



## Project Summary

# Novel and Simple Approach to Elimination of Dilute Toxic Wastes Based on Photoelectrochemical Systems

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This work investigated several basic parameters that are important for extending photocatalytic purification of water contaminated with trichloroethylene (TCE) from the laboratory to the field. Some of these variables strongly influence the decomposition kinetics of the TCE. Parameters investigated were the effect of solution pH, initial TCE concentration, presence of naturally occurring ions, temperature, and presence of "color bodies." It was found that the photocatalytic decomposition of aqueous TCE occurs more than twice as fast in the pH range 6.4 to 9 than in the range 3.4 to 5. The rate of TCE decomposition was shown to be strongly dependent on its initial concentration. Photoelectrochemically nonreactive ions such as  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ , and  $\text{SO}_4^{-2}$  did not play a measurable role in the reaction. Temperature vs TCE decomposition rate constant data exhibited non-classical dependence by yielding an activation energy of about 2 kcal/mole and a pre-exponential factor of about  $1 \text{ min}^{-1}$ . The decomposition rate of TCE was not seriously diminished by the presence of 0.059 weight percent of powdered iron oxide color bodies. Additionally, various photocatalyst materials were also tested but titanium dioxide exhibited superior activity in decomposing TCE. In this laboratory study low intensity irradiation having the

equivalent intensity of 1/4 to 1/5 Solar at AM1 was employed in order to exemplify the feasibility of large scale water purification utilizing natural solar light.

*This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Identification of Problem

TCE is a ubiquitous soil and ground-water contaminant. Its widespread appearance in the United States environment is a result of causal disposal practices and TCE's popularity as an industrial solvent. Once in the soil, its degradation does not occur at an appreciable rate. The action of rain, snow melt, and underground waters percolating or passing through the ground gradually cause the dissolution and migration of TCE from the original site of contamination into the general environment. The contaminant plume contributes to ground and surface water contamination far removed from the original dump site.

TCE and other halocarbons have been shown to be potentially deleterious to animal health and, by extension, human health as a carcinogen and/or mutagen, and it is associated with adverse effects on the heart, liver, kidney, and immune

and nervous systems at elevated concentrations. The adverse effects of low level, long duration ingestion of TCE-contaminated water has most recently and dramatically been litigated. Although the causal relationship between lengthy exposure to extremely small concentrations of TCE and adverse health effects is still being debated by the technical community, clearly it is a problem whose time has come for solution.

### Prior Cleanup Methods

Various methods, both chemical and physical in nature, have been proposed and tested for the cleanup of volatile organics (VOCs) at disposal sites. The cleanup problem can be divided into two general areas of interest; (a) cleansing or removal of soil laden with these organics, and (b) cleansing contaminated waters originally derived from these soils. For example, in one method pressurized steam injected beneath the soil was used to volatilize the organic contaminants. The resulting condensate containing the VOCs was further treated with activated charcoal. However, non-optimal adsorption isotherms for the charcoal-aqueous interphase resulted in inefficient transfer of VOCs from the aqueous phase to the charcoal phase. Other methods of extracting the VOC from the soil into an aqueous phase exist, but the subsequent problem of their destruction has not yet been surmounted. In a method for removing the aqueous VOC, the contaminated water is vigorously sparged with air. The attempt of the system's highly dispersed aqueous phase to maintain the volatiles equilibrium vapor pressure with the unsaturated air results in efficient transfer of volatiles from the water to the air. Photochemical reaction in the atmosphere supposedly results in the degradation of these volatiles. However, this is tantamount to converting water pollution into an air pollution problem. Clearly, the mitigation of contaminants at the source by chemical destruction is the best way to guarantee diminution of pollution in the general environment.

### Photocatalytic Cleanup Method

A new technology, exhibiting dramatic laboratory successes, has been shown to effect the complete mineralization of aqueous chlorinated hydrocarbons such as TCE, trichloromethane, carbon tetrachloride, pentachlorophenol and others into carbon dioxide and hydrochloric acid. In this process, solar or artificially UV irradiated semiconductor powders suspended in the water photocatalytically

oxidize the organic contaminants. Water purification based on this technology has the potential of being uncomplicated and inexpensive. This is because the semiconductor powders only have to be suspended in the water and the suspension provided with sufficient mixing to ensure replenishment of the depleted reactants at the particles' surfaces. Additionally, the powders are inexpensive, recyclable and nontoxic.

The energetic considerations of the process are the following: By absorbing photons having energy equal to or greater than the band gap, the semiconductor creates electron/hole pairs. These carriers can then transfer out of the semiconductor into the surrounding solution to do redox chemistry; alternatively, they may recombine, with the photon energy becoming lost to thermalization. In order for chemistry to proceed, the following thermodynamic conditions must be met: (1) The energy levels of the electron acceptor must be below the conduction band edge. (2) The energy levels of the hole acceptor must be above the valence band edge. (3) Redox couples satisfying the above conditions must exist simultaneously. For titanium dioxide (anatase), the valence band edge is at +3.0 V vs NHE. Holes with this energy have oxidation potentials large enough to attack most organic bonds. The electrons are injected at the conduction band edge at -0.3 V vs NHE where dissolved  $O_2$  is first reduced to  $O_2^-$  and then undergoes reactions resulting in the production of the powerful oxidizing radical species  $HO^-$  and  $HOO^-$ . The photoinduced production of the powerful oxidizing holes and  $HO^-$  and  $HOO^-$  radicals is the reason why titanium dioxide is effective at photodecomposing such a wide class of organic molecules.

The satisfaction of the above three thermodynamic conditions is necessary but not sufficient to ensure that a given reaction will proceed at an appreciable rate. The oxidation of organic molecules in the presence of  $O_2$  is energetically a "downhill" process and should occur spontaneously. This reaction may not occur if the kinetics are slow. However, the reactions proceed rapidly in the presence of irradiated, naked titanium dioxide.

### Objectives of This Study

The experiments in this study were performed with the objective of elucidating the effect of certain basic parameters on the photocatalytic decomposition of aqueous TCE expected under

field conditions. These variables (temperature, ions derived from dissolved minerals, solution pH, and initial concentration, and turbidity) had not previously been investigated. If these parameters exhibited severe practical relations to water purification in the situation existing in this laboratory, this would indicate the use of caution in committing future resources to large scale purification of industrial or municipal water sources by this technology. On the other hand, if this investigation uncovered no serious limitations in the process with respect to the variables discussed above, further large scale studies employing contaminated waters or industrial effluents would be appropriate.

## Results

### Effect of Dissolved Ions

There was no measurable effect on the photocatalytic decomposition rate caused by the presence of  $Ca^{+2}$ ,  $Mg^{+2}$ , and  $SO_4^{-2}$  ions in solution having combined ionic strength of 0.01. The presence of up to about  $1.5 \times 10^{-2}$  M dissolved  $CO_2$  did not appear to affect the decomposition of TCE.

### Effect of pH

The photocatalytic decomposition of TCE occurs at twice the rate in the pH range of 6.4 to 9.2 than in the range of 5.0 to 6.0.

### Effect of Temperature

The photocatalytic decomposition of TCE was not strongly dependent on temperature. For example, increasing the temperature by about 30°C caused a factor of 1.4 increase in reaction rate. A classical reaction having a 25 kcal activation energy would exhibit approximately a 63 fold increase in reaction rate for a 30°C increase.

### Effect of Initial TCE Concentration

The photocatalytic decomposition of aqueous TCE was shown to be strongly dependent on the initial concentration. This means that, if the decomposition rate can be described by an apparent first-order exponential decaying equation, the reaction is not first-order according to the definition. For example, the values for 100 and 20.8 ppm initial concentrations are 0.0169 and

min<sup>-1</sup>, respectively. This means that water contaminated by an initial concentration of 20.8 ppm TCE is purified almost three times as fast as water containing 100 ppm TCE.

### **New Materials as Photocatalysts**

The new materials tested for activity in photocatalytically decomposing TCE were Fe<sub>2</sub>O<sub>3</sub>, SrTiO<sub>3</sub>, WO<sub>3</sub>, and SrZrO<sub>3</sub>. All of these compounds, except for the latter, have been shown to exhibit photoelectrochemical activity. As photocatalysts for the decomposition of TCE, they were all demonstrated to be less active than TiO<sub>2</sub> by several orders of magnitude.

### **Effect of 'Color Bodies'**

By introducing 0.059 wt% of powdered Fe<sub>2</sub>O<sub>3</sub> to serve as a potentially interfering 'color body' into the 0.10 wt% TiO<sub>2</sub> slurry, the photocatalytic decomposition rate for TCE was decreased by approximately 32% of the rate for TCE decomposition in the absence of Fe<sub>2</sub>O<sub>3</sub>. The decrease in the decomposition rate is attributable to light absorption and scattering by the powdered Fe<sub>2</sub>O<sub>3</sub>.

### **Recommendations**

The laboratory results discussed above, obtained with TCE-spiked deionized water, demonstrate that a potential exists for employing photocatalysts for the removal of TCE from contaminated waters. However, the effects of variable light intensity, reactor design, and matrix

constituents in naturally occurring waters must be investigated prior to a pilot-scale investigation.

### **Light Intensity Dependence**

The light employed in these experiments had UV intensities approximately one fourth to one fifth of the solar intensity at AM1. It would therefore appear that a photocatalytic purification system could potentially be operated in most parts of the United States. Assuming the absence of diffusion limitation, the TCE decomposition rate should be directly proportional to the light intensity. However, commercial feasibility may strongly depend on exactly how the TCE decomposition rate depends on the UV light intensity. Although this will depend, to a degree, on reactor design the proportionality assumed above should be demonstrated.

### **Reactor Design**

Diffusion limitation, which occurs when reactants must diffuse through a significant quiescent layer occurring microscopically on the photocatalyst particle or macroscopically within the reactor, must be avoided by the generation of suitable fluid turbulence. The generation of good mixing is energy intensive, however, and will constitute a principal operation expense. Therefore, in order to minimize operating expenses over-mixing in the reactor must be avoided. Rudimentary reactor designs that optimize energy usage for turbulence generation must be investigated.

### **Effect of Matrix Constituents**

An attempt to duplicate some of the water constituents present in naturally-occurring water was made in this project. However, it is impossible to duplicate the dissolved minerals, natural organic products resulting from decayed vegetation and other sources, organic and inorganic man-made pollutants, organic and inorganic particulates, and other substances which occur in natural waters in the laboratory. Experiments should be performed which ascertain the recyclability of the photocatalyst in various naturally occurring waters. This would be another factor affecting this technology's commercial feasibility. Another concern is the presence of other aqueous organics which could compete with the targeted toxicant for the photogenerated oxidative species that effect decomposition. Therefore, the next logical step is to demonstrate that the photocatalytic decomposition of TCE contained in natural waters occurs at an appreciable rate. This successful demonstration would be a very important advance towards applying this technology to the decomposition of aqueous toxicants that pollute environmental waters.

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