

PHOTOPRODUCTION OF HYDROGEN IN NON OXYGEN-EVOLVING SYSTEMS

**Co-produced hydrogen as a bonus in the
photodegradation of organic pollutants
and hydrogen sulfide**

*Report prepared within the framework of Annex 10 of the
International Energy Agency's Hydrogen Programme*

by

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International Energy Agency Hydrogen Implementing Agreement

The International Energy Agency

The International Energy Agency (IEA) was established in 1974, following the first oil crisis and is managed within the framework of the Organization for Economic Cooperation and Development (OECD). The mission of the IEA is to facilitate collaborations for the economic development, energy security, environmental protection and well-being of its members and of the world as a whole.

The Hydrogen Program, or Implementing Agreement, has been in existence for more than twenty years. Its mission is to advance hydrogen technologies and accelerate hydrogen's acceptance and widespread utilization. Past collaborations have been in the areas of Thermochemical Production, High Temperature Reactors, Electrolysis, Storage, Safety, and Markets.

The following countries/organizations participate in the Hydrogen Implementing Agreement: Canada, European Commission, Lithuania, Japan, Netherlands, Norway, Spain, Sweden, Switzerland, United States.

Hydrogen

Today, hydrogen is primarily used as a chemical feedstock in the petrochemical, food, electronics, and metallurgical processing industries, but is rapidly emerging as a major component of clean sustainable energy systems. It is relevant to all of the energy sectors - transportation, buildings, utilities, and industry. Hydrogen can provide storage options for intermittent renewable technologies such as solar and wind, and, when combined with emerging decarbonization technologies, can reduce the climate impacts of continued fossil fuel utilization. Hydrogen is truly the flexible energy carrier for our sustainable energy future.

As we enter the new millennium, concerns about global climate change and energy security create the forum for mainstream market penetration of hydrogen. Ultimately, hydrogen and electricity, our two major energy carriers, will come from sustainable energy sources, although, fossil fuel will likely remain a significant and transitional resource for many decades. Our vision for a hydrogen future is one of clean sustainable energy supply of global proportions that plays a key role in all sectors of the economy. We will implement our vision with advanced technologies including direct solar production systems and low-temperature metal hydrides and room- temperature carbon nanostructures for storage.

Production

Hydrogen can be produced directly from sunlight and water by biological organisms and using semiconductor-based systems similar to photovoltaics (PV). Hydrogen can also be produced indirectly via thermal processing of biomass or fossil fuels. Global environmental concerns are leading to the development of advanced processes to integrate sequestration with known reforming, gasification, and partial oxidation technologies for carbonaceous fuels. These production technologies have the potential to produce essentially unlimited quantities of hydrogen in a sustainable manner.

Storage

Storage of hydrogen is an important area for cooperative research and development, particularly when considering transportation as a major user and the need for efficient energy storage for intermittent renewable power systems. Although compressed gas and liquid hydrogen storage systems have been used in vehicle demonstrations worldwide, the issues of safety, capacity, and energy consumption have resulted in a broadening of the storage possibilities to include metal hydrides and carbon nanostructures. Stationary storage systems that are high efficiency with quick response times will be important for incorporating large amounts of intermittent PV and wind into the grid as base load power.

Integration

Achieving the vast potential benefits of a hydrogen system requires careful integration of production, storage and end-use components with minimized cost and maximized efficiency, and a strong understanding of environmental impacts and opportunities. System models combined with detailed life cycle assessments provide the platform for standardized comparisons of energy systems for specific applications. Individual component models form the framework by which these system designs can be formulated and evaluated.

Current and Completed Annexes of the IEA Hydrogen Implementing Agreement

| | | |
|----------|---|-----------|
| Annex 1 | Thermochemical Production | 1977-1988 |
| Annex 2 | High Temperature Reactors | 1977-1979 |
| Annex 3 | Assessment of Potential Future Markets | 1977-1980 |
| Annex 4 | Electrolytic Production | 1979-1988 |
| Annex 5 | Solid Oxide Water Electrolysis | 1979-1983 |
| Annex 6 | Photocatalytic Water Electrolysis | 1979-1988 |
| Annex 7 | Storage, Conversion and Safety | 1983-1992 |
| Annex 8 | Technical and Economic Assessment of Hydrogen | 1986-1990 |
| Annex 9 | Hydrogen Production | 1988-1993 |
| Annex 10 | Photoproduction of Hydrogen | 1995-1998 |
| Annex 11 | Integrated Systems | 1995-1998 |
| Annex 12 | Metal Hydrides for Hydrogen Storage | 1995-2000 |
| Annex 13 | Design and Optimization of Integrated Systems | 1999-2001 |
| Annex 14 | Photoelectrolytic Production of Hydrogen | 1999-2001 |
| Annex 15 | Photobiological Production of Hydrogen | 1999-2001 |

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Executive Summary

This report was prepared as part of the documentation of Annex 10 (Photoproduction of Hydrogen) of the IEA Hydrogen Agreement. Subtask A of this Annex concerned photo-electrochemical hydrogen production, with an emphasis on direct water splitting. However, studies of non oxygen-evolving systems were also included in view of their interesting potential for combined hydrogen production and waste degradation. Annex 10 was operative from 1 March 1995 until 1 October 1998. One of the collaborative projects involved scientists from the Universities of Geneva and Bern, and the Federal Institute of Technology in Lausanne, Switzerland. A device consisting of a photoelectrochemical cell (PEC) with a WO_3 photoanode connected in series with a so-called Grätzel cell (a dye sensitized liquid junction photovoltaic cell) was developed and studied in this project. Part of these studies concerned the combination of hydrogen production with degradation of organic pollutants, as described in Chapter 3 of this report.

For completeness, a review of the state of the art of organic waste treatment is included in Chapter 2. Most of the work at the University of Geneva, under the supervision of Prof. J. Augustynski, was focused on the development and testing of efficient WO_3 photoanodes for the photoelectrochemical degradation of organic waste solutions. Two types of WO_3 anodes were developed: non transparent bulk photoanodes and nano-particle-based transparent film photoanodes. Both types were tested for degradation of several common organic pollutants (alcohols, aldehydes, acids, etc) and proved to be very efficient in dilute solutions. For instance, a solar-to-chemical energy conversion efficiency of 9% was obtained by operating the device in a 0.01 M solution of methanol (as compared to about 4% obtained for direct water splitting with the same device). These organic compounds are oxidised to CO_2 by the photocurrent produced by the photoanode.

The advantages of this procedure over conventional electrolytic degradation are that much (an order of magnitude) less energy is required and that sunlight can be used directly. In the case of photoproduction of hydrogen, as compared to water splitting, feeding the anodic compartment of the PEC with an organic pollutant, instead of the usual supporting electrolyte, will bring about a substantial increase of the photocurrent at a given illumination. Thus, the replacement of the photo-oxidation of water by the photodegradation of organic waste will be accompanied by a gain in solar-to-chemical conversion efficiency and hence by a decrease in the cost of the photoproduced hydrogen. Taking into account the benefits and possible revenues obtainable by the waste degradation, this would seem to be a promising approach to the photoproduction of hydrogen.

Hydrogen sulfide (H_2S) is another waste effluent requiring extensive treatment, especially in petroleum refineries. The so-called Claus process is normally used to convert the H_2S to elemental sulfur. At the Florida Solar Energy Center (FSEC) a sulfur recovery process has been developed in which the H_2S , having been absorbed into an alkaline solution is decomposed in an energy-storing solar photochemical scheme to yield not only sulfur, but also hydrogen that can be sold or used internally at the refinery. Catalyst-modified semiconductor (CdS) particles are employed to bring about this conversion process in a photoreactor. This process development was largely done before Annex 10 came into operation and is therefore not regarded as an Annex 10 activity. However, as a typical example of the photoproduction of hydrogen in a non oxygen-evolving system, a brief

description is included as Chapter 4 of this report. Also, Dr. C. Linkous at FSEC, who was in charge of this process development, has been a very active participant in Annex 10.

The encouraging results obtained in these investigations of photoelectrochemical hydrogen production combined with organic waste degradation, have prompted a decision to continue the work under the new IEA Hydrogen Agreement Annex 14, Photoelectrolytic Hydrogen Production.

1. Introduction

The use of sunlight to drive thermodynamically uphill reactions prompted a large number of studies, particularly during the last twenty years. The most widely investigated process was certainly water splitting, i.e., the photoconversion of liquid water to gaseous hydrogen and oxygen. This choice is obviously dictated by the abundance of primary material, water, as well as by the versatility of hydrogen as a clean fuel and an important chemical reactant.

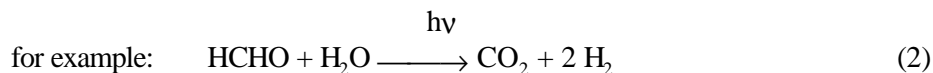
Since water is essentially transparent to radiation within the solar spectrum, most approaches to photodecompose water involved the use of semiconductors as light absorbing species, either in a photoelectrochemical or in a photocatalytic configuration.

While the photoelectrochemical (PEC) process involves the use of a semiconductor electrode associated with a metallic (or a second semiconductor) electrode to form an electrolysis cell, in the photocatalytic (PC) process involves the replacement of the electrodes by a light-harvesting semiconductor suspension. Consequently, the reduction and oxidation products (hydrogen and oxygen in the case of water splitting) that are formed separately at the cathode and the anode of the PEC cell are generated simultaneously at the surface of semiconductor particles. In the following, the application of these two kinds of processes to produce hydrogen and various oxidation products other than oxygen will be evaluated and compared to other competing technologies.

Although the photoelectrolysis of aqueous solutions of a large variety of electrolytes (such as sulphuric or perchloric acid and the corresponding sodium salts) leads to the formation of oxygen as the main oxidation product (cf. reaction 1),



the situation changes when some particular classes of reactants are present in the solution. This is, in particular, the case for various organic molecules that tend to be oxidized preferentially to form CO_2 as the final product (cf. reaction 2).



In other terms, the photoelectrolysis cell employing a semiconductor anode offers an attractive means for the treatment (and, in most of cases, the total mineralization) of organic pollutants in combination with the hydrogen production at the cathode. In view of a significant cost normally associated with the organic waste treatment, the above mentioned photooxidation alternative is to be considered as an important value added factor in the solar photoproduction of hydrogen.

2. State of the Art of Organic Waste Treatment

2.1 *Biological and Chemical Methods*

In the case of most domestic sewage waters, a biological (microbial) treatment is quite effective and has become the most important process controlling the pollution of the aquatic environment by a range of organic compounds. However, the industrial effluents also contain additional toxic compounds and heavy metal ions that are resistant to bacterial biodegradation. Similar problems arise in connection with intensive use of agricultural pesticides and herbicides, as well as other agrochemicals that produce biologically refractory organic compounds. These substances accumulate in surface and ground waters and there is clear need for new and effective methods in cleaning the polluted water. This, in turn, leads to a renewed interest in developing environmentally safe (benign) methods for detoxification, possibly by complete mineralization of a wide range of toxic substances.

Such xenobiotic chemicals have been treated by the Advanced Oxidation Processes (AOPs) in homogenous phase, which involve irradiation with UV or visible light, including sunlight (a) without or with additional oxidants such as oxygen, ozone or hydrogen peroxide and (b) with homogenous sensitizers, such as dyes, or with heterogeneous photocatalysts, such as dispersed semiconductors.

While ozone has a high oxidation potential ($E^\circ = +2.07 \text{ V}$), alone it reacts very slowly with various chlorinated compounds. Improved treatment methods involve combination of ozone with UV light, generating more reactive OH radicals. In paper industry wastewater treatment, the combination of ozone and UV appeared less effective than ozone alone. However, in all cases the cost of ozone and the electric energy consumption are the main reasons preventing its widespread use in water treatment. Another disadvantage of this technique is the need to destroy excess ozone and the failure to oxidize halomethanes, carboxylic acids and pesticides, such as atrazine. In the presence of high concentrations of bromide ions in the effluents, various brominated organic compounds are formed that, in some cases, are more toxic than their precursors (1-5).

In the case of a wastewater treatment plant, a pretreatment of the pollutants is normally done first (generally by electrochemical oxidation) and then different procedures are applied, depending on the concentrations of residual dissolved/suspended matter in the processed water. However, when observed concentrations are above 1000 g/L, burning out to ashes (incineration) is required. As long as the level stays in between 10 and 1000 g/L, chemical oxidation in the presence of oxygen at high pressure and/or temperature can be employed. In some cases, oxygen may be replaced by ozone or hydrogen peroxide. If less than 10 g/L of pollutants are present in water, no really efficient degradation technology is actually available (6).

Among alternative (non-photochemical) approaches to water treatment, one can mention ultrasonic irradiation of water at frequencies higher than 15 kHz, which causes formation of hydroxyl radicals available for oxidation. For example, sonication performed at 20 kHz and 0.1 kW/L for 1 hour produced complete degradation and mineralization of methylene chloride, tetrachloroethylene and other chlorinated organic solvents (1).

2.2 Electrochemical Methods

Environmental applications of electrochemistry have been developed that offer several promising approaches (7-11): metal ion removal and recovery, generation of redox species, degradation of harmful organics and disinfection of water, as well as methods for pollution control (12) using sensors, microelectrodes or ion-selective electrodes for monitoring of harmful species.

2.2.1 Electrochemical reduction

Chemical industries produce significant volumes of wastewater containing highly toxic organochlorine compounds. Cathodic dehalogenation presents several advantages, such as selective removal of chlorine, working at ambient temperature and absence of additional chemicals. The organic skeleton remains intact under this treatment and must be biologically digested afterwards (12-13). At the moment, the cathodic reduction of chlorine from polychlorinated biphenyls is less energy intensive than complete oxidation.

2.2.2 Electrochemical oxidation

A potentially powerful technique for controlling pollutants in industrial wastewaters is the anodic oxidation of organic material (6,9).

To oxidize organic substances in water, a low-resistivity anode material is needed with high overvoltage for oxygen gas evolution. Frequently used materials are PbO_2 and graphite, which have the disadvantage of being unstable under prolonged electrolysis, or Ti/Pt, which is stable, but expensive and, in general, less effective.

Ti/ SnO_2 electrodes efficiently catalyze the oxygen-transfer reaction and are promising in pretreatment of refractory aromatic compounds. A relatively stable and efficient electrode has been developed using SnO_2 doped with Sb to increase the conductivity (14-15). The oxidation efficiency reached with these anodes was about 5 times higher than with platinum anodes and was independent of the pH. This anode material reduces specific energy consumption on the order of 50 kWh/kg COD (chemical oxygen demand). This treatment appears to be suitable for COD concentrations between 500 and 15000 ppm (16).

This electrode was applied, for example, to phenol oxidation showing no quinone intermediate formation, (such as the very harmful 1,4 benzoquinone) and to the oxidation of sulfonic acids of benzene, naphthalene and anthraquinones derivatives (16), which represents, along with chlorinated compounds, the most toxic substances present in industrial effluents.

However, electrochemical techniques are frequently unable to perform complete oxidation of organic species unless special conditions are used, such as concentrated basic or acidic media, temperatures around 80°C and platinum-plated titanium electrodes (6,7).

2.3 Economic Assessment of the Various Waste Treatment Technologies

Any process is limited by the price of the oxidation equivalent, which varies with the reagent. Oxygen in air is the least expensive, followed by chlorine, electricity, hydrogen peroxide and finally ozone, as shown in Table 1 (17):

Table 1: Comparison of the various chemical processes vs. electrochemical oxidative destruction for the degradation of organic compounds.

| Oxidant | \$/kg equiv. | Average Yield | Invest Cost for 100 kg COD/h (M\$) [°] | Treatment Cost \$/kg COD |
|-------------------------------|--------------|------------------|---|--------------------------------|
| O ₂ * | <0.7 | | 1.3-4.0 | 0.6-2 |
| Cl | 12 | 50 % | 2.0 | 4.5 |
| H ₂ O ₂ | 30 | 55 % | 2.0 | 8 |
| O ₃ ** | 40 | 100 % | 16 | 9.5 |
| KWh | 6.7 | 56 % | 6.7 | 4 |

* Biological treatment

** Only two equivalents/mole

° Millions of Dollars

The oxidation process with oxygen at low temperatures requires a biological treatment. The use of chlorine is limited by the highly toxic by-products often formed. Electrochemical oxidation may be clean and efficient in many cases, but a greater stability of commonly used anodes is needed. Hydrogen peroxide, on the other hand, is expensive and only effective at detoxifying small quantities of wastewater. The most powerful oxidant, ozone, is also the most expensive.

Complete oxidation of organics to CO₂ and water requires the transfer of a large number of electrons and hence a very high consumption of energy. For instance, destruction of aniline requires 28 electrons per molecule. Assuming that the reaction takes place in an electrochemical cell with a voltage of 5 V and current efficiency of 100%, the cost would be 1.42 \$/lb at 0.06 \$/kWh, as shown in Table 2:

Table 2: Energy costs for electrochemical oxidation of pollutants

| Examples | Energy Cost (\$/lb) Assumption: 100% CE, 5 V, 0.06 \$/kWh |
|--|---|
| $\text{CH}_2\text{O} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$ MW30 | 0.49 |
| $\text{H}_2\text{S} + 4\text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{e}^-$ MW34 | 0.86 |
| (a) $\text{NH}_3 + 3\text{H}_2\text{O} \longrightarrow \text{HNO}_3 + 8\text{H}^+ + 8\text{e}^-$ MW17 | 1.72 |
| (b) $2\text{NH}_3 \longrightarrow \text{N}_2 + 6\text{H}^+ + 6\text{e}^-$ | 0.65 |
| $\text{C}_6\text{H}_6 + 12\text{H}_2\text{O} \longrightarrow 6\text{CO}_2 + 30\text{H}^+ + 30\text{e}^-$ MW78 | 1.41 |
| $\text{C}_6\text{H}_5\text{NH}_2 + 15\text{H}_2\text{O} \longrightarrow 6\text{CO}_2 + \text{HNO}_3 + 36\text{H}^+ + 36\text{e}^-$ MW93 | 1.42 |

EC = energy consumption (kWh/kg) = $nFV/\text{MW} \cdot \text{CE}$
CE = current efficiency

2.4 Photocatalytic Treatment

Semiconductor photocatalysis has received considerable attention in recent years as an alternative for treating water and air polluted with hazardous organic chemicals.

In contrast to the AOPs in homogeneous solutions, where the oxidant is consumed, heterogeneous photocatalytic processes use near UV and visible light to overcome the required activation energy.

Applications of heterogeneous photocatalysis to environmental cleaning involve the use of photocatalysts for the non-selective total oxidation of organic pollutants (18). Most frequently, TiO_2 or ZnO have been used as photocatalysts, since they both efficiently absorb long wavelength UV light and are chemically stable at the reaction conditions. However, both are photoactive in the UV region (below 400 nm) and, therefore, can use less than 5% of the solar energy reaching the Earth. Hence, it is evident that other materials have to be found, especially for solar applications. Nevertheless, TiO_2 is currently considered the most promising catalyst for air and water photocatalytic decontamination. Principles and mechanisms of photocatalysis on TiO_2 have been reviewed recently (19). Different classes of compounds have been investigated as substrates for photocatalytic degradation and reviewed (20-22).

The nature of the photocatalyst determines the rate and efficiency of the process. The anatase form of titanium dioxide has the desirable properties of being chemically stable, readily available, and active as a catalyst for oxidation processes. The 3.2 eV band gap matches the output of a wide variety of readily available lamps, but, as already mentioned, is not ideal for solar applications. The photoefficiency for reaction of hazardous molecules is generally low, particularly for the aqueous-phase processes. Considerable work has been directed towards modifying TiO_2 and testing other

semiconductors to identify ways to increase process efficiency and to improve the overlap of the absorption spectrum of the photocatalyst with the solar spectrum. This work involves various attempts principally in the following directions:

| | |
|---------------------------------|--|
| modified titanium dioxide | hydrophobic surface treatment |
| dye sensitized titanium dioxide | metal ion doping of TiO_2 or mixed oxides |
| metalized titanium dioxide | immobilized photocatalysts |

The number of references and related patents on heterogeneous photocatalytic removal of hazardous and toxic compounds, as well as the target compounds and applications, are numerous (21,22).

In the treatment of water contaminated with metals and organic compounds, TiO_2 was efficient as a photocatalyst for removing metal ions with standard reduction potentials more positive than 0.3V (vs. NHE). It was shown that an efficient system is realized only when both reduction and oxidation half-reactions occur rapidly, as demonstrated in experiments where organics such as EDTA, phenol, and nitrobenzene are oxidized (23-25). The possibilities for the photocatalytic treatment of water have recently been resumed by Matthews (26).

The use of TiO_2 , generally as a suspension, shows a series of disadvantages, such as filtration needed after each degradation cycle to recycle the catalyst and easy recombination of holes and electrons. This is necessary since the oxidation and the reduction processes take place on the same particle.

Several methods have been developed to stabilize the catalyst on an inert support, but only few to prepare TiO_2 photoanodes. The first films were formed from polycrystalline TiO_2 , but colloidal semiconductor solutions and thin nanocrystalline films have recently been developed and their potential applications for photocatalytic water purification and solar light energy conversion reviewed (27). The state of development and barriers to commercialization in solar photocatalytic oxidation processes (PCO) applied to water purification are presented in (28). Pilot-scale experiments have been done recently for the treatment of gaseous emissions (29-32).

3. Photoelectrochemical Degradation of Organic Effluents Combined with Photoproduction of Hydrogen. *(Based on the experimental work performed in the Electrochemistry Laboratory of the University of Geneva)*

As already mentioned, a cost-effective and efficient method for degrading pollutants present in the amounts of 1-10 g/L of solution is presently lacking. The use of titanium dioxide as a photocatalyst or as an electrode material in photoelectrochemical cells represents a possible option under investigation in a number of laboratories. The major drawback of TiO_2 , however, lies in its absorption limit (close to 400 nm), such that only a marginal portion of the solar spectrum is utilized. This means that the treatment of solutions containing more than 50-100 ppm of contaminants requires the use of artificial illumination sources (lamps).

In the search for an alternative to TiO_2 , the photoelectrochemical properties of another semiconducting oxide, WO_3 , have been extensively examined. While TiO_2 can be used in aqueous solutions over the entire range of pH (except for pHs lower than 1, where it tends to undergo photocorrosion), WO_3 delivers the highest stable photocurrents in acidic (including strongly acidic) solutions.

A photoassisted electrolysis cell employing WO_3 electrodes (developed in the Electrochemistry Laboratory of the University of Geneva) was demonstrated to efficiently oxidize most of the harmful compounds refractory to a conventional electrolytic treatment. This device can operate using solar light exclusively and requires only a small fraction of electrical energy compared to conventional electrolytic oxidation. This is due to a much lower operating voltage and because a much larger portion of the current is used to oxidize organic substances. This photoelectrolysis cell may be driven by a photovoltaic cell, thus becoming an entirely autonomous solar device. Such a device comprises a thin n-type semiconducting WO_3 film, which in the presence of illumination acts as a photoanode. A second electrode of platinum film deposited on a conducting glass substrate, for example, plays the role of a conventional hydrogen evolving cathode.

3.1 Photoelectrochemical Characteristics of WO_3 Photoanodes

For the photoelectrochemical degradation of organic compounds, two types of WO_3 photoanodes have been developed in the Electrochemistry Laboratory of the University of Geneva.

Non transparent bulk photoanodes were prepared by thermal oxidation of a tungsten sheet at 750°C in oxygen for 20-30 minutes. The resulting film consisted of relatively thick (20-30 μm) WO_3 layers with large and deep cracks exhibiting the triclinic structure. A subsequent photoanodic treatment enabled these WO_3 photoanodes to convert a significant portion of the incident solar light into photocurrent (33). This treatment consists in the prolonged anodic polarization of the WO_3 electrode under intense illumination. During the treatment, the potential of the WO_3 photoanode evolving oxygen was increased to about 1.5-1.6 V versus the reversible hydrogen electrode (RHE).

Transparent nanosized film photoanodes were formed by depositing a solution of colloidal tungstic acid on F-doped/tin oxide coated conducting glass and heating it above 500°C. Most frequently, six layers were successively deposited. The thickness of the samples obtained by this

method was 3-4 μm . The films consisted of plate-like particles with diameters ranging from 20 to 50 nm (34).

Even in the case of the oxygen evolution reaction, the quantum efficiencies attained large values: 87% for the bulk electrodes (at 390 nm) and 97% (at 400 nm) for the nanosized electrodes. The photoresponse extended to 500 nm, corresponding to a bandgap energy of around 2.5 eV (Fig. 1). As an example, Fig. 2 represents polarization curves recorded in 3M H_2SO_4 under the simulated AM 1.5 solar light illumination. For both photoanodes, the open circuit photopotential is close to 0.45V vs. RHE (reversible hydrogen electrode in the same solution) and the saturation photocurrent for oxygen evolution is higher than 3.5 mA/cm^2 .

Following addition of methanol (used as a model organic substance) to the solution (for the example shown in Fig. 2, 0.1 mol/L was used), the open circuit photopotential is shifted by approximately 50 mV to a more cathodic value. The observed large enhancement of the initial photocurrents (for small anodic bias) reflects the ability of methanol to compete more efficiently than water molecules with surface hole recombination. The corresponding saturation photocurrents increase by a factor of 1.7 for the bulk electrode and by a factor of 2 for the nanosized electrode. The persistence of the photocurrent multiplication at large anodic bias in the solutions containing methanol (and other small organic molecules) is due to the so-called photocurrent-doubling effect known to occur in the case of some multi-step reactions. Here the hole transfer from the valence band of the semiconductor to the reactant in the solution (or adsorbed) is followed by the injection of an electron to the conduction band of the semiconductor by an easily oxidizable reaction intermediate (35).

The photoelectrochemical activity of the WO_3 photoanodes normally decreases when the pH of the solution increases, but this effect is more marked for the bulk material. For example, changing the pH from 0 to 2 causes a decrease in the photocurrent (at 0.8 V for the 0.1 mol/L methanol solution oxidation) by 23% for the bulk electrode compared to only 6% for the nanosized one. This suggests that by using the nanosized WO_3 photoanodes the photoelectrochemical degradation of organic compounds may be performed efficiently with relatively high photocurrents providing only small pH adjustments.

Figure 1: Spectral photoresponses associated with oxygen evolution at an activated bulk WO_3 electrode (A) and at a nanosized electrode (B) in 3M H_2SO_4 .

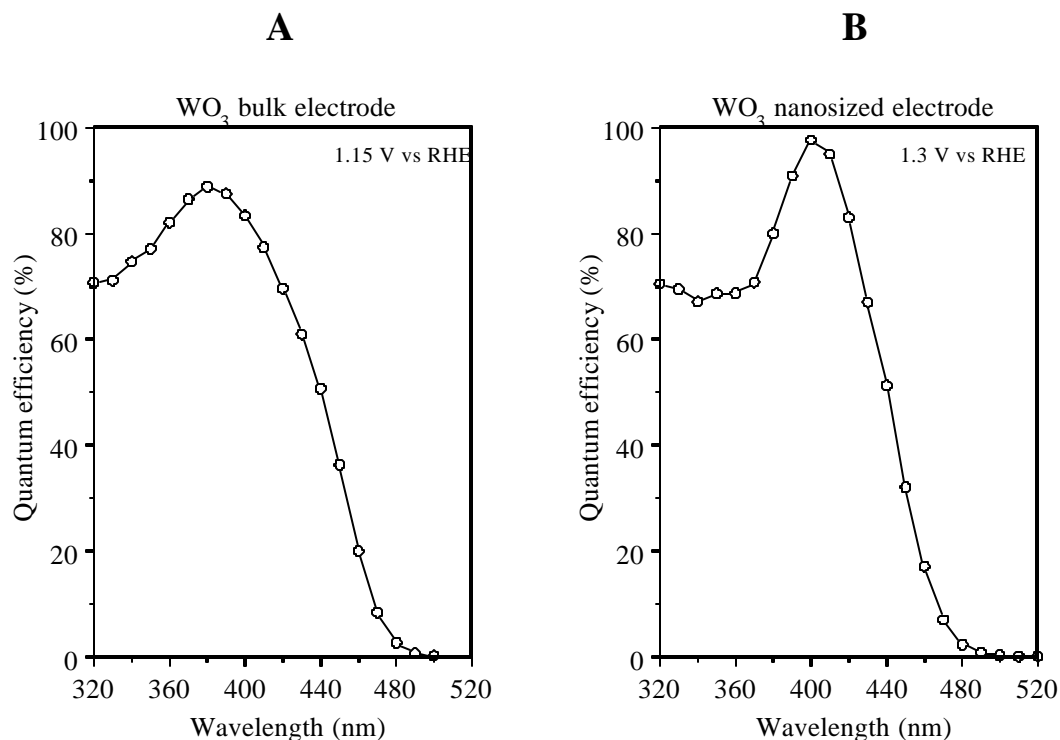
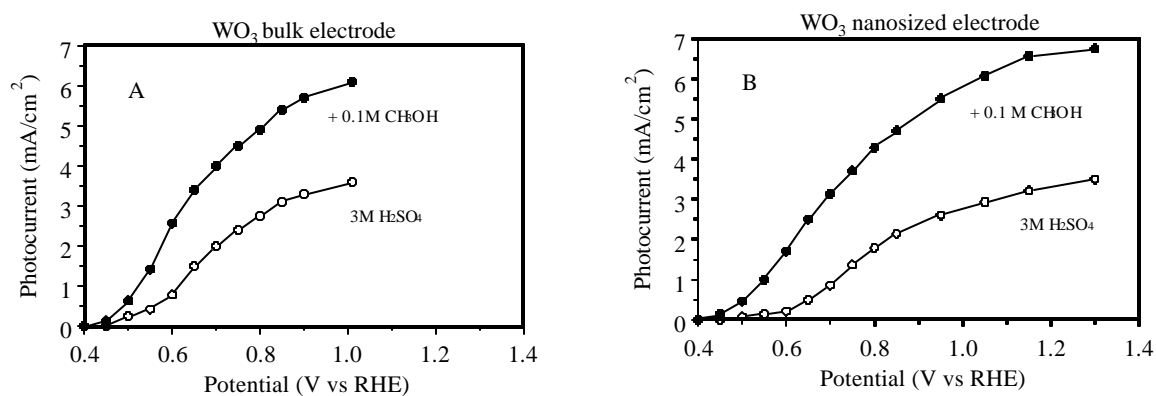


Figure 2: Photocurrent/potential curves recorded at 5 mV/s in 3M H_2SO_4 for the bulk (A), and the nanosized (B) WO_3 electrodes under simulated solar light (1 sun AM 1.5).



The ease with which various organic substances undergo preferential photooxidation at the WO_3 surface may be evaluated from the photocurrent multiplication factor. For this comparison a series of 0.01 mol/L (corresponding to 300-1200 ppm) aqueous solutions of organic substances frequently present in chemical effluents was used (see Table 3).

In order to evaluate the practical ability of the photoelectrochemical cell to degrade organic chemicals, 30-60 cm^3 of 0.01 mol/L solutions of a series of organic compounds (including methanol, formic acid and formaldehyde) were electrolyzed using a 0.8 cm^2 WO_3 photoanode illuminated with simulated solar light (AM 1.5). The platinum counter electrode was placed in a second compartment and separated with a Nafion membrane. Due to their diverse uses, these compounds are frequently present in various effluents from which they have to be removed in order to avoid damage to the aquatic environment. While an indirect electrochemical treatment via hydrogen peroxide formed in situ at a carbon cathode has been described (36) for formaldehyde, it enables only a partial oxidation to formic acid.

Table 3

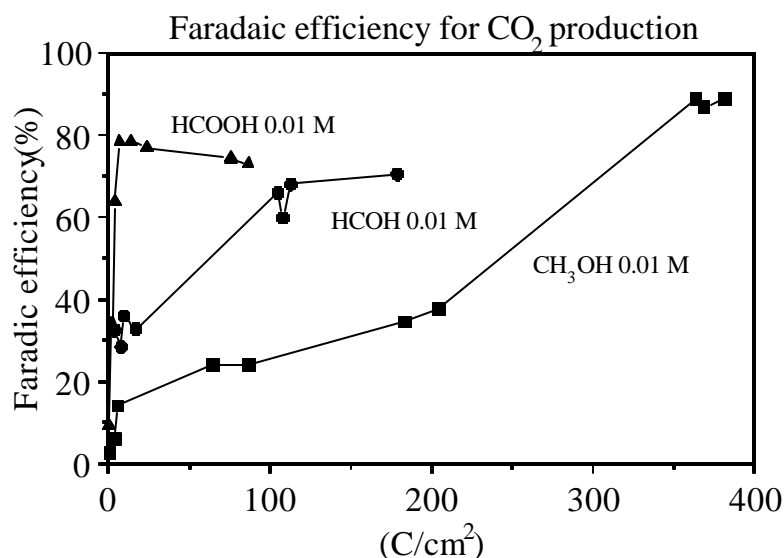
| Bulk photoanode | | Nanosized photoanode | |
|---|------|--|------|
| H_2SO_4 1M pH = 0.5 (0.8 V vs. RHE) 1 sun AM 1.5 | | Na_2SO_4 1M pH = 2 (1 V vs. RHE) 1 sun AM 1.5 | |
| Compound | M | Compound | M |
| Formic acid | 1.5 | Formic acid | 1.2 |
| Acetic acid | 1.1 | Acetic acid | 1.41 |
| Benzoic acid | 1.6 | Benzoic acid | 1.2 |
| EDTA | 2.25 | EDTA | 2.15 |
| Ethanol | 2.0 | Oxalic acid | 1.2 |
| | | Malic acid | 1.9 |
| Methanol | 3.0 | Methanol | 2.0 |
| Formaldehyde | 1.8 | Formaldehyde | 1.8 |

3.2 Photodegradation Experiments Conducted Using Bulk WO_3 Photoanodes.

The photoelectrolyses conducted under an external bias of 0.8 V showed that the oxidation of CH_3OH , HCOOH and CH_2O at the WO_3 photoanode leads, in all cases, to the formation of CO_2 . Apparently the photooxidation of methanol proceeds step-wise with the first 2e^- step giving formaldehyde, which is converted in a second 2e^- step into formic acid and in a third 2e^- step to CO_2 . This 3-step reaction is also reflected by the results presented in Fig. 3, where instantaneous current efficiency for CO_2 formation is shown. For the oxidation of methanol, the efficiency is progressively rising from an initial value of 15% to about 90%.

For the photooxidation of formaldehyde, the efficiency rises more rapidly from 33 to 80% and in the case of degradation of formic acid the current efficiency rapidly reaches 70-80 % to remain essentially stable along the entire run.

Figure 3 : Instantaneous faradaic efficiencies for CO₂ production during the photoelectrolyses on a bulk WO₃ photoanode polarized at 0.8V vs. RHE (60 ml of methanol, formaldehyde or formic acid, initial concentration 10⁻² mol/L in 1 mol/L H₂SO₄, 1 sun AM 1.5). The efficiencies are represented as a function of the total amount of charge (Coulombs/cm²) passed during the photoelectrolyses.

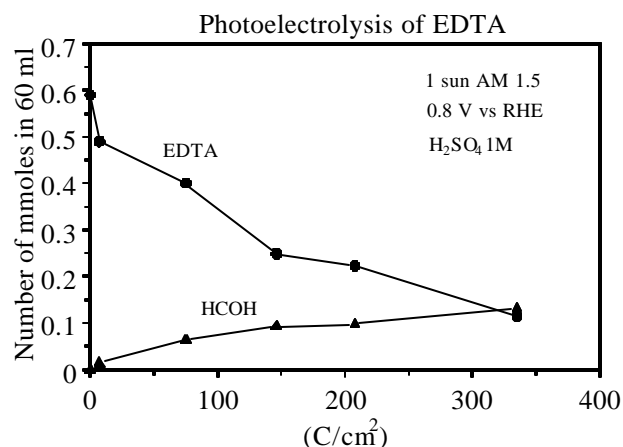


During the photoelectrolysis of formaldehyde, the concentration of the initial compound could be continuously analyzed by a chemical method (reaction with chromotropic acid). Electrolyses of small amounts of solutions (15 cm³) for 24 hours and in the absence of nitrogen led to a final concentration of less than 10⁻⁵ mol/L, corresponding to the disappearance of 99.9% of the initial compound.

EDTA (ethylene diamine tetraacetic acid) is frequently used as a fertilizer or in industry (textile, paper, pharmacy, photography, nuclear plants). It is also present in detergents. Because EDTA is not volatile, it is released in waste water. Unfortunately, EDTA is neither transformed by microorganisms nor adsorbed in the sewage sludge. One form, Fe(III)-EDTA, undergoes direct photolysis (37), but one of the degradation products is formaldehyde.

At pH 0.5 all of the EDTA is in acidic form. It is under those conditions that the photoelectrochemical degradation of this compound has been demonstrated (Fig. 4). The formaldehyde production does not present a problem, since its decomposition into CO₂ under the same experimental conditions has already been demonstrated to occur quite effectively.

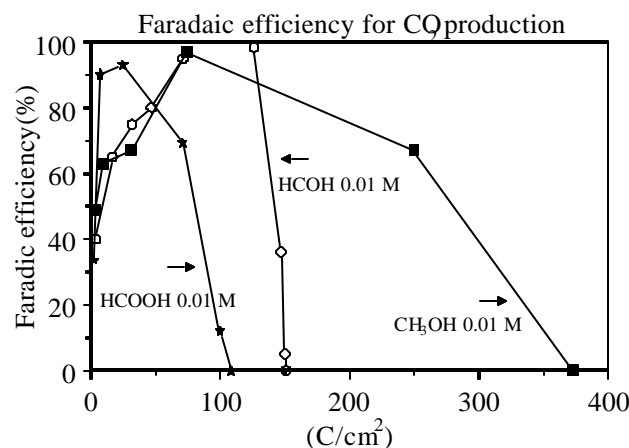
Figure 4: Photoelectrolytic degradation of EDTA in 1M H₂SO₄ solution on a bulk WO₃ photoanode polarized at 0.8V vs. RHE (60 ml, initial concentration 10⁻² M, 1 sun AM 1.5).



3.3 Photodegradation of Organic Compounds at Transparent WO₃ Photoanodes

The photoelectrolyses conducted using the transparent, nanosized WO₃ photoanodes also showed the total oxidation of CH₃OH, HCOOH and CH₂O to form CO₂. The occurrence of the 3-step methanol oxidation is confirmed by the results presented in Fig. 5, showing instantaneous current efficiencies for CO₂ formation. The efficiency for the oxidation of methanol is progressively rising, from an initial value of 50% to about 100%. In the case of formaldehyde and formic acid, the efficiencies increase more rapidly to reach 100%. The total amount of organic carbon remaining in the solution at the end of the photoelectrolyses (TOC) is listed in Table 4. Despite a low residual concentration level of the organic species attained during these photoelectrolyses, the mean current efficiencies remained close to 80%.

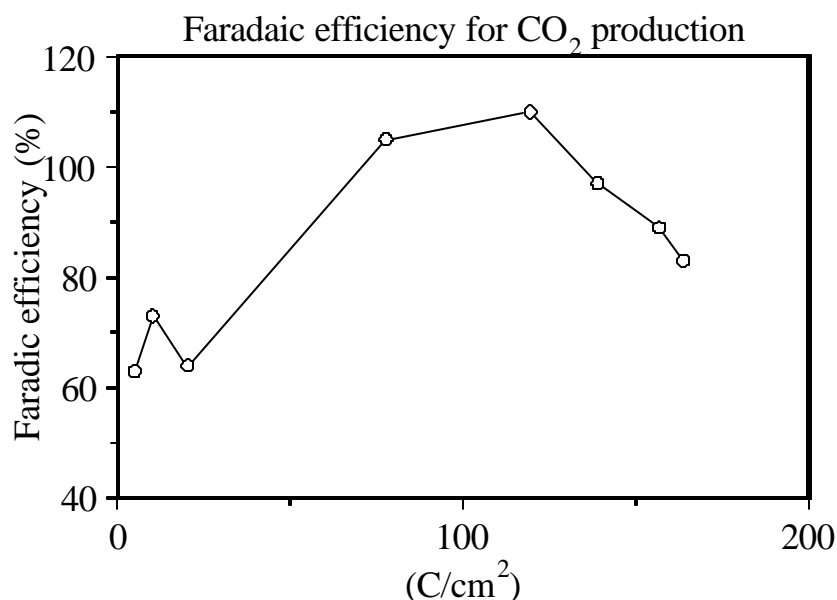
Figure 5 : Instantaneous faradaic efficiencies for CO₂ production recorded during the photoelectrolyses on a nanosized WO₃ photoanode polarized at 1V vs. RHE (30 ml of 10⁻² M methanol, formaldehyde or formic acid in 1M Na₂SO₄, pH 2, 1 sun AM 1.5).



| Table 4 : | Compound | TOC (ppm) | Mean faradaic efficiency for CO ₂ evolution |
|-----------|--------------|-----------|---|
| | Methanol | 1.3 | 78 % |
| | Formaldehyde | 3.0 | 87 % |
| | Formic acid | 4.1 | 75 % |

In a similar way, the photooxidation of oxalic acid to form CO₂ occurs with even higher faradaic efficiencies due in part to its photochemical activity in solution (Fig. 6). It should be noted that, in this connection, the degradation of oxalic acid by conventional electrolysis is inefficient.

Figure 6: Instantaneous faradaic efficiencies for CO₂ production during the photoelectrolysis of 10⁻² M oxalic acid on a nanosized WO₃ photoanode polarized at 1V vs. RHE (in 30 ml of 1M Na₂SO₄ solution of pH 2) 1 sun AM 1.5.



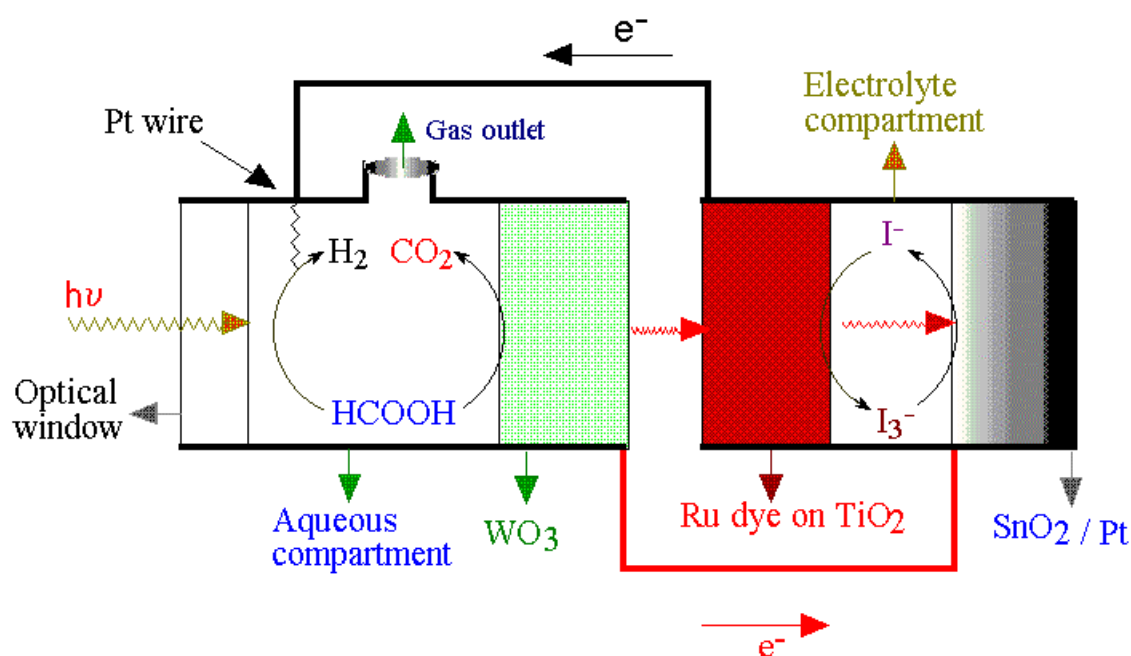
3.4 Combined Degradation/Hydrogen Production Experiments Using Tandem Device

As a part of the collaborative research project with the group of Prof. M. Graetzel at the Swiss Federal Institute of Technology in Lausanne, within the framework of the IEA program, photodegradation experiments were also performed using an autonomous tandem device. Such a device consists of a dye-sensitized liquid-junction photovoltaic cell (38) connected in series with the

photoelectrolyzer, including a transparent WO_3 electrode (represented schematically in Fig. 7). The two cells are superimposed, taking advantage of their complementary light absorption in the visible range. The thin film nanocrystalline tungsten trioxide absorbs the blue part of the solar spectrum and the dye-sensitized TiO_2 electrode absorbs the green and red part of the spectrum. The latter is placed directly behind the WO_3 film, capturing the light transmitted through the WO_3 electrode.

The photovoltaic cell provides the bias required by the photoelectrolyzer to produce hydrogen at the cathode and to oxidize organic compounds at the photoanode. As an example, the photoelectrolysis of a 0.01M solution of methanol (taken as a model substance), performed in the tandem device configuration, produced the amount of H_2 corresponding to an approximate 9% overall solar-to-chemical conversion efficiency.

Figure 7 Schematic representation of the tandem cell used for the photoelectrolysis of organic waste.



3.5 Tentative Economic Assessment

As demonstrated by the above examples, an application of the photoelectrochemical device to remove organic chemicals from waste streams offers two potential advantages over the electrochemical method. In fact, while conventional electrochemical oxidation of most organic compounds requires high-oxygen-overvoltage anodes (and consequently large cell voltages of the order of 4-5 V), the WO_3 photoanodes using solar light as an energetic input can operate under a five times lower bias, i.e., 0.8-1 V. In addition, the above compounds undergo preferential

photooxidation (with respect to water) at the WO_3 photoanode, in contrast with their electrochemical oxidation exhibiting, in general, low current efficiencies. Even assuming that the mean current efficiency associated with the photoelectrochemical process is only two times higher than that of the equivalent electrolytic process, the specific energy requirement of this new process is ten times lower than that of the conventional one. This means that the energy requirement for the removal of 1 kg of COD (chemical oxygen demand, cf. section 2.2.2) from the waste stream would be on the order of only 5 kWh instead of the 50 kWh estimated for the electrochemical oxidation(15). In other terms, the energy cost would be only 0.30 \$/kg instead of 3 \$/kg COD. A more drastic difference in the energy cost may be expected for the degradation of the substances exhibiting low current efficiencies in the case of electrochemical oxidation (e.g. acids such as formic, oxalic or maleic).

Taking into account the diffusion limitations inherent of relatively low concentrations of organic effluents considered for the present application, i.e., 1-10 g/L, the photocurrent densities, in the range of few mA/cm² reached at the WO_3 electrode under 1 sun illumination are not a real drawback. For the treatment of more concentrated solutions of toxic substances, the use of moderately concentrated (up to 10 suns) sunlight will lead to a sensitive increase of the anodic photocurrents and to a concomitant reduction of the investment costs.

Feeding the anodic compartment of the photoelectrolysis cell with the solution of organic effluents instead of a usual supporting electrolyte will bring about a substantial increase (or even a doubling) of the photocurrent at a given illumination. This large photocurrent multiplication factor observed for several organic compounds is characteristic of the species undergoing adsorption at the electrode surface followed by a direct hole transfer (34,39).

From the standpoint of hydrogen production, the replacement of the photooxidation of water by the photodegradation of organic waste will be accompanied by a gain in solar-to-chemical conversion efficiency and, consequently, by a decrease in the cost of the photoproduced hydrogen. Still, this analysis does not take into account an important added value represented by the otherwise energetically expensive waste elimination.

According to a report published by the IEA in 1994 by J. Bolton (40), the economically acceptable investment cost for solar generation of H_2 from water is 165 \$/m² of collector area. In 1994, the estimated capital cost for a combination of the photovoltaic (PV) cell with the conventional electrolyzer was on the order of 600 \$/m² (approximately 4 times higher than the acceptable number). Since 1994, the cost of the commercial PV cells and, consequently, the expected capital cost associated with H_2 generation, have been significantly lowered. Under such conditions, the use of a PV cell/photoelectrolyzer option (instead of the PV cell/electrolyzer) proves viable when the hydrogen generation is coupled with the photodegradation of organic waste. In the latter case, the higher investment cost associated with the use of a photoelectrolyzer (having larger surface area), instead of the conventional electrolyzer, will be easily counterbalanced by its much lower (10 times or more) energy requirement.

4. Photocatalytic Recycling of Hydrogen in Hydrodesulfurization *(Based on the experimental work performed in the Florida Solar Energy Center, University of Central Florida, reported by C.A. Linkous)*

4.1 Introduction

Environmental regulations have required oil and gas refineries to develop waste minimization technologies for the treatment of sulfur-containing compounds, principally hydrogen sulfide (H_2S) within their facilities. Current technology typically involves a solvent absorption/stripping process to separate the acid gases, a Claus reactor to perform a partial oxidation of the sulfide to free sulfur and water, and a tertiary treatment, whose specifics can vary greatly, but must effect at least another hundred-fold reduction in H_2S concentration.

In this report, a new tail gas sulfur recovery process is described in which the H_2S , having been absorbed into an alkaline solution, is decomposed in an energy-storing solar photochemical scheme to yield not only sulfur, but also hydrogen that can be sold or used internally at the refinery. Catalyst-modified semiconductor particulates are employed to facilitate the reaction.

Past experiments have shown that cadmium sulfide (CdS) can be used successfully in the production of hydrogen from hydrogen sulfide and that the use of platinum as a catalyst increases the yield of hydrogen production. In a paper by Bühler et al (41), a batch reactor design was demonstrated in which it was shown that a mixture of sulfide and sulfite ions produced a rate corresponding to a four fold rate increase in hydrogen production. However Linkous et al (42), found that issues of reaction kinetics, alkaline scrubber efficiency, ease of sulfur recovery, and market economics combine to discourage addition of sulfite ion as a carrier for photoproducted sulfur.

Figure 8 depicts a system design for a semiconductor particle-based photoreactor. H_2S from the stripper is passed into an alkaline scrubber solution to produce sulfide ion, S^{2-} (aq). The sulfide solution is then sent into a photoreactor, which consists of a bed of catalyst-activated semiconductor particles distributed in a thin array. As the solution is passed over the surface of the photo-energized semiconductor particles, sulfide ion is oxidized and water is reduced to sulfur and hydrogen, respectively. The H_2 gas percolates countercurrent to the top of the reactor where it is collected. The sulfur-containing solution is then recycled back to the scrubber, where it is again mixed with H_2S , precipitating the sulfur and beginning the cycle anew.

The rate of sulfur production is determined by a number of factors: intensity of incoming radiation, sulfide ion concentration, particle size and means of dispersion, and fundamental rate constant, as determined by the catalyst employed. Typical immobilized particle densities vary in the range of 1.0-5.0 mg/cm^2 for the 1-micron CdS powder.

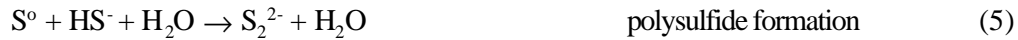
4.2. Process Chemistry

The Photoelectrochemical Particle, or PEP, process is designed to be cyclical in nature, where H_2S is the only input, and H_2 and elemental sulfur are the only outputs. The following are the necessary equilibria to complete the system:

First, in the alkaline scrubber unit, H_2S stripped from a monoethanolamine unit or other purifier is bound in solution by acid/base equilibria:



Bisulfide ion, HS^- , is thus generated and sent to the photoreactor, where the light-induced redox steps produce hydrogen and sulfur that is complexed as polysulfide:



The mechanism given above shows formation of the smallest and simplest polysulfide ion, the disulfide. Actually, there are a number of longer chain polysulfides known, which, in the presence of excess sulfur, can build themselves up from sequential addition, in general:

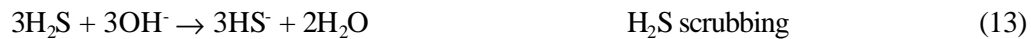


Sulfur saturation studies by Giggenbach (43) showed that n can be as high as 5 in aqueous solutions. Even then, the pentasulfide only exists as a small component in equilibrium with the tetrasulfide, S_4^{2-} . Under typical operating conditions (0.1 M total sulfide concentration and pH 8-12), the tetrasulfide ion is the predominate species.

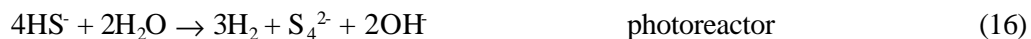
The above mechanisms must then be rewritten to reflect tetrasulfide chemistry. In the photoreactor, we have:



In the scrubber/S-recovery vessel:



By adding the net reactions from photoreactor and scrubber:





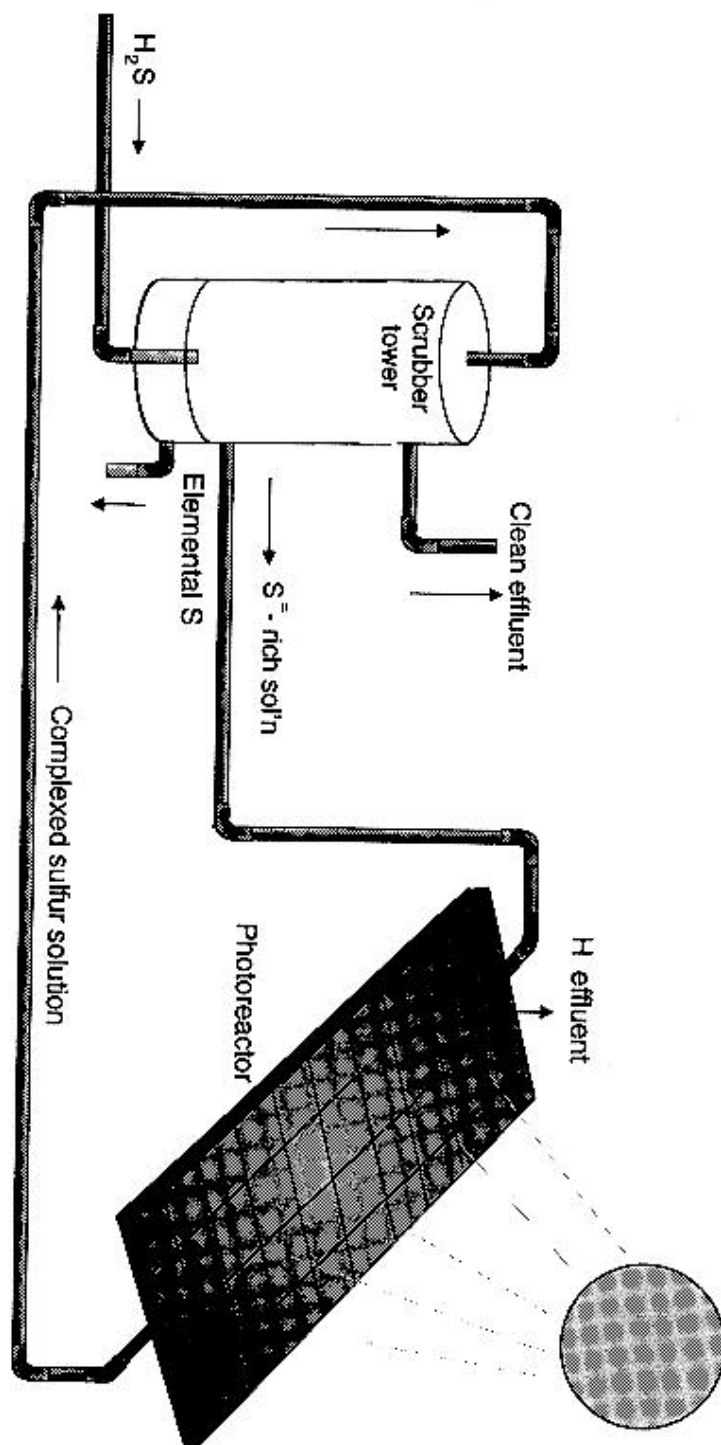
The overall reaction is shown to be the decomposition of H_2S to its constituent elements.

4.3. *Economic Considerations*

Since the PEP process generates hydrogen in equimolar proportion to sulfur, and most modern refineries require more hydrogen than they can produce in-house, one can count a credit of 126 lb of H_2 per ton of sulfur recovered. To scale things up somewhat, a refinery producing 300 tons of sulfur per day due to desulfurization would also generate 18.8 tons of H_2 if the PEP process were being used. At a price of \$8/mbtu for the H_2 , this represents a cost savings of \$15,200/day. The electricity, at \$0.05/kWh, assuming an optimum 100% light generation efficiency and unity quantum efficiency for the photochemical process, would cost only \$3,888. While the ultimate cost differential will undoubtedly be less, a cost ratio of greater than 31 provides substantial room to accommodate practical loss factors.

The economics for the PEP process are much more favorable when considered as a tail gas treatment process, i.e., geared toward environmental compliance, than as a substitute for the entire sulfur recovery system, since the cost of removing or recovering the last few percent of the sulfur equals that of the primary process.

Figure 8: Schematic of PEP Process



Schematic of PEP process for H_2S and sulfur recovery.

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