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ADVANCED OXIDATION AND REDUCTION PROCESSES: CLOSED-LOOP APPLICATIONS FOR MIXED WASTE

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At Los Alamos we are engaged in applying innovative oxidation and reduction technologies to the destruction of hazardous organics. Non thermal plasmas and relativistic electron-beams both involve the generation of free radicals and are applicable to a wide variety of mixed waste as closed loop designs can be easily engineered. Silent discharge plasmas (SDP), long used for the generation of ozone, have been demonstrated in the laboratory to be effective in destroying hazardous organic compounds and offer an alternative to existing post-incineration and off-gas treatments. SDP generates very energetic electrons which efficiently create reactive free radicals, without adding the enthalpy associated with very high gas temperatures. A SDP cell has been used as a second stage to a LANL designed, packed-bed reactor (PBR) and has demonstrated DREs as high as 99.9999% for a variety of combustible liquid and gas-based waste streams containing scintillation fluids, nitrates, PCB surrogates, and both chlorinated and fluorinated solvents. Radiolytic treatment of waste using electron-beams and/or bremsstrahlung can be applied to a wide range of waste media (liquids, sludges, and solids). The efficacy and economy of these systems has been demonstrated for aqueous waste through both laboratory and pilot scale studies. We will present recent experimental and theoretical results for systems using stand alone SDP, combined PBR/SDP, and electron-beam treatment methods

I INTRODUCTION

Historically, combustible wastes (including those with radioactive metal contamination) within the DOE and DOD complexes have been incinerated to reduce volumes and, in the case of hazardous mixed wastes contaminated with organics, to destroy the hazardous organic constituents. Growing legislative and social concerns are leading to an increased demand for a reduction in the amount of wastes released to the environment through flue gas stacks, liquid waste streams, and other sources. EPA and RCRA regulations on the release of hazardous compounds to the environment will become increasingly stringent in the next decade. Although the EPA still considers incineration the best demonstrated available technology for many combustible wastes, public acceptance of incineration has declined to a point where alternatives must be evaluated. Similarly, licensing of an incinerator in today's climate may take seven or more years. Combining the incineration problem of hazardous organics with the potential for the release of radioactive materials in mixed waste treatment has virtually rendered conventional incineration as a totally unacceptable solution. Thus the DOE and DoD complexes must proceed to develop environmentally acceptable mixed waste treatment technologies, particularly those which minimize (or eliminate) uncontrolled emissions

The conventional approach to organic destruction is through combustion of the material. Although this can usually be a one-step process, difficult, noncombustible materials such as polychlorinated biphenyls (PCBs) require a two stage process, with the second stage running at a very high temperature. In all cases, the chemistry is dependent on the generation and propagation of free radicals such as O(^{3}P), OH, and H. The efficiency of production for these free radicals depends primarily on the temperature of the combustion. For waste materials that do not contain highly combustible organic materials, fuel (such as hydrogen, methane, and methanol) that can generate the high temperatures required

TCA, Freon TF, and CCl_4 with flow rates of up to 215 slm of oxidizing gas and 6 grams per minute of liquid mixtures.

Thermal PBR technology has several distinct advantages for the treatment of combustible liquid wastes: First, the PBR operates below normal flammability limits and relies upon an external energy source to initiate and control the chemical reactions. Second, the heat of reaction can be used to sustain the operation of the PBR once the organic flow begins; hence, reducing or eliminating further electrical input. Third, because the technology is relatively simple, the overall initial and operating cost should be modest. Fourth, since the technology is relatively simple and rugged, the scalability, survivability, and maintainability of a PBR system should be extremely high.

A diagram of the treatment system with the PBR as the first stage is shown in Fig. 2. The PBR consists of the following major parts: main reactor enclosure (cylindrical metal pipe), bed packing material (alumina pellets), and an electric furnace. As currently designed, the bed reactor is a tube with an outer diameter of 16 4 cm and a length of 105 to 120 cm. The liquid is atomized above the bed using a simple axisymmetric, oxidizer-gas-assisted nozzle. The liquid gasifies with passage through the bed and reacts with the oxidant and products of thermal decomposition producing easily handled materials (primarily CO_2, H_2O, and HCl) before reaching the bed exit. After exiting the bed, the gas is cooled down by passing through a heat exchanger, analyzed to determine its composition, and sent through additional stages and treatment processes as necessary. Historically, for applications like stack gas purification or catalytic enhanced processes, PBR systems have used a large variety of bed materials and hence, reaction mechanisms. For our current process, alumina appears to be a good bed material. Other materials such as calcium carbonate could be added to enhance the removal of certain compounds such as HCl. The initial heat source for the reactor is an external electric tube furnace. An operating temperature between 500 and 1300 degrees C is generally required depending on the fluid being treated. While the current furnace limits the bed reactor to a maximum diameter of about 16 5 cm, tube furnaces are commercially available up to about 100 cm in diameter.

The current data is primarily from the 6 4 cm OD reactor. Initial testing of a 15 cm ID PBR has recently been completed. This system will allow studies of gas and liquid chemical conversion processes at gas flow rates up to a range of 300 to 700 slm and organic liquid injection rates up to about 100 grams per minute (about 6 kg/hr), depending on the water/organic ratio. Based on current data from the 6 4 cm OD reactor, a system designed for operation at a liquid injection rate of 1 kg/minute would have an OD of about 30 to 45 cm with a bed length of about 1 meter.

IV ELECTRON-BEAM TREATMENT

High energy electron beams, x rays (bremsstrahlung) belong to a class of technologies generally referred to as radiolytic methods. These methods have been demonstrated, both in the laboratory and in pilot plants, to effectively destroy hazardous organic wastes, particularly chlorinated hydrocarbons [4] We have established collaborations with industry, academia and other national laboratories to promote radiolytic (electron-beam) waste treatment technology. The hazardous components of particular concern in mixed wastes are those on the EPA Superfund list of toxic organics and other fluids which are typically found in process streams, stored materials, and ground water. Within DOE EM 30 and EM 40 need aqueous and mixed waste technologies that address the following key points:

- Process must handle a broad spectrum of hazardous wastes (present aqueous treatment technologies do not do, not handle higher solids content or sludges, and are too compound selective at their optimum performance, therefore cost of present technologies too sensitive to waste type)
- Process should provide high throughput and, hence short residence times

- Standoff capability (major part of equipment not in contact with radioactive components) desired for mixed wastes.
- Process should provide broad dynamic range of treatment capability.

Existing technologies fail to provide effective and economical means of addressing these problems. Radiolytic treatment technology shows promise for addressing these needs as well as contributing solutions to mixed radiochemical waste treatment problems of key importance to the DOE Complex.

Radiolytic treatment has advantages over existing industrial waste treatment technologies because it is not sensitive to the treatability of the contaminant or the particular target species; it treats waste streams of varied composition (including solids characteristic of mixed wastes), has a short residence treatment time, and is a superior de-halogenator. As evidenced by earlier studies, radiolytic treatment technology has an established engineering base, is presently economically competitive with other methods, see figure 3 [5], and is envisioned to be less expensive when new accelerator technology is implemented. Hanford, for example, has identified the need for removal/destruction of organic compounds, nitrates, and ferrocyanides from single-shell tank wastes. Radiolytic processes show promise for the removal of these wastes, and the treatment of sludges as well, because of the presence of both oxidative and reductive free radicals.

V EXPERIMENTAL RESULTS

V-1 SDP Treatment of Off Gases:

The prototype SDP laboratory at Los Alamos uses a planar cell to treat waste streams at up to 10 liter/min. The cell has approximate dimensions of 71-cm long, 18-cm wide and 2.5-mm gap, giving a mean discharge area of 1236 cm^2, and an active volume of 310 cm^3. A cylindrical cell designed for operation at higher temperatures can be inserted in a surrounding furnace. Higher temperature operation is desired because reaction rate coefficients involving OH increase with temperature. This cell has an active volume of 215 cm^3. The planar cell was used for the data reported here. Our main electrical power supply is a series inverter which switches charged capacitors through a high-quality pulse transformer by high power thyristors. This unit supplies up to 4 kW of power at repetition rates to 3 kHz. Other driving circuits include commercial systems built for ozonation, fast pulse forming networks and simple audiofrequency amplifiers.

In order to determine the destruction efficiency of any process, two measurements must be made. The first is the power supplied to the system. The usual method of deriving electrical power, $<W> = V*I$ is difficult to implement for SDP due the transient nature of the current. A formula, using easily measured parameters, for the average power dissipated within a silent discharge has been developed by Manley [6]:

$$<W> = 4 f V_i C_d [V_0 - ((C_d+C_g)/C_d) V_i].\qquad (1)$$

Where f is the frequency of the applied voltage in Hz, C_d and C_g are the dielectric and gas capacitances, respectively, in Farads, and V_i and V_0 are the gas ignition and peak applied voltages, respectively, in Volts. Both V_i and V_0 are taken from a measurement of the total voltage appearing across the cell, V_{cell}. This equation has proven to be useful for a wide range of applied voltage waveforms. An alternative method uses a simple integrating circuit to measure the transported charge, Q. At an applied voltage, the gas does not breakdown and Q is proportional to and in phase with V_{cell}. Above breakdown, losses within the gas discharge phase shift Q and the Q-V plot generates a figure whose area corresponds to the power dissipated in the gas per cycle. Calculations using equation 1 and the area of the Q-V plot agree to 5%, well within the error of the original measurements

The effluent from the SDP reactor is distributed to a gas manifold for the second measurement: chemical analysis. Analytical capabilities include IR spectrometry, mass spectrometry (MS), and gas chromatography. The IR and MS systems are used primarily to search for, and identify, intermediate compounds produced in the discharge. The gas chromatograph (GC) monitors the concentration of the specific contaminant under study.

To determine optimal treatment conditions we have conducted power scaling experiments with TCE and CCl_4. Figure 4 shows a representative plot of measured destruction rates for the listed gas flow and composition. The TCE and CCl_4 are diluted into a 78/19/3 mix of argon/oxygen/H_2O. Other compounds destroyed using SDP include: hyrocarbons, CFC's, toluene, xylene, p-cumene, dichlorobenzene, NO_x and SO_x. System optimization continues.

In order to compare varied experimental conditions, a figure of merit, can be determined by the energy delivered to the plasma per hazardous molecule removed from the gas stream. The average power, <W>, is divided by the flow rate, Q, and hazardous compound concentration, [C]. Using convenient units, this can be expressed as kW-hr/kg - or the number of kilowatt-hours needed to remove one kilogram of hazardous compound. For the data in Figure 4, we calculate a figure of merit of 84 kW-hr/kg for >>99% removal of TCE, and 270 kW-hr/kg for >90% removal of CCl_4. These results are consistent with the modeling efforts underway at LANL and our coworkers at the U of Illinois and Auburn [7]

V-2 Combined PBR/SDP Treatment of Liquids

The SDP and PBR sub-systems have been integrated to treat contaminated cutting oils. The PBR gaseous effluent was sent directly to the SDP reactor (after condensing most of the liquid) for further treatment. Chlorocarbons in the final effluent were well below 100 ppb. Results (using an infrared spectrophotometer, a gas chromatograph (GC), and a mass spectrometer for diagnostics) indicate that chlorocarbon compounds such as TCE and CCl_4 can be removed by the PBR to 0.1 ppm levels during steady state operation. During start up, transient behavior in the PBR does allow larger concentrations of chlorocarbons and reaction products to remain in the effluent stream. During this startup period, the power applied to the SDP stage would be increased to reduce the effluent concentrations to acceptable levels. Figure 5 shows a time history of the effluent during a TCE test measured with the GC

A series of test runs have determined the effectiveness of PBR/SDP treatment of 1,2-dichlorobenzene (DCB). The system successfully reduced DCB levels to below 1 ppm. The EPA suggests DCB as a surrogate for PCB's which are controlled by TSCA. The index of incinerability for DCB is 24, compared to 30 for PCB. The lower the number, the more difficult to incinerate. Tests were conducted for both pure samples and samples mixed with 80% oil. During startup data show DCB levels around 3 ppm. This is reduced to around 2 ppm as the CO concentration decreases. It appears that the addition of oil assists the combustion of the DCB. Treatment of the PBR off gasses by the SDP substantially reduce DCB levels. At a delivered energy density of 2.6 kJ/liter DCB levels are below 500 ppb. For a delivered fraction of 20% DCB this corresponds to better than 99.99% destruction - for an unoptimized system. As the run progressed, the flow rate was increased to 1.0 l/min. The CO level continued to fall as did the DCB level from the packed bed. Thermocouple data suggest a longer, higher temperature zone within the bed, which increases the residence time of the DCB in the reaction zone. Additional studies will optimize the temperature profile in the packed bed

To assess the feasibility of destroying nitrates with the PBR/SDP system we processed a 3M solution of $NaNO_3$ in water through our small PBR with and without a reducing gas, and analyzed the effluent with a FTIR spectrometer. The preliminary results are encouraging. Figure 6 represents a composite of three separate figures show — FTIR traces of the PBR effluent with different effluent

compositions. Panel (a) shows an FTIR baseline trace of the PBR effluent with argon only. The CO_2, water, etc. peaks are due to residual reactions and contamination from PBR processing of oils. The trace shown in Panel (b) displays the apparent generation of NO_x products with a feed of argon + the 3$\underline{M}$ $NaNO_3$ solution, presumably produced through thermal cracking of the $NaNO_3$. Panel (c)shows an effluent trace after introduction of a (4.8%) I_2/argon mixture into the PBR with the $NaNO_3$ solution. The NO_x peaks are no longer visible. Although further testing and full diagnostic implementation is required for complete verification and assessment system performance and products, these initial runs indicate that the nitrate concentration is reduced by processing through a heated PBR (~900 C) operating with a hydrogen-containing atmosphere. The second stage SDP reactor will remove any NO_x from the exhaust.

The design of a pilot plant is influenced by waste type and treatment throughput. Based on the results discussed above, it is reasonable to conclude that an oil/solvent processing pilot, based on a closed-lopp PBR/SDP design, is straightforward in concept. In conjunction with our work for Rocky Flats, we have explored specific plant designs and based on a modular design. For example a system operating in the range of 3-10 kg/hr would use three or four 15-cm PBRs and two stacks of SDP cells operating in parallel (figure 7). The system is low cost, simple to construct and easy to maintain. The system proposed [8] is shown in figure 8.

V-3 Electron-Beam Treatment

We have configured an existing electron accelerator for technology evaluation studies and demonstrated the destruction of two hazardous organic compounds characteristic of priority mixed wastes. The test bed operates in single-pulse mode (65-ns pulse width), typically producing beam voltages of 1.5-2.0 MeV and doses in the range 4-7 Mrad (40×10^3-70×10^3 Gy). To better understand the waste removal process and explore e-beam treatment scaling issues, we have employed a computer-based chemical kinetics model to predict the expected removal efficiency and to compare standard electrostatic accelerators to pulsed accelerators in terms of reactive free radical production. Typical measured single-pulse destruction for TCE are in the range 90-95%, in good agreement with our model. We have found that radical production efficiencies are significantly lower for high dose rate than lower dose rates (due to radical-radical recombination). However, simulations of pulse-profile effects indicate that a suitable application of repetitive, short-duration pulses (e.g., 10 kHz, 100 ns) gives radical concentrations and organic removals similar to a DC dose (see TABLE 1).

Recent technology developments have lead to a new generation of pulsed linear induction accelerators driven by solid state electrical power conditioning elements. These are considered to be less expensive per unit delivered e beam dose, physically smaller, modular, and more reliable than conventional electrostatic accelerators. It is speculated that these repetitively pulsed accelerators, developed by industry and the national laboratories, will produce better chemical destruction as well, although this remains to demonstrated. At present, we have found no data comparing waste destruction by repetitively pulsed accel erators with that of conventional electrostatic accelerators. Once demonstrated these new accelerators would allow a considerable simplification in treatment plant architecture.

Table 1: TCE Destruction Calculated for Different Doses and Methods of Application

Dose Method	Fractional Destruction (%)	
	100-krad dose	150-krad dose
100-ns pulse	37.5	46.1
1-kHz pulse train	68.0	92.2
10-kHz pulse train	68.8	95.9
DC	69.4	96.8

Notes: initial TCE concentration is 100 ppm; residence time is 0.1 sec.

Potable water or natural water normally contains radical scavengers (e.g., carbonates) that decrease the average radical concentrations and consequently decrease the destruction efficiency. To reproduce the results from the Florida facility, our initial concentrations had to be increased by a factor of 50 because these calculations were based upon a simple, one-step removal mechanism and did not include radical scavenging effects. We have modified our model to account for radical scavengers and more complete destruction mechanisms for TCE and CCl_4. Figure 9 shows the remarkable agreement between model and experiment. This will be particularly important for real wastes (both mixed and otherwise) that will contain scavengers like nitrate and carbonate.

For mixed-waste applicability, we can get some guidance from recent electron-beam irradiation experiments on high carbonate/hydroxide-containing simulants carried out at Sandia [9]. In these studies, it was found that, using a high instantaneous dose rate, the percentage of organic carbon in simulated mixed waste sludge decreased by more than 40% for a cumulative dose of 400 Mrad. Preliminary data from radiolytic experiments carried out on simulants characteristic of real Savannah River wastes by our Florida International University collaborators also show that benzene, phenol, nitrobenzene, and 4-nitrophenol can be removed to a relatively high degree by modest irradiation doses (< 800 krad). These results are encouraging in showing promise for the treatment of real mixed wastes by electron beams. A general survey of the literature also shows that it may be possible for electron-beam irradiation to play a role in the removal of heavy metals from aqueous solutions, as the solubility of Cd, Cr, Cu, and Zn are significantly reduced under modest e-beam irradiation.

VI CONCLUSIONS

Closed loop systems offer definite advantages for treating mixed wastes. Radiolytic treatments are applicable over a wide range of waste streams (liquids, solids and sludges) and the efficacy of silent discharge plasma has been demonstrated, both as a primary and secondary stage, for an expanded list of RCRA and TSCA wastes. An application for an EPA RD&D permit has been submitted to the state of New Mexico for the treatment of LANL wastes using a closed-loop PBR/SDP system. Commercialization of both technologies is promising and industrial CRADAs (with EPRI and others) are being pursued.

VII ACKNOWLEDGMENTS

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CAPTIONS

FIGURE 1. Schematic showing the flat dielectric barrier configuration used to produce silent discharge plasma microdischarges.

FIGURE 2. Schematic of combined SDP/packed bed reactor waste processor used in this work for combustion of scintillation fluids and machining oils with entrained hazardous components.

FIGURE 3. Cost diagram of various waste water treatment methods.

FIGURE 4. Summary of experimental data showing destruction of TCE and CCl_4 by the LANL SDP cell.

FIGURE 5. Effluent concentration as a function of PBR running time. Influent: 3% TCE in machining oil.

FIGURE 6. Data demonstrating PBR destruction of Nitrates.

FIGURE 7. Schematic of existing stacked SDP module containing four planar cells, operating in parallel.

FIGURE 8 Proposed closed-loop system for treating mixed wastes.

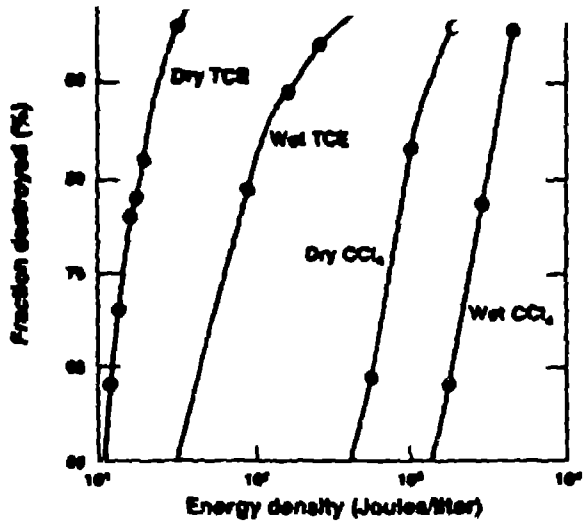FIGURE 9 Comparison of model and experiment for e-beam irradiation of TCE contaminated water.

Dielectric Barrier

Metal Electrode

HVAC

Gas Space

Microdischarge

Fg 1

Reservoir

Gas In

Atomizer

Alumina Beads in Reactive Bed

Furnace

Treated Gas

Water

Electrical Discharge Cell

Water

Heat Exchanger Condenser

Particulate Filter

Condensates

Fg 2

Landfill

Incineration

Deep Well Injection

Biological

Model SCWO

1000

Dollars per thousand gallions

100

GeneSys GPV SCWO

WEDECO UV/O₃

ULTROX UV/O₃/H₂O₂

E-beam (Phenol)

10

Electron-beam

1

Purox pure UV/H₂O₂

0.1

10   100   1000   10000   100000

Organic concentration (ppm)

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CLS 92-377

Fg 3

Fg 4

Fg 5

Fg 7
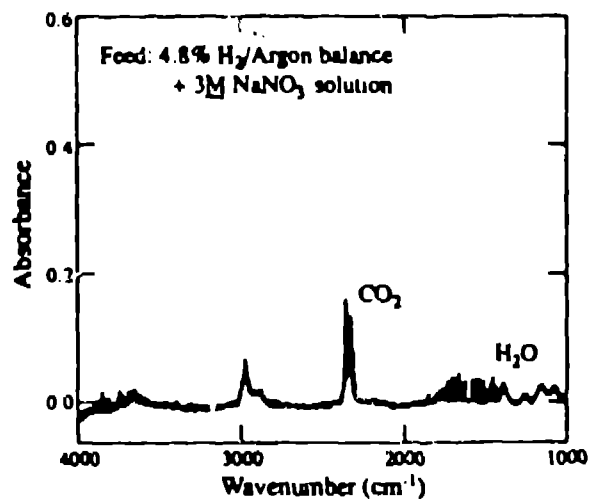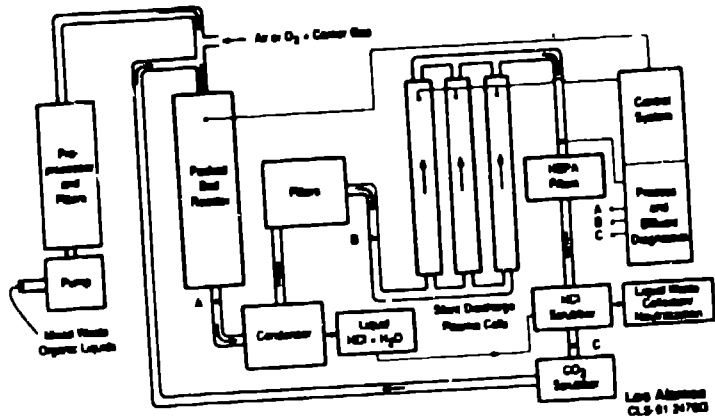
(a) Baseline trace; no $NaNO_3$ in feed
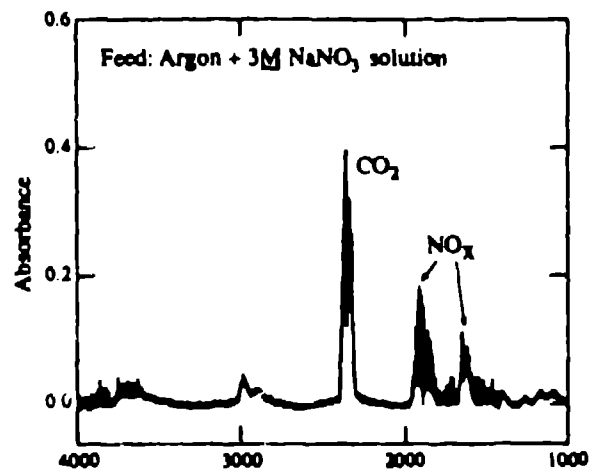
(b) Non-reducing atmosphere with $NaNO_3$ in feed

(c) Reducing atmosphere with $NaNO_3$ in feed
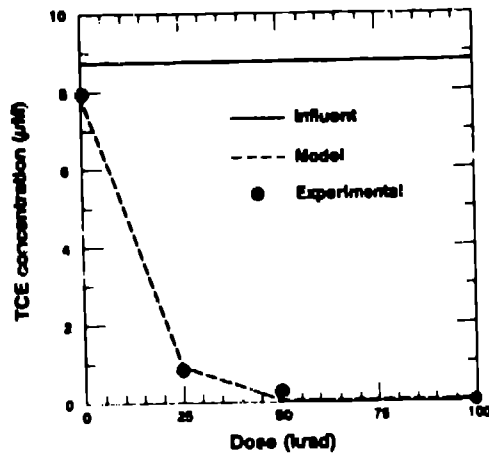
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