CONCENTRATION OF TRANSIENT REACTIVE SPECIES AT SEVERAL DOSES USING HIGH ENERGY ELECTRON IRRADIATION.

	e^-_{aq}	H·	OH·	H_2O_2
DOSE (Mrad)			mM	
1	2.7	0.6	2.8	0.7
2	5.4	1.3	5.6	1.4
4	10.8	2.6	11.2	2.8

High energy electron beam irradiation is the only process that is capable of forming both highly oxidizing and highly reducing reactive species in aqueous solutions at the same time and in relatively the same concentration. Furthermore, no other advanced oxidation process has the capability of generating as high an overall free radical yield per unit energy input as high energy electron beam treatment.

Aqueous Electron. The e^-_{aq} is a powerful reducing reagent with an E° ($e^-_{aq} + H \text{ ---> } \frac{1}{2}H_2$) of 2.77. The reactions of the e^-_{aq} are single electron transfer, the general form of which is:

$$e^-_{aq} + S^N \text{ -----> } S^{N-1} \quad [2]$$

The e^-_{aq} reacts with numerous organic chemicals and of particular interest to the field of toxic and hazardous wastes are the reactions with halogenated compounds. A generalized reaction is shown below:

$$e^-_{aq} + RCl \text{ -----> } R\cdot + Cl^- \quad [3]$$

Thus, reactions involving the e^-_{aq} may result in the dechlorination of organohalogen compounds. Further reaction of the organic radical formed could result in the complete destruction of the compound. The e^-_{aq} also reacts with other organic compounds and would contribute to the removal of these compounds from aqueous solutions.

Hydrogen Atom. The hydrogen atom accounts for approximately 10% of the total free radical concentration in irradiated water. The H· undergoes two general types of reactions with organic compounds, hydrogen addition and hydrogen abstraction.

An example of a typical addition reaction with an organic solute of interest in contaminate source water is that of benzene:

$$H\cdot + C_6H_6 \text{ -----> } C_6H_7\bullet \quad [4]$$

The second general reaction involving the H· is hydrogen abstraction:

$$H\cdot + CH_3OH \text{ -----> } H_2 + \cdot CH_2OH \quad [5]$$

Because of the relatively small second order reaction rate constant of H· with the common radical scavengers found in natural waters, it is possible that this transient radical may be important in removing some of the compounds of interest in drinking water treatment. This treatment process is the only one in which this particular radical is formed.

Hydroxyl Radical. The types of reactions that involve the OH· are addition, hydrogen abstraction, electron transfer, and radical-radical recombination.

Addition reactions occur readily with aromatic and unsaturated aliphatic compounds. The resulting compounds are hydroxylated radicals:

$$OH\cdot + CH_2{=}CH_2 \text{ -----> } HOCH_2\text{-}CH_2\bullet \quad [6]$$

Hydrogen abstraction occurs with saturated and many unsaturated molecules, e.g., aldehydes and ketones:

$$OH\cdot + CH_3\text{-}CO\text{-}CH_3 \text{ -----> } \cdot CH_2COCH_3 + H_2O \quad [7]$$

Case Studies. All case studies presented in this paper were conducted in Halle-Dieskau, Germany, utilizing a mobile electron beam treatment unit. The electron beam and ancillary equipment are mounted in a 48 foot tractor trailer. The trailer is completely self contained, self-shielded, and has the capability of treating waste flows of up to 50 gpm.

In all cases a 1 m^3 sample of the waste to be treated was transported by tank truck to the mobile unit and transferred into an internal 2 m^3 nalgene vessel. The waste stream was then recirculated through the electron beam treatment process, at a flow rate of 25 gpm, for a total of anywhere between 50 and 199 minutes (a total of 3 to 14 recirculation passes based on time), depending on the wastewater characteristics. The electron beam was maintained at full power for the entire study. Influent and effluent samples were collected by German scientists every one or two recirculation passes; again depending on the waste stream treated.

RESULTS

Table 1 summarizes the results obtained from one of the case studies. The results obtained in this study were typical of those observed for all studies conducted.

TABLE 1. SUMMARY OF ELECTRON BEAM REMOVAL OF VARIOUS ORGANIC COMPOUNDS FROM CASE STUDY #1.

Analyte		Zero Dose	0.7 Mrad	1.4 Mrad	2.8 Mrad	Overall % Removal
Σ Phenol	$\mu g\ L^{-1}$	2230	220	60	20	99.10
Benzene	$\mu g\ L^{-1}$	6200	150	10	3.5	99.95
Toluene	$\mu g\ L^{-1}$	498	9	<1	BMDL	100
Ethylbenzene	$\mu g\ L^{-1}$	118	2	BMDL	BMDL	100
m/p-Xylene	$\mu g\ L^{-1}$	201	4	<1	BMDL	100
o-Xylene	$\mu g\ L^{-1}$	108	2	BMDL	BMDL	100
Σ Aromatics	$\mu g\ L^{-1}$	7125	167	10	3.5	99.95
Naphthalene	$ng\ L^{-1}$	15207			<20	>99.87
Fluorene	$ng\ L^{-1}$	728			<20	>97.25
Phenanthrene	$ng\ L^{-1}$	48			<10	>79.17
Anthracene	$ng\ L^{-1}$	138			<10	>92.75
Pyrene	$ng\ L^{-1}$	56			BMDL	100
Benzo-(a)anthracene	$ng\ L^{-1}$	12			BMDL	100
Fluroanthene	$ng\ L^{-1}$	86			<10	>88.37
Σ PAH	$ng\ L^{-1}$	16277			BMDL	100

BMDL = below method detection limit.

CONCLUSIONS

Work to date has demonstrated that high energy electrons generated by electron beam accelerators can effectively and efficiently treat complex mixtures of hazardous compounds from aqueous solutions. Additionally, the electron beam equipment used for this study can easily be scaled up to handle increased waste stream flows, thereby making this innovative technology economically competitive with existing treatment processes.

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INTRODUCTION

High strength organic wastewaters are encountered at hazardous waste sites in the form of leachate and in some cases groundwater. The ZenoGem™ Process is designed to remove biodegradable materials, including most organic contaminants, from wastewater to produce a high quality effluent. This technology was accepted into EPA's Superfund Innovative Technology Evaluation (SITE) program in summer 1992; this paper summarizes the technology demonstration performed at a Superfund site in 1994.

DESCRIPTION OF THE TECHNOLOGY

The ZenoGem™ Process consists of an integrated bioreactor and ultrafiltration membrane system, or ultrafilter. After equalization, wastewater enters the bioreactor, where contaminants are biologically degraded. In this tank, a biomass develops which contains bacterial cultures that break down organic contaminants. Ideal conditions for biomass growth are maintained, including introduction of air to assure sufficient aerobic conditions and optimal process temperatures. The contents are constantly mixed by the introduction of air bubbles through a series of manifolds from the tank bottom. The tank is totally enclosed; air is recycled and a purge is emitted through a carbon adsorption unit before being discharged into the atmosphere. A mixture of sludge solids and un- filtered wastewater from the ultrafilter is recycled back to the bioreactor and remains in the treatment system for periods of several weeks. The bioreactor's size is significantly reduced because of this long sludge retention time. Conversely, the hydraulic residence time in the bioreactor is relatively short.

The ultrafilter receives feed flow from the bioreactor. It separates treated wastewater from biological solids and soluble materials with higher molecular weights. Ultrafiltration (UF) is a pressure-driven (typically at 60 to 70 pounds per square inch) cross flow filtration process in which the water to