

A Feasibility Study of the Destruction of Chemical Weapons by Photocatalytic Oxidation

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The destruction of existing arsenals or deposits of chemical weapons is an important obstacle on the way to the successful implementation of the Chemical Weapons Convention which was opened for signature in 1993. Many approaches have been proposed and none can be seen as a panacea. Each has its merits and shortcomings. In this paper we review the different technologies and propose a new one, photocatalytic oxidation, which has the potential to fill an important gap: a cheap, small, mobile facility for chemical warfare agents which are difficult to transport or are deposited in a remote area. We report some relevant experimental results with this technology for the destruction of chemical weapons.

INTRODUCTION

After many years of negotiation, a convention banning the production, possession and use of chemical weapons was opened for signature in Paris on January 13, 1993.¹ The convention, once it is ratified, will provide a framework and a program for the destruction of chemical weapons by the nations party to it. The framework will cover such topics as definitions of terminology, general rules of verification and verification measures, level of destruction of chemical

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weapons, activities not prohibited under the convention, and investigations in cases of alleged use of chemical weapons. The program will require that countries with chemical weapons shall start their destruction not later than one year after they have ratified the convention, and that they shall complete it within a ten year period. For this period involved countries are required to declare their plans for destruction. These plans have to include a time schedule for the destruction process, an inventory of equipment and buildings to be destroyed, proposed measures for verification, safety measures to be observed during destruction, specification of the types of chemical weapons and the type and quantity of chemical fill to be destroyed, and specification of the destruction method.

Before the convention was opened for signature, only three nations had officially acknowledged possession of chemical weapons: the US in 1987, the USSR, one year later, and Iraq whose stockpile has been destroyed under international control. Quite a few other nations are suspected of possessing chemical weapons. In some cases those weapons have been deposited in their territory by previous invaders: this is the case in Manchuria, where the Japanese allegedly left 3 million munitions behind, or Belgium, where there are still some chemical agents brought by the Germans during the first world war! At the time the convention was signed, the entire extent of the distribution of chemical weapons in the world was not public knowledge.² It is generally expected, though, that when the chemical convention enters into force several nations will report the possession of chemical warfare agents in one form or another which will have to be destroyed. A variety of technologies exist or have been suggested for the disposal of chemical warfare agents but they may not be appropriate for all situations. In this paper we describe a possible approach to the destruction of chemical weapons which has not yet been widely discussed and which may turn out to be very useful in specific instances; e.g., when what is needed is a destruction technology which can fit in a truck and can therefore be very easily moved around.

There are at least two methods of classification of chemical warfare agents: medical and military. For medical purposes, chemical agents are usually classified according to their pharmacological properties. However, it is often more appropriate to classify them according to their overall effects on combat efficiency. Both classifications are shown in table 1. Of all the types of agents listed in table 1 the most lethal are the nerve agents, and it is these agents about which there is most concern in the 1993 convention. In this paper we shall focus on these types of agents, although as table 1 indicates, there are a range of other, less obnoxious agents which also need to be destroyed.

Table 1: Medical and military classification of chemical agents.

Medical Classification	Military Classification
nerve agents (e.g., Tabun, Sarin)	lethal agents (nerve)
lung damaging agents (choking agents; e.g., phosgene and chlorine)	lethal agents (choking)
vesicant agents (blister agents; e.g., sulphur mustard, Lewisite)	damaging agents (blister)
psychotomimetic agents (incapacitants; e.g., LSD)	incapacitant agents (mental)
cyanogen agents (blood agents; e.g., hydrogen cyanide)	lethal agents (blood)
riot control agents (vomiting agents)	riot control agents— incapacitating agents (physical)

The first nerve agent, Tabun, was discovered in 1936 during research into organophosphorus compounds. This class of chemical became, and still is, the most toxic type absorbed into the body through inhalation or skin penetration. The compounds in this class are active in very low dosages, with effects similar to those caused by anticholinesterase drugs. Since the discovery of Tabun, many related compounds have been found, some of which are even more potent. Most nerve agents are liquid organophosphorus esters whose volatilities vary over a range similar to that found when going from petrol to a heavy lubricating oil. They can be classified into three types: Tabun (GA), Sarin (GB) and Soman (GD), and V-agents (VX); the letters in the brackets correspond to the military code use, which is the way they are usually designated. The chemical structures of these organophosphorus nerve agents are shown in figure 1. As can be seen, Sarin and Soman are quite similar, differing only by the ester group, which leads to differences in their volatility. Sarin, which was released in March 1995 by a terrorist group in subways in Tokyo, is the most volatile.

In appearance these nerve agents are pale yellow to colorless, and they are nearly odorless, although Tabun has a faint, fruity odor. They are fairly soluble in water, except for Tabun which is only slightly soluble.^{3,4} They are all very slowly broken down by hydrolysis, yielding less toxic products. Additionally, they can be destroyed by strong alkalis and bleaching powder, as discussed below. Table 2 summarizes some of the physical properties of two of the nerve agents, Sarin and VX.^{5,6}

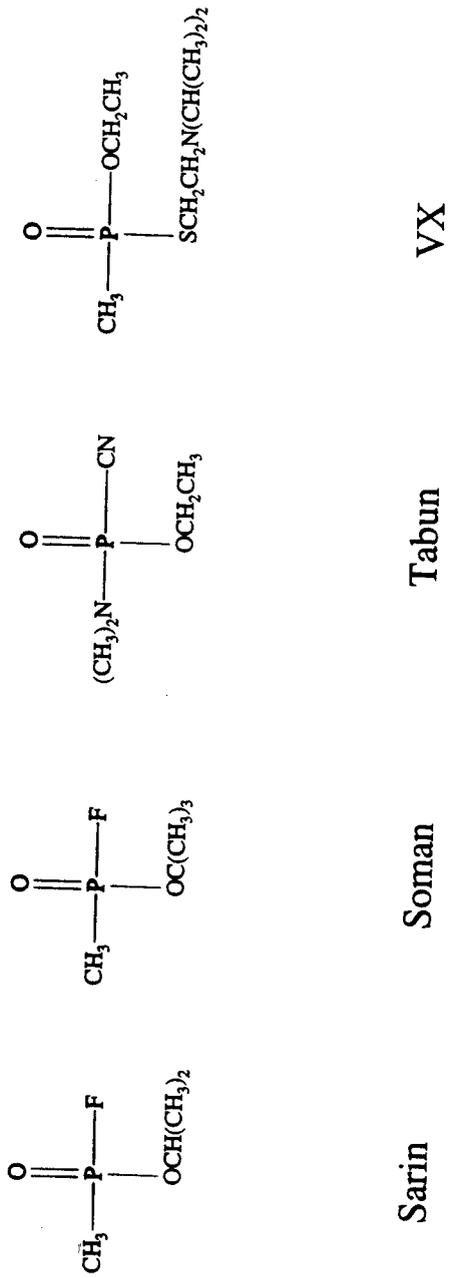


Figure 1: The chemical structures of the most common phosphorus-containing chemical nerve agents.

Table 2: Physical properties of Sarin and VX.

	Sarin	VX
liquid density at 20°C/g cm ⁻³	1.0887	1.0083
solubility in water at 20°C/g (100 g) ⁻¹	100	1-5
volatility at 20°C/mg m ⁻³	12,100	3-18
boiling point/°C	158	298
freezing point/°C	-56	<-51

The destruction of chemical weapons presents significant technical and economic problems. Any destruction technology must take cognizance of a number of requirements and considerations.⁷ For example, a number of process streams need to be treated, such as those coming from the chemical agent and from reaction products, and an integrated system of unit processes will therefore be required for the different steps. Waste streams must also meet environmental standards and agent release must be avoided. The time for development of any technology cannot be extensive since the international treaty deadlines mentioned above need to be met. Finally, the costs of any methods of destruction need to be considered as well. The cost, difficulty and efficiency of alternative approaches vary, but none is a panacea.⁸

We now briefly review most of the methods which have been proposed for the destruction of chemical agents. A more detailed account can be found in reference 6.

OVERVIEW OF POSSIBLE METHODS FOR THE DESTRUCTION OF CHEMICAL WEAPONS

Background

Since 1969, the US Army has disposed of over 7000 tons of chemical warfare agents at their test sites on The Johnston Atoll and at the Tboele Army depot in Utah (CAMDS). Early tests used incineration and/or chemical neutralization to destroy the chemical agent but neutralization was soon abandoned in favor of incineration. The neutralization process was regarded as being too complex, producing too much solid waste and requiring too much capital and

expenditure. Although countries like France, Great Britain or Canada did not have publicly-acknowledged chemical weapons arsenal at the time of the signature of the convention, they have shown active interest in developing neutralization techniques.

Although the US has used incineration exclusively since 1976, in 1984 an National Research Council (NRC) Committee on Demilitarizing Chemical Munitions and Agents considered alternative technologies such as placement in deep oceans, chemical processes, pyrolysis by steam generated with nuclear power, underground combustion or caustic hydrolysis, and high temperature pyrolysis.⁹ It was concluded that incineration was the preferred method. However, a fresh consideration of the importance of alternatives to incineration was prompted by public opposition to the transfer of chemical weapon destruction facilities from the remote site on Johnston Atoll (JACADS) to the US mainland. Concern was also expressed over possible health risks associated with incinerator effluent, the possibility that the facilities would be used for other types of waste disposal once the stockpile was destroyed, the proximity of the destruction facilities to major population centres, and the risk to citizens in communities near chemical weapons storage sites during munition transport from storage igloos to the on-site incinerator facility. Greenpeace sponsored a report in 1991 reviewing biological, chemical, photochemical, electrochemical and thermal processes as alternatives to incineration and suggested that a range of techniques be combined to manage the various components of the chemical weapon stockpile.

In 1992, the NRC Committee on Alternative Chemical Demilitarization Technologies was set up after an instruction from the US Congress to recommend disposal technologies for all sites as alternatives to the established "Baseline Technology" (i.e., incineration). The primary task of the committee is to objectively characterize alternative technologies, assess their state of development, identify their advantages and disadvantages for chemical demilitarization, and identify the R & D they would require if they were to be used in demilitarization.

The language used in the Chemical Weapons Convention does not restrict the destruction technology as long as it converts chemical agents irreversibly to a form unsuitable for the production of chemical weapons and renders munitions and other devices unusable. As a result, the NRC committee proposed two strategies for demilitarization: Strategy 1 is on-site disassembly and agent detoxification to a level that meets treaty demilitarization requirements and permits transportation to another site or continued local storage of residues, and Strategy 2 is conversion of agents and disassembled weapons to salts, carbon dioxide, water, and decontaminated metal.

At the moment, the US Army has achieved the objectives of the second strategy by means of their "Baseline Technology" which is component disassembly of munitions, followed by incineration and treatment of the off-gases by a pollution abatement system. In particular, the chemical weapons are treated using a four stream process. The munitions are transported from storage to the destruction facility, where they are received in an unpacking area. Unpacking munitions, draining agent, and disassembling weapons produces four primary waste streams: (1) dunnage (packing materials); (2) energetics (explosives and propellants); (3) metal parts; and (4) liquid agents. These streams are processed in separate incinerators. Each of the four furnaces is equipped with an afterburner and a pollution abatement system to clean exhaust gases which then exit through a common stack.

Most of the technologies which the NRC committee is considering as alternatives to this "Baseline Technology" are, in fact, unit processes. These technologies represent only part of a system of processes required to demilitarize the US stockpile. For example, separation of the agent itself from munitions and explosives, chemical neutralization of the agent, oxidation of the neutralization products, and oxidation of remaining agents on the metal parts are all unit processes which together might represent an alternative demilitarization system. Such alternative demilitarization processes might partly or wholly replace, or be used in addition to the current "Baseline Technology" for handling agents, energetics, metal parts, dunnage, or any other waste streams potentially contaminated with agents.

There are, though, a number of factors which need to be taken into account when considering alternative strategies for chemical weapon demilitarization. For example, chemical warfare agents can be found in a variety of environments. One possibility is inside a warhead, in which case the destruction requires either extraction of the chemical warfare agent from the warhead or the destruction of the whole warhead. The agents can be stored in containers, but in some instances the containers have deteriorated and this makes the retrieval and transport of the chemical warfare agents difficult. In other instances transport is less problematic. Thus, mobility and environmental impact of any destruction technology are important considerations. Another aspect of environmental impact is that all chemical agents are composed of carbon, hydrogen, oxygen, and some contain fluorine, nitrogen, phosphorus or sulfur. Therefore, all of these elements will be present in the waste streams independent of the choice of destruction technology. Ideally, carbon dioxide and water would be the final products from destruction of compounds containing carbon, oxygen and hydrogen while the need to find environmentally acceptable sinks for heteroatoms favors relatively insoluble calcium

salts, such as CaF_2 , CaSO_4 and $\text{Ca}_3(\text{PO}_4)_2$, which would be appropriate for landfill as final waste products. However, because these salts are only readily formed under alkaline conditions, many alternative destruction technologies would require a pH adjustment stage. Moreover, in many cases, the salts must be dried before they can be sent to landfill and this produces contaminated waste streams.

Other aspects which need to be taken into consideration for any chemical weapon demilitarization technology are the final form of the agent after treatment (degree of destruction), throughput, cost, maturity and operationability or degree of development of the technology, and the efficiency of the method. All of these factors have to be evaluated for a variety of situations where a technology has to be applied, and, although there are a wide range of possible technologies, when they are evaluated against the criteria given above, it appears that no one technology can solve all the problems. In particular, chemical weapon demilitarization is not supposed to be a long term problem. Therefore, only technologies which can demonstrably be made operational in the short term qualify. As a result, only a few technologies can realistically be considered as potential contributors to the solution of the chemical weapon demilitarization problem.

A very brief review of such technologies is given below. More detailed information about the various techniques is given in Appendix A.

Approaches to Chemical Weapon Demilitarization other than the "Baseline Technology" (i.e., Incineration)

Strategy 1: Detoxification

In this category are included "low temperature liquid phase detoxification" and "wet air oxidation (WAO)."

Strategy 2: Mineralization

In this category are included "supercritical water oxidation (SCWO)," "low temperature, low pressure oxidation processes," and "high temperature, low pressure pyrolysis processes."

A variety of other technologies have been mentioned and proposed for chemical weapon destruction (see Appendix A) but none has become a serious candidate. They are either too immature yet to have a chance to be developed in time, or have disadvantages in comparison with more mature technologies.

One technology which was discarded from the NRC report for political reasons, but which belongs to any serious broad range technical discussion of chemical weapon demilitarization, is the use of underground nuclear detonations.^{10,11} Although a deeper technical analysis reveals that this approach is not devoid of problems, it still has the potential to help in the destruction of large arsenals. The two most obvious advantages of this approach are, first, that given the physical conditions created by a nuclear explosion large quantities of chemical agent can be atomized in an instant, and, second, there would be no need to dismantle live munitions, although they would still have to be transported which is the most delicate and expensive phase of chemical warfare destruction. Although the idea seems to be a non-starter in the West, the nuclear option may be attractive to Russia. It has the advantage of leading to the destruction of large quantities of chemical weapons in a relatively short time and it may still be the least inconvenient solution for destruction of large quantities of chemical warheads. But much detailed analyses needs to be done before nuclear destruction of chemical weapons could be considered a safe, clean and unambiguously cost-effective approach.

SUMMARY OF DESTRUCTION METHODS

While there are quite a number of possible technologies which could be applied to the problem of chemical weapons destruction, very few of them have actually been employed, and even with those that have, there are drawbacks and limitations.

Methods proposed under Strategy 1 would not lead to adequate destruction of the chemical warfare agents since there would not be a satisfactory level of destruction of the P-Me bond. For the more aggressive methods proposed under Strategy 2, there are the problems associated with incomplete conversion of the organic species to inorganic compounds; i.e., incomplete mineralization of all the elements in the original agent. Consequently, in many of the high temperature combustion or pyrolysis processes, an afterburner is required to completely mineralize waste gases. Furthermore, there are problems which are specific to particular methods. For example, corrosion of the reactor lining by fluoride ions is particularly a problem for SCWO whereas sorption of chemical agent onto microbial cell mass or immobilized enzyme support matrices is a problem specific to biological methods.

The realistic possibilities for the near future appear to be incineration along the lines of the JACADS program and perhaps the use of underground explosions in the exceptional situations which pertain to Russia. Both of these

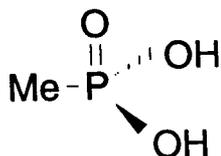
techniques are costly and have rather rigid requirements, and neither is conducive to allowing a mobile method of destruction. And even if they could be used for the destruction of the US and most of the Russian arsenals, they may be less suited to destruction of arsenals in other countries. For the latter use especially, there appears a need to add to chemical weapon destruction methods, technologies which do not require expensive chemicals or capital equipment, which are environmentally friendly, and which can be used in mobile modes to allow the treatment of non-transportable stocks of chemical weapons.

To this end, we have explored the use of photocatalytic processes to see whether they could fill a gap in the techniques of chemical weapon demilitarization and could be made operational in time for the implementation of the convention. This approach is an extension of the use, mentioned already, of UV light to generate OH^\cdot radicals. The method suggested earlier was to decompose oxidizing agents such as O_3 or H_2O_2 . This process requires, however, a continual supply of these reagents. The photocatalytic approach studied here consists of generating OH^\cdot in situ by photooxidation of water on a catalytic surface. Before describing the results of our preliminary investigations, we first outline the underlying chemical physics of heterogeneous photocatalysis.

PHOTOCATALYTIC OXIDATION

The physics of the process is described in some detail in Appendix B. In a nutshell, UV is used to illuminate a semiconductor (titanium dioxide). UV photons have enough energy to excite electrons into the conduction band of titanium dioxide and thereby create an electron-hole pair. If the electron is removed before it has time to recombine with the hole, the energy of the hole is then great enough to oxidize almost any organic compound and, in particular, to break the P-C bond.

There is considerable work being done to explore the possibility of using this principle for the treatment of waste water.¹² Here we report on experiments aimed at investigating the prospects of the approach for the oxidation of nerve agents. Because of the inherent dangers in using actual nerve agents we have chosen to use methylphosphonic acid (MPA) as a test chemical.



Methylphosphonic acid

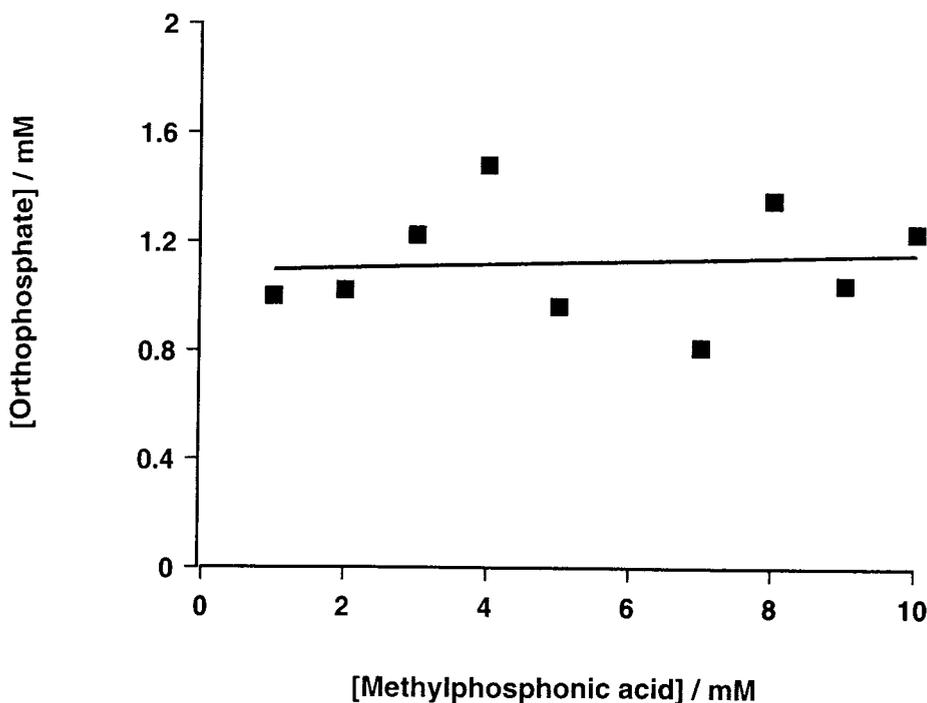


Figure 2: The yield of orthophosphate as a function of the initial methylphosphonic acid concentration for 0.5 g dm^{-3} titanium dioxide and after 45 minutes of irradiation.

MPA has strong similarities with Sarin, the latter being obtained by substituting one OH by F and one H by iso-propyl. The feasibility of destroying the P-C bond in the butyl, benzyl and phenyl homologues of MPA has already been demonstrated.¹³ However, the destruction of the P-Me bond, the most persistent remnant of the chemical nerve agents after degradation, has not been reported. We would expect the destruction of the methyl phosphonic acid to be similar to that of the nerve agent, although, of course, different by-products would be produced. Nevertheless, achieving the cleavage of the P-Me

bond would strongly suggest the potential application to more lethal materials. The photochemical oxidation was effected by simultaneously irradiating and aerating aqueous dispersions of titanium dioxide containing MPA. The extent of the reaction was then determined by detecting the concentration of inorganic phosphate (orthophosphate) generated by the reaction; details of this procedure are given in Appendix C.

A detailed technical discussion of our results and their scientific implications can be found in Appendix D. Figure 2 shows a plot of orthophosphate yield against initial MPA concentration. The reaction appears to be zeroth order in MPA. Figure 3 shows the yield against titanium dioxide concentration. The plots for the two different MPA concentrations superimpose, in agreement with apparent zeroth order dependence of this species, as just discussed. Figure 4 shows a typical plot of yield as a function of irradiation time. These results clearly show that titanium dioxide catalyzed photooxidation of MPA can be achieved by irradiating aerated aqueous dispersions of titanium dioxide containing the organic species. In particular, 4 ml samples of methylphosphonic acid of concentrations $0.5 \text{ mM} \leq [\text{MPA}] \leq 10 \text{ mM}$ were completely mineralized to orthophosphate in less than 100 minutes by irradiating with the 200 W mercury-xenon arc lamp.

However, while it is clear that photocatalytic oxidation can effectively destroy and mineralize an organophosphonic acid similar to those used as nerve agents such as Sarin, Tabun, etc., several important questions have not been addressed in our studies and need to be answered. For example, "How complete is the photocatalytic oxidation?" Or, in other words, how many '9s' of conversion can be achieved by the process? This aspect is under active consideration as is the optimization of the process for the destruction of MPA. Further results will be published shortly. It can be noted here, though, that since a treated sample can be recycled repeatedly, it should be possible to achieve a high degree of destruction. Other points which need to be considered concern the rate of destruction which can be achieved and the practicality of applying this technique to the large scale destruction of nerve agents.

First, we can consider the relative ease of mineralizing nerve agents compared to the mineralization of MPA. As has been mentioned earlier, the major obstacle to be overcome in destroying most nerve agents is that of breaking the P-C bond. The presence of F in, for example, Sarin and Soman will weaken the P-Me bond and hence facilitate its rupture. However, the effect of fluorine on the photocatalyst is not known and needs to be investigated. If there is a poisoning effect then this would have to be overcome, possibly by hydrolysis of the P-F bond prior to photocatalytic treatment for the much more difficult P-C bond cleavage. The generation of fluoride ions should not present a problem

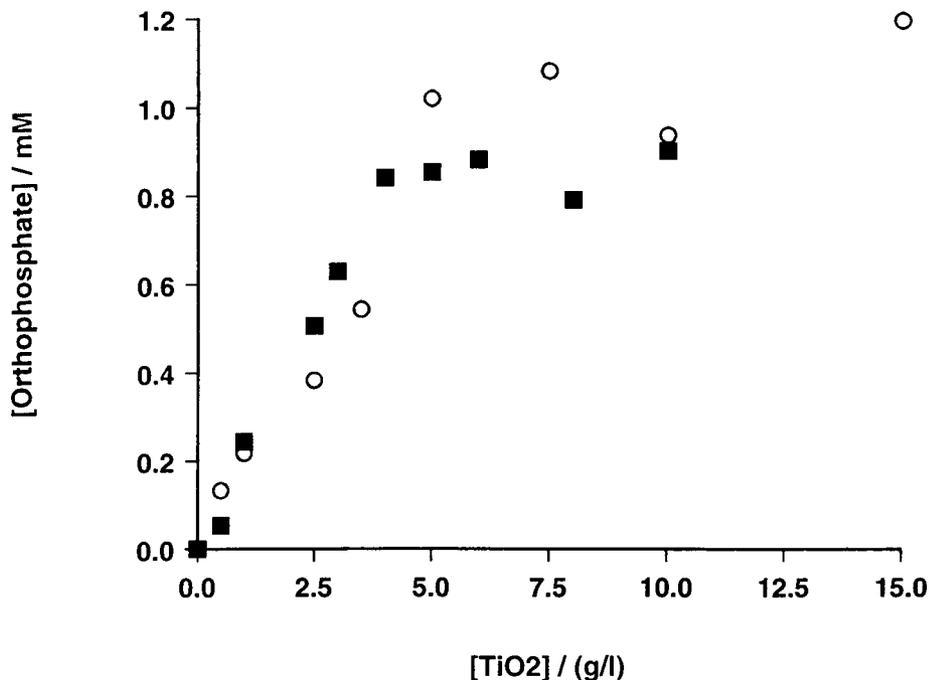


Figure 3: The yield of orthophosphate as a function of titanium dioxide loading for initial MPA concentrations of ■ 1 mM and ○ 0.2 mM and or 10 minutes of irradiation.

for either disposal or reactor etching provided that treatment is undertaken in dilute solution and, in any case, the glass walls of a photocatalytic reactor would be protected from fluoride etching by titanium dioxide. Other substituents such as CN, esters and thioesters will readily hydrolyze and undergo complete mineralization. Therefore, at least chemically, the concept of photo-oxidation should be applicable to nerve agent destruction.

Let us now consider the feasibility of destroying, say, one ton of nerve agent per annum. Figure 4 shows that without any significant attempts at optimization it has been possible to destroy 1 mM of MPA dissolved in 4 cm³ in a period of ~10 minutes. Assuming that the degree of destruction of MPA achieved in our experiments is an acceptable standard, this corresponds to

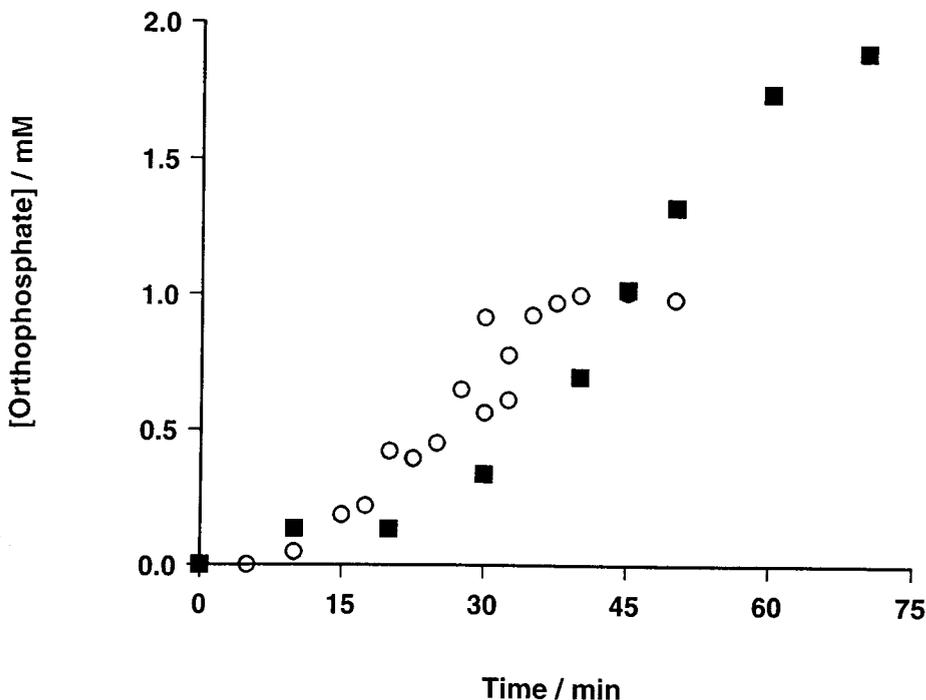


Figure 4: The yield of orthophosphate as a function of irradiation time for initial MPA concentrations of 0.1 mM and ■ 2 mM and for 0.5 g dm^{-3} titanium dioxide.

$\sim 0.5 \text{ mg}$ in 10 min. To destroy one ton per year, or $\sim 2 \times 10^4 \text{ mg}$ in 10 min, will therefore require a scale-up of 4×10^4 . If it is assumed that the efficiency of destruction cannot be improved, for example by improving the input of light into the reactor or by using a more powerful light source—and this is perhaps being overly pessimistic—then the only way to increase the rate of destruction is by enlarging the reactor. The volume of liquid treated in this study was 4 cm^3 held in a boiling tube of about 1.5 cm diameter. Thus lengthening the reactor tube to 1.25 m gives a factor of about 50. Doubling the reactor tube diameter and having the UV light all around the reactor circumference will lead to a total throughput increase of approximately 400. One hundred reactor tubes would then give the required amplification in destruction rate of 4×10^4 .

This number of tubes in a square array of 10 x 10 with UV lights arranged appropriately would occupy a total area of $\sim 1 \text{ m}^2$. The total volume required to accommodate the reactor array and lamps would not be much greater than 1 m^3 . This is a small volume which could easily fit into a mobile system, and this feature could be of great importance from an environmental point of view since it would not require transport of the nerve agents themselves.

The lamp used for the experiments described in this paper was 200 W. The arrangement of the lamps with respect to the meter length tubes will determine the total power required; it will be about 15 kW. From a three phase 250 V supply this will need about 20 A per phase, which is not unreasonable and could readily be provided on site for a mobile reactor. Additionally, since the preliminary experiments have been with a very weak solution of the organophosphonic acid, it will be necessary to dilute the nerve agent. Taking Sarin as an example, with MW = 140 there are ~ 7 moles in a liter. So a dilution factor of ~ 3500 will be required, although a lower factor may be required if the net rate of destruction can be enhanced. An advantage, though, of working with very dilute solutions is that the effluent will be correspondingly dilute and will require very little, if any, additional treatment before discharge to waste.

FINAL COMMENTS

In conclusion, one can say that our experiments demonstrate that photocatalytic oxidation has the potential to be the basis for a cheap, versatile and very mobile system of destruction of non-transportable chemical warfare agents, which are located at scattered sites in not too large quantities. This approach would be appropriate in instances where incineration, preceded or not by detoxification, would not address the problem. The technology described in this work is the only technology (with the possible exception of the plasma torch developed by Westinghouse¹⁴) that has a realistic potential of dealing with such cases.

Just how important having a mobile system could be has recently been highlighted by the news that in the US leaking chemical weapons will pose a significant hazard over the next decade and that the US army will have to develop an emergency plan for disposing of rockets and warheads.¹⁵ A mobile system could also be valuable in disposing of the small amounts of nerve agents which have recently been uncovered in Japan in the possession of a religious group.

In the particular situation that one expects to find in countries where chemical agents have been deposited by past invaders,¹⁶ this technology may offer the best hope for a flexible, mobile, small scale, and cheap chemical weapon destruction system. Easy access to the technology may also remove an important obstacle for some Third World nations to join the chemical weapon convention.

APPENDIX A: REVIEW OF DIFFERENT METHODS OF CHEMICAL WEAPON DEMILITARISATION

A.1 Strategy 1: Detoxification

Low Temperature Liquid Phase Detoxification

This generally refers to neutralization by caustic hydrolysis. Chemical neutralization of Sarin with aqueous sodium hydroxide liberates sodium fluoride reducing toxicity considerably, and although neutralization of VX by aqueous sodium hydroxide does not effect a similar reduction in toxicity, toxic products resulting from the neutralization process are readily destroyed by the addition of hydrogen peroxide. Chemical neutralization, though, does not break the P-C bond which is the most difficult bond to form in the manufacturing process.¹⁷ Since the energy of a P-C bond is not greater than that associated with other phosphorus bonds (e.g., the P-C bond energy is $\sim 300 \text{ kJ mol}^{-1}$, and the P-O bond energy is approximately the same, while the P=O energy is 500 kJ mol^{-1} and the P-F bond energy is $\sim 460 \text{ kJ mol}^{-1}$), breaking the P-C bond tends to require a much higher activation energy, especially when the alkyl is methyl, and as a result the bond is very robust.^{18,19} This characteristic of the bond may, in fact, be used for the detection of the production of chemical agents in waste streams since the P-Me bond will appear in the degradation products of the compounds of interest in the form of MPA and other derivatives.²⁰

Wet Air Oxidation (WAO)

In WAO, organic materials are oxidized in a dilute, aqueous, liquid matrix at temperatures of 200° – 300°C ; the pressures required to maintain a liquid phase are in the range 16–186 bars. In this process, air (or air enriched with oxygen) and an aqueous feed mixture are compressed, heat is added as needed and the mixture flows to a reactor. In WAO, compounds containing phosphorus break down rapidly but yield a substantial amount of low molecular weight material that then oxidizes much more slowly; the P-C bond is believed to react slowly.

A.2 Strategy 2: Mineralization

Supercritical Water Oxidation (SCWO)

Supercritical water is an attractive medium for oxidation reactions as it offers high solubility for both organic compounds and oxygen and because the usual transport and mixing problems associated with reaction in two or more phases are absent. The properties of supercritical water (i.e., water at temperatures

above 450°C and pressures above 250 bars) are quite different from those of liquid water at ambient conditions. They resemble more closely those of steam. The dielectric constant for liquid water is about 2 at 450°C and 250 bars, and the ionic-dissociation constant falls from 10^{-14} to a value of about 10^{-23} . Supercritical water acts as a nonpolar fluid. Its solvation properties resemble those of a low polarity organic fluid and whereas hydrocarbons are highly soluble, inorganic salts are almost totally insoluble. Heteroatoms converted to inorganic compounds in high oxidation states can be precipitated as salts with the addition of some base. Reaction rates can be rapid and oxidation can proceed to completion, in contrast to the WAO process.

Low Temperature, Low Pressure Oxidation

A - Chemical Oxidation

Chemical oxidation means the addition of powerful oxidants such as peroxydisulfate salts, organic peroxy compounds, chlorine dioxide, hydrogen peroxide and ozone. For example, the Lawrence Livermore Laboratory has proposed the use of electrochemically generated peroxydisulfate, although this process produces a considerable waste stream of sulfate and sulfuric acid.

B - Electrochemical Oxidation

Mediated electrochemical processes generate reactive ions such as Ag^{2+} , Co^{3+} , or Fe^{3+} , which can react with an organic compound and water to produce carbon dioxide. Heteroatoms in organic compounds may also be oxidized: sulfur to sulfate, phosphorus to phosphate, etc. One disadvantage, though, is that the estimated electric energy required to destroy one ton of Sarin is 800kW for 24 hours, which is several times larger than the heat of combustion of the agent. Another disadvantage is that the organic material being decomposed may undergo a polymerization resulting in insoluble materials. However, a recent bench-scale study has achieved a 99.9999 percent destruction efficiency with Sarin.

C - Biological Oxidation

The most promising approach appears to be direct detoxification of stockpiled organophosphorus nerve agents using cellular or enzyme-based reactions, biodegradation and mineralization of reaction products from chemical destruction of the nerve agents Sarin and VX, and biodegradation used as a final polishing process for aqueous effluents from other detoxifying processes such as chemical or thermal oxidation. Recently, an organophosphate hydrolase has been isolated that can destroy munition-grade Sarin in less than one hour at concentrations up to 1.1M. Several enzyme and cellular systems have been identified that are capable of cleaving the P-C bond and degrading the meth-

ylphosphonate products of agent hydrolysis.²¹ However, residual toxicity from the partitioning or sorption of agents onto microbial cell mass or immobilized enzyme support matrices must be considered. In addition, the capability of enzyme or cellular-based processes to completely degrade agents (e.g., to greater than 99.99 percent destruction efficiency) has not been demonstrated in a practical reactor system. Furthermore, any biological treatment of process waste streams would most likely require a prior reverse osmosis or evaporation stage to remove the salts accumulated from pH neutralization and the halogen ions released from agent degradation.

D - Processes Mediated by UV Light

UV radiation decomposes ozone or hydrogen peroxide to hydroxyl radicals which, in turn, can oxidize most organic compounds. Not much has been published on treatment by this method of concentrated organic wastes or chemical warfare agents, and the best application of this technology would appear to be for the final treatment of dilute solutions after bulk destruction and oxidation have been accomplished by other means.

High Temperature, Low Pressure Pyrolysis Processes

A - Molten Metal Processes

Metals, such as copper, iron, or cobalt are used at ~1650°C to decompose organic compounds thermally and dissolve inorganic materials to form a slag. The material to be destroyed is pumped into the bottom of the vessel containing the molten metal. The waste material dissociates into small molecules or atoms and is distributed throughout the bath. The gases formed are emitted to an air pollution control system in which oxidation is completed and solids are removed. A molten inorganic slag, insoluble in the liquid metal rises to the top and is skimmed off. The baths are potentially capable of destroying chemical agents and energetics. They could melt metal parts while destroying any agent residues on them. However, the metal furnace does not eliminate the need for a combustion process; the product gases would be oxidized in a separate unit. These gases would likely be very dirty, containing soot from the metal pyrolysis and possibly some slag particulate matter.

B - Plasma Arc Torches

These generate ionized plasmas at temperatures of 3000–12000K. At such high temperatures, waste materials can be completely pyrolyzed. Organic compounds in the presence of a small amount of oxygen are oxidized to a product gas consisting principally of hydrogen, carbon monoxide, carbon dioxide, and small hydrocarbons such as methane, ethene, and ethane. The source of oxygen may be steam or air used for the plasma. The gaseous product is a fuel

with a low heating value, which would be burned with added air. One advantage of plasma arc over incineration is that it acts as a two-stage system: first, as a detoxification reactor (the plasma arc), and second, as a destruction reactor (such as a burner or catalytic oxidizer). Arc furnaces have very short start-up times (of about 5 minutes to stable operation) and shutdown times. This feature is well suited to the decontamination of metal parts.

C - Gasification

This is the process by which partial oxidation of pulverized coal with steam and air produces a fuel gas. It has been proposed that chemical warfare agents be mixed with the feed to the gasification reactor and thus, it would be destroyed by a two-stage process: an initial steam reforming at high temperature followed by combustion. Common to many high temperature high pressure processes, it is envisaged that attack on refractory linings by acidic reaction products, such as HF, might be a problem.

D - "Synthetica" Detoxifier Process

In this process, the feed material is evaporated into high temperature steam (700°C), where pyrolysis and some reaction with steam occurs. A promising evaporator for applications to chemical warfare agents is the moving bed evaporator, which consists of a descending bed of uniform-sized solid balls containing a reactive alkaline material which would partially neutralize the agent. The vapor leaving the evaporator, consisting of remaining organics, steam and products of the steam reforming process, passes to a detoxification reactor. In this reactor the material is heated electrically to a higher temperature, typically about 1300°C. The final gas stream is neutralized. The principal advantage of steam reforming lies in the product distribution obtained. The reaction with steam leads to different products than those obtained by the reaction with oxygen. Equilibrium calculations indicate that troublesome products such as NO_x, SO_x and solid particulates are not formed at the very high reforming temperatures used.

High Temperature, Low Pressure Oxidation

A - Catalyzed Fluidized Bed Oxidation

This method uses a fluidized, granular solid as a heat transfer medium. The material is kept in suspension by the gas flow, which is primarily air. The bed acts as a well-mixed reactor with high thermal inertia. Temperatures are kept relatively low, at roughly 800–1000°C, reducing potential emissions of NO_x, dioxins, and CO. Slurries of organic materials with up to 25 percent water have been successfully destroyed in a commercial size unit. To achieve high levels of destruction with a fluidized bed, an afterburner would be needed to

complete the destructive process. Fluidized bed equipment can be used to treat both hydrolysis products and explosives. Solids such as shredded dunnage and metal parts could also be handled. Importantly, when the bed is lime or dolomite, a large fraction of the acidic components are removed.

B - Molten Sodium Carbonate

At 900°–1000°C the melt is used with air as a medium in which to oxidize mixtures of combustible solids, organic liquids, aqueous solutions, and/or slurries. Acidic products from agent oxidation would react to form salts that would dissolve in the molten salt bath. The gaseous effluents would need to be filtered to remove some of the fine particulates formed in the bath, and the process would probably require an afterburner. Alternatively, a molten salt counter-current tower design could be used as an afterburner for the removal of acid gases in waste streams from other processes.

C - Catalytic Oxidation

This process uses an oxidation catalyst with natural gas to heat the catalyst to an operating temperature of about 500°C. This technology is usually applied to very dilute gas streams for final cleanup. With some modification, possibly with electrical heating, it could be used to replace the "Baseline Technology" combustion-based afterburner.

Other Technologies

Some other techniques not directly related to Strategies 1 or 2 are being considered as alternatives to "Baseline Technology," but their suitability is uncertain because of a lack of understanding of both the chemistry involved and of the nature of the reaction products. In each case, no destruction of chemical warfare agents have been reported, but the argument for their consideration is that they have been successfully used in the treatment of other environmental pollutants (e.g., PCBs). In particular, the use of ionizing radiation and reaction with hydrogen and sulfur are mentioned in the report by the NRC committee.²²

Penetrating Ionizing Radiation

X-rays, ⁶⁰Co gamma radiation, and radiation from spent nuclear fuel elements, can be used to rearrange the chemical structure of compounds and this technique is being actively investigated. The approach could possibly be applied to weapons containing chemical warfare agents. This process could occur within loaded weapons, such as artillery shells, land mines, and rocket warheads that contain agent and, therefore, could potentially detoxify agent before removal.

Hydrogenation

Organic materials containing a high concentration of sulfur are commonly treated with hydrogen to eliminate the sulfur, as H_2S . The hydrogenation process is now being developed to attack chlorine similarly. Presumably other heteroatoms, such as P and F, would also be reactive with hydrogen under appropriate conditions; this remains to be demonstrated.

The Adams Process

This process relies on the reactivity of elemental sulfur to destroy organic materials at temperatures of 500° – $600^{\circ}C$. Gaseous and solid products are formed. Gases such as CS_2 , COS , HCl , and H_2S require recovery or further destruction. The solid formed is a high molecular weight carbon-sulfur material of uncertain composition, probably containing some of the heteroatoms (P, Cl, F, or O) of the original organic materials.

APPENDIX B: HETEROGENEOUS PHOTO-CATALYTIC OXIDATION

Semiconductor photocatalysis has its origins in the substantial research effort, in the seventies and early eighties, into photoelectrochemical systems and micro-photoelectrochemical systems for solar to chemical energy conversion.²³ The efficacy of heterogeneous photocatalysis for the total oxidation of organic species has been previously demonstrated.^{24,25,26,27,28} This photocatalytic activity is sometimes undesirable, as in the breakdown of binding agents in paint, and sometimes desirable, especially in the decomposition of toxic contaminants.²⁹

Oxidative decomposition is usually carried out using suspensions, or sometimes fixed beds, of semiconductor particles in aqueous solutions irradiated with near-UV light and in the presence of O₂ leading to the complete mineralization of the organic compounds. Owing to their relative stability, oxide semiconductors are preferred for this kind of application, and, among them, the most widely used is titanium dioxide which has been shown to be an effective photocatalyst for the oxidative degradation of a wide range of organic products.³⁰

A semiconductor is a material characterized by a discontinuous distribution of energy levels. A gap exists between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The HOMO and LUMO orbitals are also called valence and conduction bands respectively. By thermal or optical excitation, electrons (e⁻) can be excited and promoted to the conduction band producing an equal number of holes (h⁺) in the valence band. Once promoted, the electron within the conduction band moves randomly through the crystal structure and at some stage recombines with a hole and returns to the valence band of one of the atoms. When this recombination process occurs, the hole and electron are no longer free. The average time that a hole or an electron exists between production and recombination is known as the lifetime of the charge carrier. Lifetime values range from 10⁻⁹ to 10⁻⁶s.³¹ Electrons in the conduction band and holes in the valence band have a particular energy with respect to species in solution. Their reactivity towards such species can be described energetically by a redox potential, which is a measure of the electron affinity of a redox system. The more positive the redox potential the greater the affinity for electrons, or the lower the tendency to give up electrons.³²

There are many different semiconducting materials which are readily available, but only a few are suitable for catalyzing the photomineralization of a wide range of organic pollutants. In the case of water purification, a catalyst must be photoactive, be able to utilize near UV or, preferably, visible light, be biologically and chemically inert, and be photostable (i.e., not liable to photo-

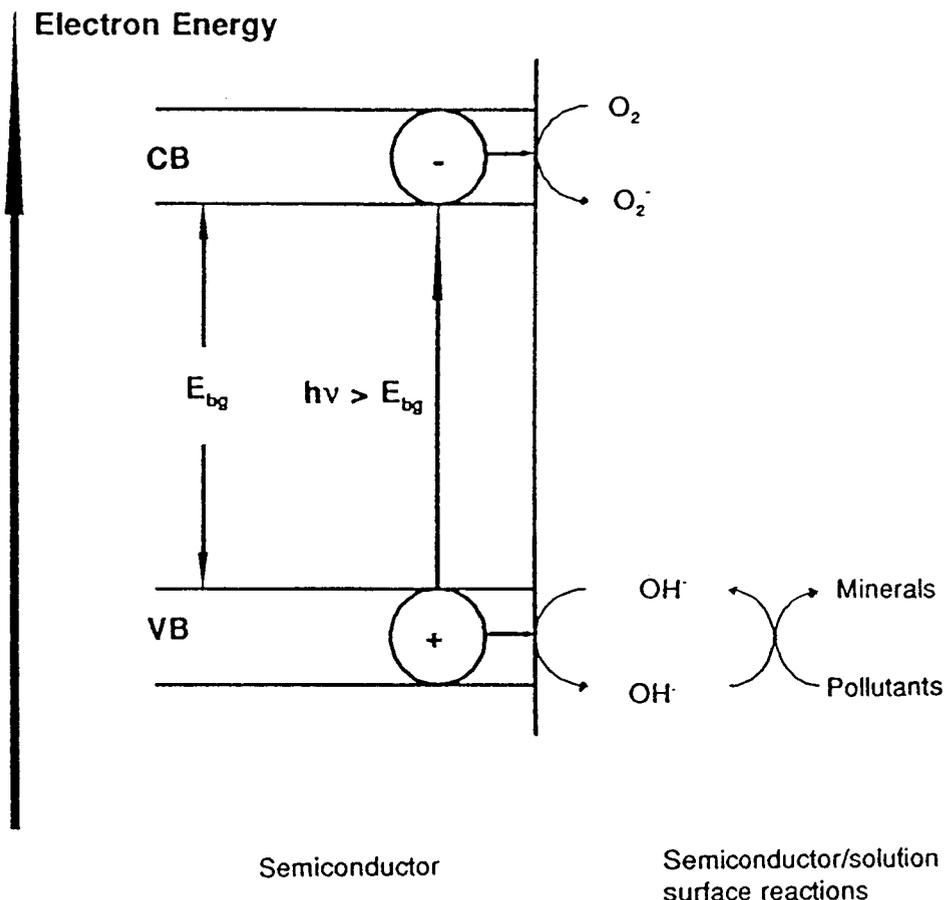


Figure 5: Schematic representation of the band energy model of the overall process of semiconductor photocatalysis for water purification.

anodic corrosion) and cheap. In order for a semiconductor to be photochemically active as a catalyst for mineralization, the redox potential of the photogenerated valence band must be sufficiently positive to generate adsorbed OH^\cdot radicals which can subsequently oxidize the organic pollutant, and the redox potential of the photogenerated conductance band electron must be sufficiently negative to be able to reduce O_2 . A schematic representation of the energetic associated with the overall process is given in figure 5.

From different semiconductor photocatalytic investigations, titanium dioxide appears to be the most active.³³ In addition, although titanium dioxide is only a UV absorber (band gap energy $E_{bg} = 3.2$ eV), it is cheap, insoluble under most conditions, photostable, and non-toxic. In figure 6, the photocata-

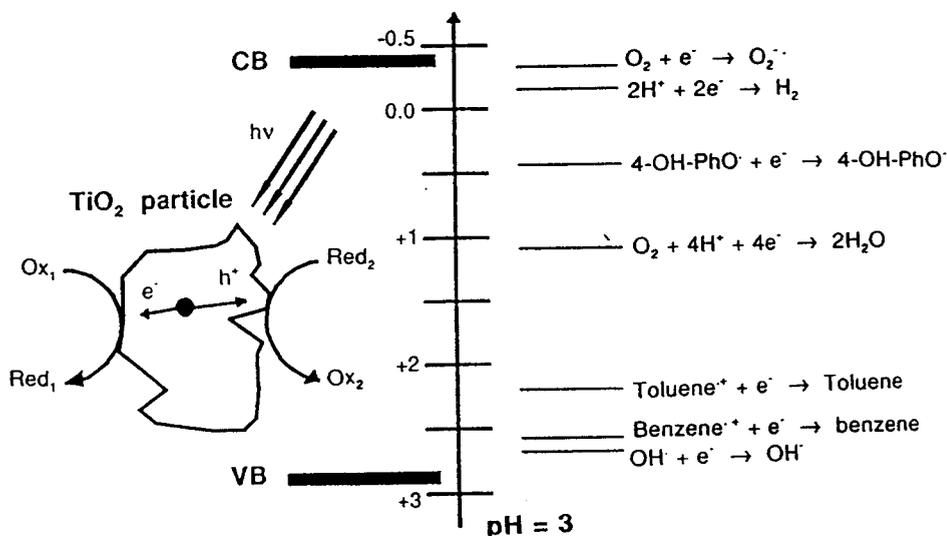
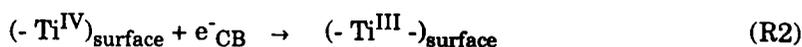
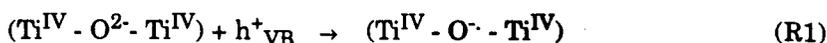


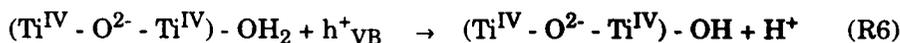
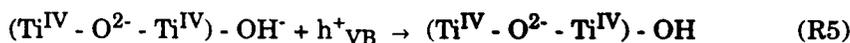
Figure 6: Simple view of a semiconductor particle under irradiation and the ensuing redox reactions. The redox potential scale shows the potential (vs. SHE) of the valence and conduction bands of anatase and some redox couples.

lytic oxidizing ability of titanium dioxide is compared to some redox couples. The wide range of applicability of the material is apparent. The mechanism by which the oxidation occurs is still not entirely clear, though. What is clear is that for a photocatalyst to be efficient, the different interfacial electron transfer processes, involving e^- and h^+ reacting with adsorbed species, must compete effectively with the major deactivation route of electron-hole recombination. This can happen either in a single event or in a series of multiple steps involving surface irregularities, sometimes called surface states. Examples of competing reactions are shown in reactions (R1) – (R4).



The rapid rate of electron-hole recombination requires that Red_2 and Ox_1 need to be preadsorbed prior to light excitation of the titanium dioxide photocatalyst.

There is abundant evidence, though, that a titanium dioxide surface exposed to an aqueous solution undergoes extensive hydration and hydroxylation and the consensus is that very few Ti^{IV} sites are available for direct oxidation of organic species by holes. Therefore, hole trapping by interfacial electron transfer primarily yields surface bound OH^\cdot radicals ((R5) and (R6)) which act as the major route for photocatalytic oxidation of organic molecules in solution.



Clearly, H_2O is an essential species in the photomineralization of organic compounds: no, or very little, photodegradation occurs in the absence of H_2O . This supports the mechanism based on OH^\cdot radical formation and subsequent oxidation by this species. In addition, though, adsorbed oxygen is also essential since this traps electrons thereby delaying electron-hole recombination:



Again very little photooxidation occurs in the absence of oxygen.

Even though the oxidation of organic compounds appears to occur primarily by OH^\cdot radical attack, direct hole oxidation of an adsorbed organic substrate to give an organic radical cation cannot be completely discounted since holes, as the primary oxidizing species, have been described in non-aqueous photoassisted oxidation. In aqueous solutions, therefore, both mechanisms are described in more recent bibliographies as possible pathways. When OH^\cdot radical attack does occur, though, this photogenerated oxidizing species does not migrate very far from the photogenerated active site on titanium dioxide, and the degradation process must occur at the photocatalyst surface or within a few atoms of distance from the surface. Therefore, pre-adsorption of the organic species is still needed.

APPENDIX C: DETERMINATION OF ORTHOPHOSPHATE

When aqueous solutions of inorganic phosphate (orthophosphate) and acidified ammonium molybdate are mixed together, they are known to react to form a yellow phosphomolybdate complex,³⁴ that may be quantitatively determined by UV/Vis absorbance. In particular, we found that analysis at 320 nm of solutions containing nine parts 4 mM ammonium molybdate and one part orthophosphate was appropriate for the determination of orthophosphate samples in the concentration range 0.1 mM to 1 mM. Consequently, it was proposed that orthophosphate determination might be used as a means of following the extent of MPA degradation.

To proceed with the study, we made the assumption that the degradation of MPA to orthophosphate did not generate significant concentrations of phosphorus-containing intermediates. Consequently, we inferred that at all times the sum of the concentrations of MPA (reactant) and orthophosphate (product) was equal to the initial MPA concentration (conservation of mass). On the basis of this assumption, we obtained figure 7, a working curve for orthophosphate release from the photocatalyzed oxidation of a 1 mM solution of MPA. Each point on this curve was obtained by measuring the absorbance at 320 nm of a mixture of nine parts 4 mM orthophosphate and one part 1 mM total phosphorus (sum of MPA and orthophosphate concentrations). A least mean squares fit to the data is also plotted in figure 7 and the equation for this line, including the standard deviation, is given below.

$$\text{Absorbance} = (1.220 \pm 0.036) \text{ Orthophosphate Concentration} + (0.592 \pm 0.048) \quad (1)$$

Figure 7 was also applied to product analysis of reactions for which the initial MPA concentration was higher than 1 mM by diluting the samples down to 1 mM prior to the test. For samples of lower than 1 mM initial concentration, the test was appropriately modified so that the mixture of sample and ammonium molybdate reagent contained 0.1 mM total phosphorus and 3.6 mM ammonium molybdate (the standard test conditions).

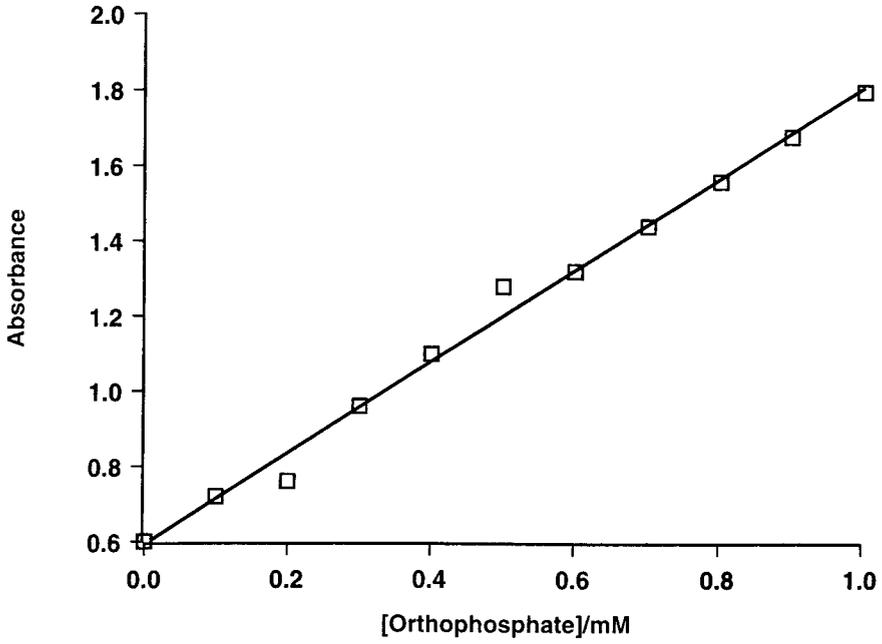


Figure 7: Calibration curve for the release of orthophosphate during the degradation.

APPENDIX D: DISCUSSION OF THE EXPERIMENTAL RESULTS

Initially, an experiment was undertaken to determine whether orthophosphate, the anticipated product from the oxidation of MPA, adsorbs to titanium dioxide powder under the conditions of our photocatalysis studies. A solution containing 1 mM orthophosphate and 0.5 g dm^{-3} titanium dioxide was irradiated for one hour and then analyzed for orthophosphate using the phosphomolybdate test described in Appendix C. The result of this analysis showed that the concentration of orthophosphate had not decreased during the period of irradiation and, therefore, that orthophosphate had not significantly adsorbed to the titanium dioxide photocatalyst. Consequently, it was concluded that orthophosphate detection should be used to monitor the extent of MPA destruction by titanium dioxide photocatalysis.

Figure 4 shows a typical plot of orthophosphate concentration as a function of irradiation time obtained from studies of the photooxidation of MPA in a 0.5 g dm^{-3} titanium dioxide dispersion. It should be noted that data from studies of the two different MPA concentrations (1 mM and 2 mM) are compared and the initial curvature of the product transients are seen to correspond quite well. Similar results were obtained for [MPA] of 0.5 mM and 1 mM. These results demonstrate that in the initial stages of the reaction the rate was zeroth order with respect to MPA, a conclusion reached by Fox *et al.* for the degradation of phenyl-, butyl- and benzyl- phosphonic acids.³⁵ This behavior is characteristic of heterogeneous reactions obeying Langmuir-Hinshelwood kinetics,³⁶ and it implies that a surface process rather than the transport of MPA to the titanium dioxide surface was rate determining. Further evidence of zeroth order kinetics has already been presented in figure 2, a plot of orthophosphate yield against initial MPA concentration for experimental conditions where the sample had been irradiated for 45 minutes in the presence of 0.5 g dm^{-3} titanium dioxide.

Although the rate of reaction was zeroth order with respect to MPA, it was clearly a more complex function of the reaction time, as is demonstrated by the data plotted in figure 4 for the photooxidation of a 2 mM MPA solution. In particular, the rate of reaction was observed to increase to a limiting value during the first 45 minutes of irradiation and then to remain constant until most of the MPA had been degraded.

The observed steady increase of the rate during the first 45 minutes of irradiation was shown to exhibit Arrhenius behavior; i.e., $\ln(\text{rate})$ was proportional to the reciprocal of absolute temperature. Although the initial temperature of the sample was measured to be 21°C , after approximately 45 minutes irradiation, its temperature reached a limiting value of 50°C . Therefore, it was decided to preheat the samples to this temperature prior to irradiation and to then study the yield of orthophosphate with time. Figure 8 compares the data

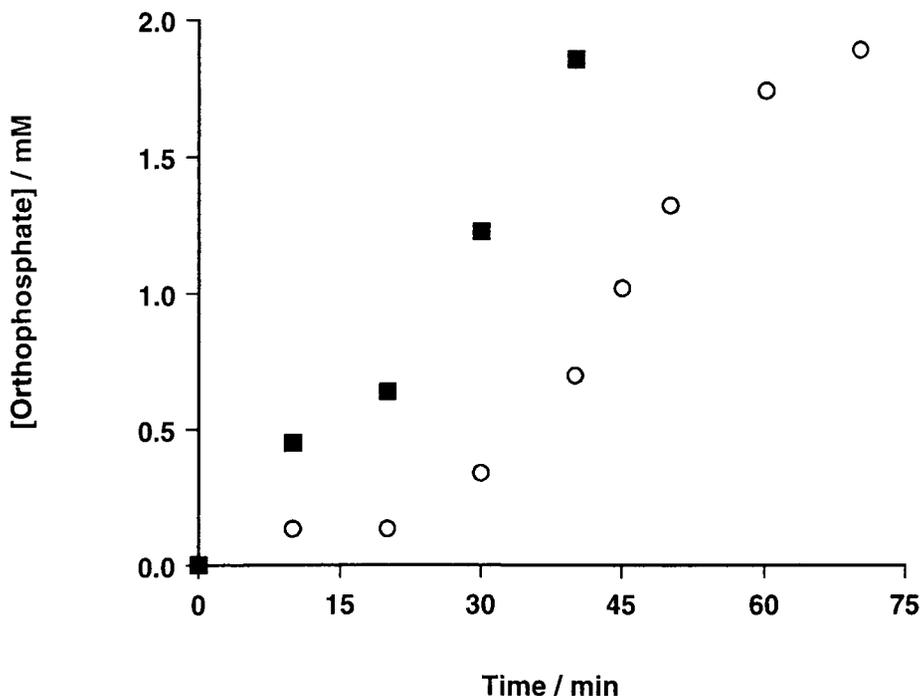


Figure 8: The yield of orthophosphate as a function of irradiation time for an initial MPA concentration of 2 mM and for 0.5 g dm^{-3} titanium dioxide. The initial sample temperature was 0 20°C and ■ 50°C.

which was obtained with and without preheating, and importantly demonstrates that after preheating, the reaction rate did not vary with time but had the same value as the limit derived from figure 4, i.e., $45 \mu\text{M min}^{-1}$. To rule out the possibility that MPA had degraded thermally at 50°C, a blank experiment was undertaken in the absence of irradiation. Orthophosphate analysis of a 1 mM MPA sample that had been maintained at 50°C for one hour showed that no degradation to orthophosphate had occurred and, therefore, that MPA is stable to thermal degradation at 50°C.

The Arrhenius analysis of all the data shown in figure 4 for the destruction of 2 mM MPA yielded an activation energy of 130 kJ mol^{-1} , a value not inconsistent with a bond cleavage activation process such as adsorption. However, the activation energy for adsorption itself is probably much lower than 130 kJ mol^{-1} because a value of 30 kJ mol^{-1} was reported for the adsorption of the dimethyl ester of MPA,³⁷ this process occurs by activation of the bond common to both compounds, the phosphorus-oxygen double bond. It should be noted, though, that an activation energy determined from an Arrhenius plot for a heterogeneous process may include contributions from more than one process,³⁸ e.g., mass transfer, adsorption, bond cleavage, surface diffusion.

The importance of oxygen for the photochemical process was investigated by purging the dispersions with nitrogen during simultaneous irradiation. After 45 minutes of irradiation no orthophosphate was detected and it was thus concluded that oxygen was essential for reaction. However, only a slight increase in the rate of reaction was observed when the source of oxygen was pure oxygen rather than air.

Finally, a study of the variation of the reaction rate with titanium dioxide concentration was made. Figure 3 shows a plot of orthophosphate yield as a function of titanium dioxide concentration for concentrations of 1 mM and 2 mM MPA and for an irradiation time of 10 minutes. The plots for the two different MPA concentrations superimpose, in agreement with the apparent zeroth order dependence of this species and as discussed above. The shape of the plots is such that the yield of orthophosphate increases linearly to a limiting value as the concentration of titanium dioxide is increased. The linear relation (below 5 g dm^{-3} titanium dioxide) is predicted by Langmuir-Hinshelwood kinetics because under conditions of high light intensity, the reaction rate is limited by the number of catalyst surface states able to trap photogenerated holes.

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