
In Situ Hydrogen Peroxide Generation for Use as a Disinfectant and as an Oxidant for Water Recovery by Aqueous Phase Catalytic Oxidation

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ABSTRACT

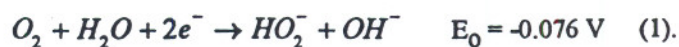
The initial development effort is described for an electrochemical hydrogen peroxide generator and pervaporation module capable of producing and delivering hydrogen peroxide to a contaminated waste water stream as an oxidant or to a pure water stream for use as a disinfectant. A three chambered cell is used to generate hydrogen peroxide by a combined electrodialysis and electrochemical process. Each chamber is separated from its neighbor by a membrane allowing selective production of peroxide anions and hydrogen ions under controlled pH conditions followed by migration to form hydrogen peroxide. Concentrations greater than 6,500mg/L have been produced in this manner. The effects of voltage, pH, membranes, electrode materials, and method of oxygen introduction are delineated. Hydrogen peroxide is then transferred to the end-use stream by pervaporation. The impact of pH, relative flow rates, and ionic strength of sink and source solutions on pervaporation rates is detailed. The use of hydrogen peroxide as a superior disinfectant and as an oxidant is also described.

INTRODUCTION

This paper details the initial development and characterization of an electrochemical hydrogen peroxide (H_2O_2) generator and pervaporation module capable of producing and delivering hydrogen peroxide for on-demand use as a disinfectant or oxidant. A schematic of the electrochemical generator and pervaporation loop is shown in Figure 1. A three chambered cell is used to generate H_2O_2 by a combined electrochemical process including electrolysis and electrodialysis sub-processes. Each chamber within the cell is separated from its neighbor by an ion exchange membrane allowing selective migration of anions and cations produced at the cathode and anode, respectively. The cathode chamber's strong alkalinity (1M KOH) enables the generation of high concentrations of peroxide anions (HO_2^-) due to the suppression of a second, 'parasitic' reduction of HO_2^- to OH^- . The anode reaction of water produces O_2 and H^+ which then migrates toward the central compartment under the action of the electric field. The anode chamber's low pH (1M H_2SO_4) is maintained by this oxidation reaction. The migrating

species, H^+ and HO_2^- , meet in the central chamber forming H_2O_2 . Acidic H_2O_2 solutions in excess of 6,500mg/L have been produced within the central compartment of the breadboard H_2O_2 generator. The effects of voltage, pH, membrane and electrode materials, and method of oxygen introduction on H_2O_2 production rates will be described. Following electrochemical synthesis within the central chamber, H_2O_2 is then transferred to the end-use stream by pervaporation. The impact of pH, relative flow rates, and ionic strength on hydrogen peroxide pervaporation rates is described. The production of H_2O_2 using only oxygen and electrical power is intended to advance the state of the art for environmental control in Advanced Life Support (ALS) systems.

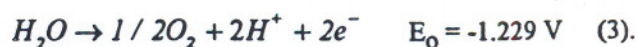
Peroxide is generated from O_2 in an electrochemical cell consisting of a dimensionally stable anode (DSA) consisting of IrO_2 covered titanium, and a composite cathode formed from porous graphite and graphite felt. The anode and cathode chambers are separated from the central compartment by cation and anion exchange membranes, respectively.¹⁻⁴ These membranes form three separate compartments. Oxygen is reduced in the cathode compartment forming HO_2^- anions in a 1M KOH solution according to reaction (1):



Further reduction of HO_2^- to form OH^- proceeds according to reaction (2):



Protons are formed from H_2O in the acidic anode (1M H_2SO_4) chamber producing O_2 according to reaction (3):



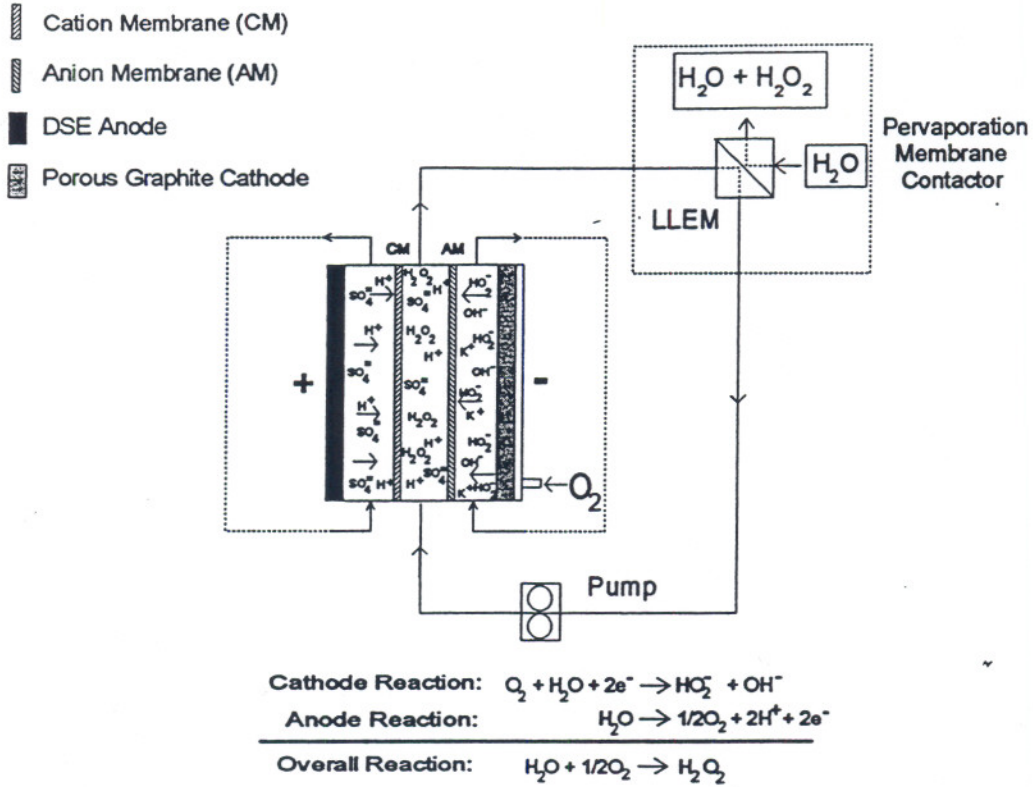


Figure 1. Electrochemical Process for Generation and Separation of H_2O_2

In the central compartment, H_2O_2 is formed by migration of H^+ and HO_2^- through the ion exchange membranes from adjacent compartments. The central compartment contains 0.1M H_2SO_4 as an electrolyte. All solutions are continuously recirculated. The cathode solution receives a steady supply of O_2 while excess O_2 in the anode compartment is continuously removed or may be recycled to the cathode chamber.

Based on the standard potentials of reactions (1)-(3), the reduction of O_2 to OH^- is thermodynamically favored. The second 'parasitic' reduction eliminates the desired product, HO_2^- . When the OH^- concentration in the cathode chamber is raised, this parasitic reduction is suppressed and the desired product, HO_2^- predominates. Combining half reactions (2) and (3), illustrates this point through the equilibrium expression relating HO_2^- and OH^- given by (4),

$$HO_2^- \rightarrow 1/2 O_2 + OH^- \quad \Delta E_o = -0.359 V$$

$$\text{and } K = \frac{[O_2][OH^-]}{[HO_2^-]} = 5.19 \times 10^{-6} \quad (4).$$

This expression indicates that high pH favors HO_2^- formation relative to OH^- .

Electrodialytic migration of charged species formed at the two electrodes occurs under the applied electric field. Protons formed at the anode migrate across the anode chamber, through the cation exchange membrane, and into the central compartment. Since the initial OH^- concentration in the cathode compartment is high, OH^- form the bulk of initial anionic species which migrate into the central

compartment. The counter migration of H^+ into the central compartment forms H_2O in the central compartment. As the HO_2^- concentration in the cathode chamber builds due to electro-reduction of O_2 , HO_2^- replaces OH^- as the major anion exchange membrane migrant. When this latter condition holds, H^+ and HO_2^- react in the central compartment under acidic conditions. According to the dissociation equilibrium for H_2O_2 given by (5),

$$H_2O_2 \rightarrow H^+ + HO_2^- \quad \text{and}$$

$$K = \frac{[H^+][HO_2^-]}{[H_2O_2]} = 1.5 \times 10^{-12} \quad (5)$$

H_2O_2 will be the predominant species at the pH of the central compartment. The overall electrochemical reaction produces H_2O_2 from water and oxygen according to reaction (6):



Factors which determine the rate of production of HO_2^- in the catholyte and its transfer rate into the central compartment include voltage, secondary parasitic reactions, membrane resistance, membrane leakage, the availability of O_2 for reduction at the cathode-gas-liquid interface, and the concentration of OH^- in the cathode compartment.

The H_2O_2 produced by the generator is contained in a 0.1M H_2SO_4 solution within the central compartment. The delivery of H_2O_2 to a pure water stream is accomplished by pervaporation of H_2O_2 through a Liquid-Liquid Exchange

Module (LLEM) composed of a bundle of hollow fiber membranes in the tube-in-shell configuration shown in Figure 2. The acidic H_2O_2 solution from the electrochemical cell's central compartment recirculates through the shell side of the

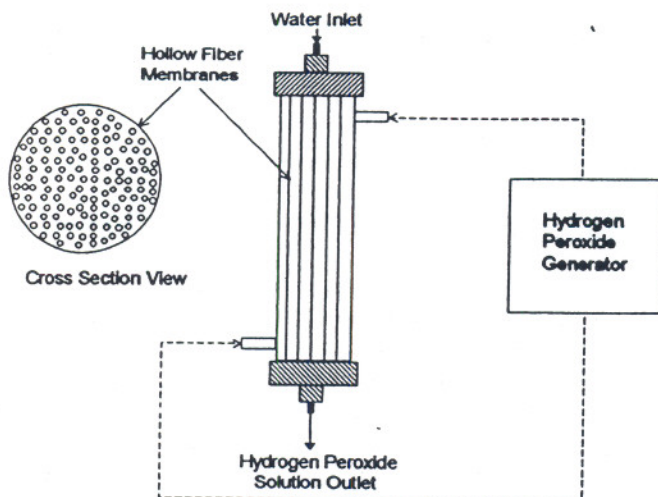


Figure 2. Pervaporation of H_2O_2 Through a Tube-in-Shell Hollow Fiber LLEM.

LLEM. The water stream flows through the tube side of the LLEM. The tube side is formed from microporous hollow fibers. This type of membrane allows vapor phase transport of H_2O_2 through gas filled pores. Since H_2O_2 is the only volatile component other than H_2O contained within the electrochemical cell, a very effective separation from ionic species is achieved. The use of small hollow fibers makes efficient mass transfer possible due to high membrane surface to liquid volume ratios in concert with short diffusion distances.^{5,6} The gas phase membrane transport of H_2O_2 across microporous tubing is driven by the concentration gradient between the two streams. The volatilization of H_2O_2 is governed by Henry's Law (7),

$$k = \frac{p\text{H}_2\text{O}_2}{\chi} \quad (7),$$

where k is the Henry's Law constant, $p\text{H}_2\text{O}_2$ is the partial pressure of hydrogen peroxide vapor, and χ is the mole fraction of hydrogen peroxide in the sulfuric acid solution. The value of k is sufficiently large to ensure a reasonable permeation rate.

EXPERIMENTAL SECTION

Materials and Apparatus.

Chemicals. Reagent grade sulfuric acid, potassium hydroxide, hydrogen peroxide, urea, and acetic acid were purchased from Aldrich (Milwaukee, WI). Horseradish peroxidase (EC 1.11.1.7), and o-dianisidine were obtained from Sigma (St. Louis, MO). R2A culture media was purchased from VWR Scientific (Seattle, WA). 1MΩ deionized (DI) water was prepared using mixed ion exchange beds and carbon adsorption (Culligan). Breathing quality

compressed oxygen was purchased from Pacific Airgas (Portland, OR).

Analytical Instruments and Methods. Hydrogen peroxide and urea determinations were made by the horseradish peroxidase-dianisidine, and BUN methods respectively, using a Hewlett-Packard 8452A diode array UV-visible spectrophotometer. Total Organic Carbon (TOC) was determined using an ASTRO 2001 TIC/TOC analyzer. Acetone was quantified using a Hewlett-Packard 5710A gas chromatograph with flame ionization detection and a packed SP-1000 stainless steel column (Alltech).

Electrodes. A 5cm x 10cm dimensionally stable anode (DSA) of IrO_2 over titanium and a reticulated vitreous carbon cathode (# 45 PPI) were purchased from Electrosynthesis Company (Lancaster, NY). Kynol carbon fabric was provided by American Kynol (Pleasantville, NY). Fine woven carbon felt was acquired from Alfa Aesar Chemical (Ward Hill, MA). A porous carbon brick (# 7196) was supplied by National Electronic Carbon (Cleveland, OH). An Ag/AgCl reference electrode was purchased from Microelectrodes, Inc., (Londonderry, NH).

Materials. CR67-HMR-412 sodium form strong acid cation exchange, and 204-UZL-386 chloride form strong base anion exchange electro dialysis membranes were purchased from Ionics (Watertown, MA). Tokuyama Soda (TS) brand Neosepta CM-2 sodium form strong acid cation exchange and AMH chloride form strong base anion exchange membranes were purchased from Electrosynthesis (Lancaster, NY). Prior to use, cation exchange membranes were converted to the hydrogen form by contact with 1M sulfuric acid for 16 hours. Anion exchange membranes were converted to the hydroxide form by contact with 5% (w/v) potassium hydroxide for 16 hours. Non-porous polydimethylsiloxane (Silastic) hollow fiber membranes with 0.031 cm internal diameter and 0.016 cm wall thickness (0.031cm ID x 0.064cm OD) were purchased from Dow Corning (Midland, MI). Microporous polypropylene hollow fibers with 0.05μm pore diameter, 0.040cm internal diameter and 0.003cm wall thickness (0.040cm ID x 0.046cm OD) were donated by Hoechst-Celanese (Charlotte, NC). Ethylene-propylene rubber (EPDM) gasket material was acquired from Chavers Gasket Corp. (Laguna Hills, CA). Teflon gasket material was obtained from Small Parts, Inc. (Miami Lakes, FL). High density polypropylene purchased from several suppliers was used to form the three chambers in the hydrogen peroxide generator.

Electrochemical Cells (EC). Two electrochemical cells were fabricated and evaluated during the Phase I effort. Each incorporates three distinct flow paths. The catholyte chamber (1.0M KOH) is formed between the cathode and anion exchange membrane, and flow recirculates through an O_2 source (either saturator or gas injector), a reservoir, and a peristaltic pump. The central chamber contains an acidic solution (0.1-0.5M H_2SO_4) which accepts peroxide anions from the catholyte and protons from the anolyte. This

chamber recirculates via a second peristaltic pump channel, reservoir combination. The anolyte (1.0M H_2SO_4) flows between the anode and an electroalytic cation exchange membrane, and recirculates through a reservoir, membrane degasser, and third peristaltic pump channel.

In operation, recirculating streams flow at different rates through each chamber. The applied electric potential is precisely controlled relative to a Ag/AgCl reference electrode in the catholyte chamber using a Pine Instruments (Grove City, PA) AFRDE-4 Potentionstat. The peroxide anion competes with the matrix hydroxide ions for electroalytic migration through the anion membrane. Electrodialysis of HO_2^- becomes more efficient at higher concentrations. Product O_2 is vented via a degasser in the anode chamber recirculation loop.

First Generation Cell (EC1): The initial cell configuration consisted of a series of 10cm by 15cm elements sandwiched together and separated by Teflon spacers, polypropylene blocks, and EPDM gaskets. Inside, three chambers are formed. The anode chamber is bounded by the DSE at the external face, and the cation exchange membrane at the internal face. The central chamber is bounded on the anode side by a cation exchange membrane and on the cathode side by an anion exchange membrane. The cathode chamber is bounded by the inner anion exchange membrane and by the cathode at the outer face. A variety of cathode materials were investigated using this cell. The cell is held together by two 1.27cm (0.5inch) aluminum frame mounts fronted by polypropylene blocks with fourteen 7.62cm (3inch) screws

evenly spaced around the edge of the frame. Four alignment pins were located in the corners of the cell, with stainless steel pins used for the initial alignment of all the gaskets and membranes. A hole was cut in the center of each plate of the frame to allow the electrical connections to be made to each electrode. Flow paths to each compartment were cut directly into the thick EPDM gasket material and polypropylene backing blocks. A hollow fiber membrane oxygen saturator was used to oxygenate the solution flowing into the anode compartment. Degassing was achieved by venting from the reservoir.

Second Generation Cell (EC2): The second cell illustrated in Figure 3 incorporates features which were intended to produce a substantial improvement in performance. The recirculating aqueous streams are introduced directly into each chamber via injection ports located at the end of each polyethylene chamber. This arrangement utilizes the full electrode surface by eliminating stagnant areas through better flow dynamics. In the new configuration, the thick EPDM spacers are replaced with polyethylene spacers of the same dimensions, with thin 1 mm EPDM gaskets between them to allow a proper seal between the plastic blocks. The membranes are separated from the polyethylene spacers by thin layers of EPDM. The polyethylene spacers are perforated with three 0.159cm (1/16inch) holes on the top and bottom surfaces to allow even distribution of flow throughout the body. Each chamber is independently plumbed in an up flow configuration, rather than along a

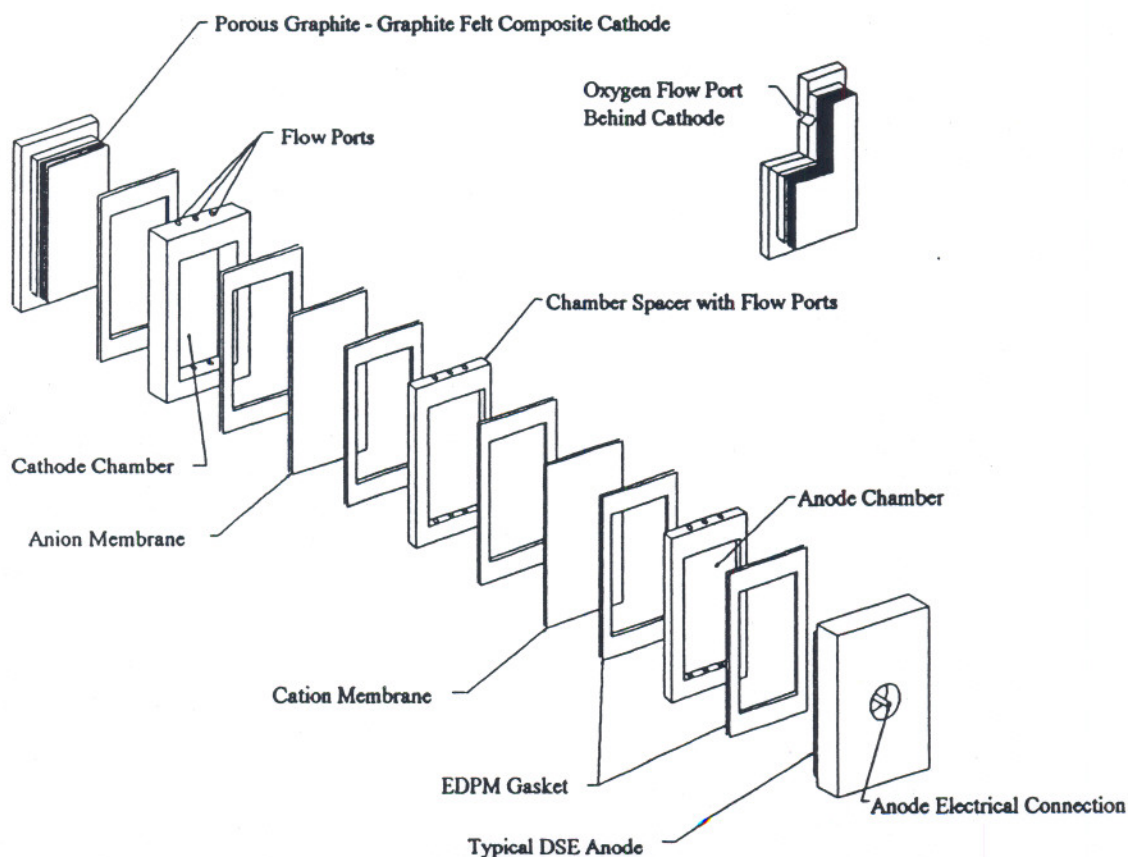


Figure 3. Second Generation Electrochemical Cell, EC2.

flow path including holes in the electrode block and vias cut into each gasket. A short length of hard Teflon tubing is inserted in each port and attached to flexible Tygon tubing. The ports to and from each chamber are connected together as a manifold using polyethylene tees. Two different methods of O_2 introduction were employed. Oxygen was introduced through a porous carbon cathode via an inlet line plumbed directly behind the cathode chamber into a hollow in the polypropylene backing plate. A 1mm thick EPDM spacer is used to create a chamber that allows gas contact with the full length of the cathode block. The second method employs direct introduction of O_2 bubbles into the recirculating flow just prior to the catholyte chamber. The cathode electrical connection is made by a screw inserted into a graphite post. The reference electrode is inserted through the central outlet port, directly into the cathode block.

Liquid-Liquid Exchange Module (LLEM). The LLEM is a tube-in-shell membrane pervaporation contactor designed to transfer H_2O_2 from an acidic solution (representing the central flow compartment of the electrochemical cell) on the shell side of the contactor, to a deionized water stream flowing countercurrent through the tube side of the contactor as previously shown in Figure 2.

The LLEM was constructed using 72 microporous polypropylene hollow fibers inside a polytetrafluoroethylene-co-hexafluoropropene (FEP) shell. The unit is 290cm in length. The hollow fibers are attached to flow distributing end-caps with epoxy cement. The internal volume within the shell and the hollow fiber bundle is 27.4mL and 6.6mL respectively. Active membrane surface area available for mass transfer within the module is 1,312cm². Flow in tube and shell sides of the LLEM are controlled independently.

Oxygen Saturator. An O_2 saturation module was assembled in order to oxygenate the influent to the cathode chamber of the first EC cell. This module consists of a hollow fiber bundle formed from non-porous polydimethylsiloxane membranes in a tube-in-shell arrangement similar to the LLEM. The saturator uses a bundle of 114 fibers inside a cylindrical polyvinylchloride shell, 26.7cm in length and 2.54cm in diameter with a fiber internal volume of 2.3mL and an active area of 251cm². The gas outlet to the shell is dead ended. The hollow fibers are attached to manifolds at the inlet and outlet faces by an epoxy potting compound. The module is designed to equilibrate a gas phase in the shell with an aqueous stream flowing through the hollow fibers. At equilibrium, a balance exists between O_2 vapor and dissolved aqueous O_2 as described by Henry's Law.⁷ Collection of dissolved O_2 after saturation at higher than atmospheric pressures confirmed the saturator's performance.

Low Temperature Aqueous Phase Catalytic Oxidation Reactor. As shown in Figure 4, the catalytic oxidation system consists of temperature control and reactor sub-systems. The temperature control unit is comprised of silicon oil bath, coiled heating element (Watlow), mixer, and Omega Series CN 1200 temperature controller. A type K thermocouple submerged in the oil bath provides temperature input to the controller which regulates power to the heating element. This control scheme maintains oil bath and reactor temperatures within $\pm 0.5^\circ\text{C}$.

The reactor unit consists of a packed catalyst bed, oxygen saturator, influent preheating coil, effluent cooling coil, pressure relief valve, Eldex A-30-VS metering pump, and Nupro model SS-RL354 back-pressure regulator. The preheating and cooling coils were prepared using 6.1meter

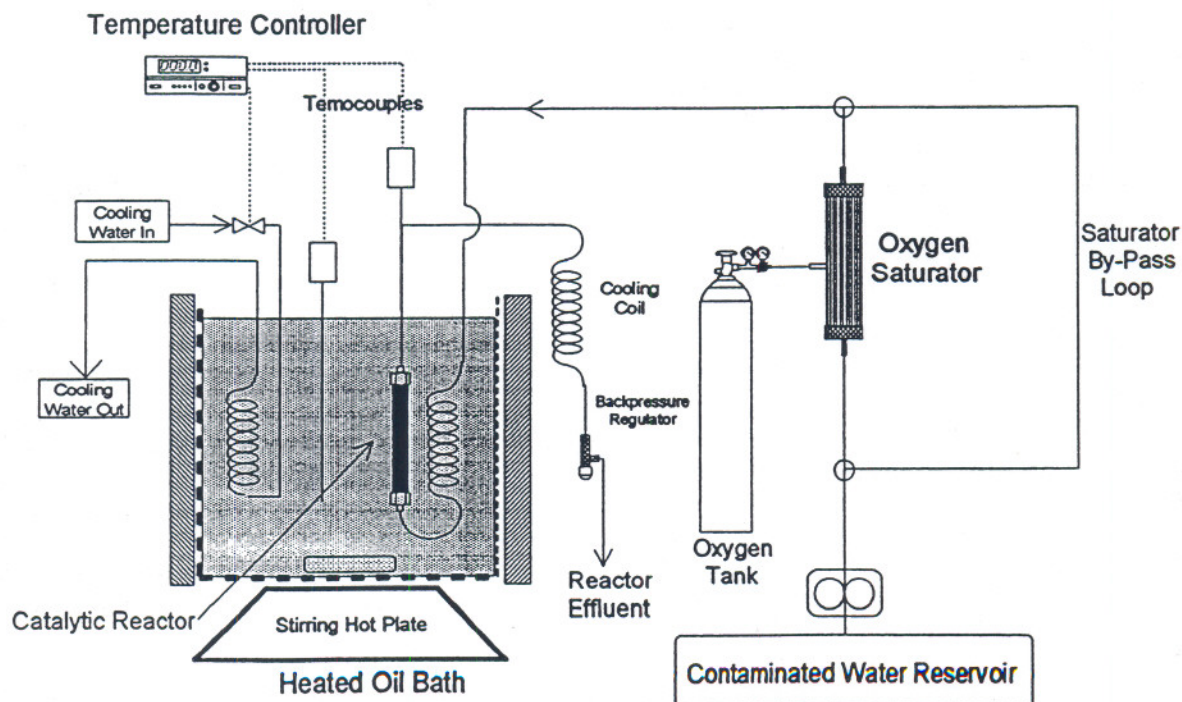


Figure 4. Aqueous Phase Catalytic Oxidation System.

lengths of 316 SS tubing with an internal diameter of 0.318cm and 0.09cm wall thickness. Several different catalyst beds were used. The packed catalyst beds were configured as plug flow tubular micro-reactors, confined within 1.27cm diameter and 0.09cm wall thickness 316 stainless steel housings of various lengths and volumes. Plug flow conditions were determined based on catalyst particle size, flow rates, and reactor size.^{8,9}

In operation, sufficient pressure is applied to the shell side of the O₂ saturator to achieve the desired dissolved O₂ concentration in the reactor influent. The oxygen saturated stream then passes through the heating coil which brings it to the specified reactor operating temperature. The contaminant laden aqueous stream then flows into the packed catalyst bed where the oxidation reactions are initiated. The reactor outflow passes through the cooling coil where heat is dissipated by forced air convection. The cooling coil produces an ambient temperature effluent. The back-pressure regulator maintains reactor operating pressure. Operation of this type of reactor has been previously described in much greater detail.¹⁰⁻¹⁵ This reactor was used for the experiments using O₂ as the oxidant. A second reactor was assembled differing only in the absence of the O₂ saturator. This unit was used to study the use of hydrogen peroxide as oxidant.

Experimental Approach.

The main objectives of the research were to demonstrate: 1) the electrochemical generation of peroxide anions in an oxygen saturated recirculating basic solution (pH>12), 2) electrodialytic transport of peroxide ions across an anion exchange membrane into an acidic stream forming undissociated hydrogen peroxide, and 3) introduction of the product hydrogen peroxide into a flowing water stream by membrane pervaporation. Subsequent tests were also performed to determine the effectiveness of H₂O₂ as a sterilizing agent and as an oxidant for low temperature aqueous phase catalytic oxidation.

Two experimental systems were investigated concurrently. The production and transport of HO₂⁻ was studied using an electrochemical cell which evolved as enhancements were incorporated in the cell design. The membrane separation of H₂O₂ from a high ionic strength acidic stream was studied using a LLEM module. Each of these experimental systems is discussed in greater detail below.

Electrochemical/Electrodialytic Cell. Experiments were performed to determine means for generation of acceptable levels of peroxide by the reduction of O₂ at the cathode, and to transport the product into the central chamber. Hydrogen peroxide concentrations in the cathode compartment and in the central chamber were monitored as functions of time and applied electric potential. Important factors investigated were applied voltages and resulting currents, cell resistance, cathode composition, electrode surface area, configuration of the cathodic compartment, techniques for O₂ introduction into the catholyte, and relative performances of different types of anion and cation exchange membranes. Experimentation began using the first EC1 cell design. The deficiencies in

this cell were used to aid in the design of a second cell (EC2), intended to substantially improve performance.

Liquid-Liquid Exchange Module. The LLEM module was used to study the delivery of hydrogen peroxide into a DI water stream through vapor phase transport across a hollow fiber bundle of microporous polypropylene tubing (pervaporation). Experiments performed with the LLEM module used recirculating solutions with initial hydrogen peroxide concentrations between 0.5-1% in 1M H₂SO₄ on the shell side of the module and studied peroxide transport to the pH neutral solution flowing through the hollow fibers as functions of concentration, flow rate, and temperature.

Aqueous Phase Catalytic Oxidation. Experiments were performed to assess the relative efficacy of H₂O₂ as an oxidant for aqueous phase catalytic oxidation of dissolved organics at temperatures between 100 and 120 °C as compared to O₂. The first comparisons were made for urea oxidation. Urea is a problematic contaminant due to the inability of many oxidative systems to efficiently process this compound and its byproducts. The study was conducted using two identically configured catalytic reactors with a 1% Pt/Al₂O₃ catalyst under identical conditions of temperature and pressure. The two reactors differed only in the presence or absence of an O₂ saturator. Stoichiometrically equivalent concentrations of O₂ and H₂O₂ were used. Effluent TOC levels were monitored. To facilitate comparison between the two oxidants, catalyst activity, reactor temperature and space velocity were manipulated to achieve only partial conversion of the reactant. A second set of experiments investigated the capacity of a H₂O₂ based reactor to treat higher levels of influent than would be practical using O₂. These studies used high concentrations of acetic acid (500mg/L) as the contaminant.

Biocidal Activity of H₂O₂ Solutions on Biofilm and Planktonic Microbial Activity.

The effectiveness of H₂O₂ as a biocide was investigated for the control of planktonic microorganisms and biofilms. Free floating or planktonic microorganisms were obtained directly from laboratory deionized water. These planktonic microbial forms are pertinent to ALS water reclamation systems since they are sloughed organisms originating from biofilms present in the deionizing equipment. Solutions containing a known level of planktonic microorganisms were challenged with various H₂O₂ concentrations, and residual microbial activity was determined as a function of exposure time. Biofilms were grown on cleaned microscopic slides in deionized water. Slides were immersed in a culture medium consisting of 1.5g of R2A medium in 1.5 liters of deionized water. Each slide was angled at ~30 degrees from vertical along the edge of a glass dish. This solution was slowly stirred for six days with periodic addition of deionized water to maintain the liquid level. These slides were then exposed to different H₂O₂ concentrations, and residual microbial activity was determined as a function of exposure time.

RESULTS AND DISCUSSION

Electrochemical H_2O_2 Generation. Using the EC1 cell, series of tests were conducted to compare the effect of cathode composition on the rate of H_2O_2 production, using a variety of carbonaceous materials including reticulated carbon block, layered carbon felt, shredded carbon felt, Kynol felt, and porous carbon block. The influent to the cathode chamber was saturated with 40mg/L of O_2 at a flow rate of 18mL/min. The cathode voltage of 1.5V relative to the Ag/AgCl reference electrode produced a 20mA current. Ionics (Watertown, MA) ion exchange membranes were used. The results are shown in Figure 5. HO_2^- production using the porous carbon block as cathode was at least double that of any of the other materials. This material was incorporated in subsequent cell designs.

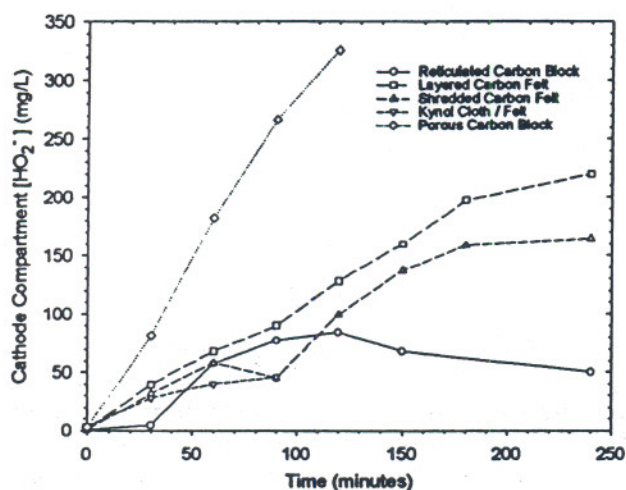


Figure 5. HO_2^- Production for Different Cathode Materials.

A second experiment conducted using the EC1 cell compared rates of transport of HO_2^- into the central compartment by Ionics and Tokuyama Soda anion membranes. In both cases, the Ionics cation exchange membrane was used. The catholyte solution contained 1000mg/L of HO_2^- and was recirculated through a porous carbon block cathode at 18mL/min. The potentiostat delivered 43mA at +0.4V relative to the Ag/AgCl reference. The results indicated only a small difference in performance between the two membranes, with the Tokuyama Soda membrane performing slightly better than the Ionics membrane. The differences were attributed to the thickness of the more robust Ionics membrane.

Initially, the low rates of peroxide production in EC1 were attributed to O_2 mass transfer limitations at the cathode. To improve O_2 availability at the cathode, two changes were incorporated into the design of EC2. The hollow fiber membrane saturator was replaced with direct injection of O_2 . In addition, a layer of graphite carbon felt were attached to the porous carbon block using a carbon based conductive epoxy resin. Oxygen was then injected through the rear face of the porous carbon into the carbon felt. This composite cathode was intended to maintain higher levels of O_2 availability for peroxide production, by moving the gas-

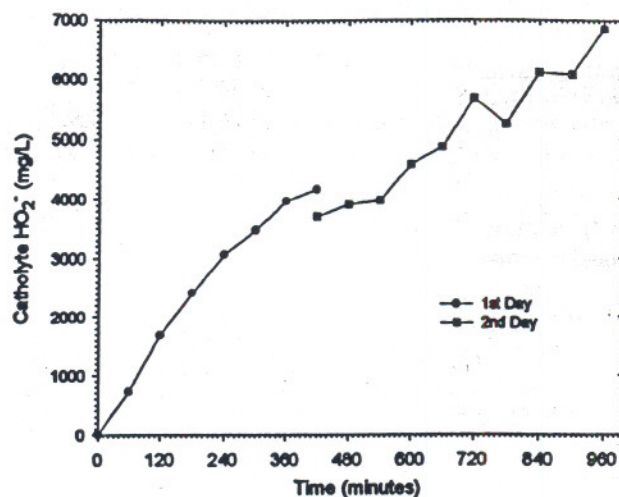


Figure 6. Cathodic Production of Peroxide Anion, EC2.

liquid interface to a region of high surface located inside the cathode.

Using this new arrangement, the EC2 cell produced $\approx 7,000$ mg/L of peroxide in the recirculating catholyte as shown in Figure 6. This experiment was conducted at 0.6V and ~ 20 mA with 20 mL/min flow rates. The Tokuyama Soda anion membrane was used. The production of H_2O_2 in the central chamber is given in Figure 7. While cathodic production of HO_2^- was good, the membrane transport of the anion was not. Further work focused on identification of the conditions needed for efficient peroxide delivery into the central compartment. Important factors include: the driving voltage which is very low at 0.6V; the concentration gradient for HO_2^- , which rises with time; and poor mixing of HO_2^- in the cathode compartment, especially near the anion exchange membrane.

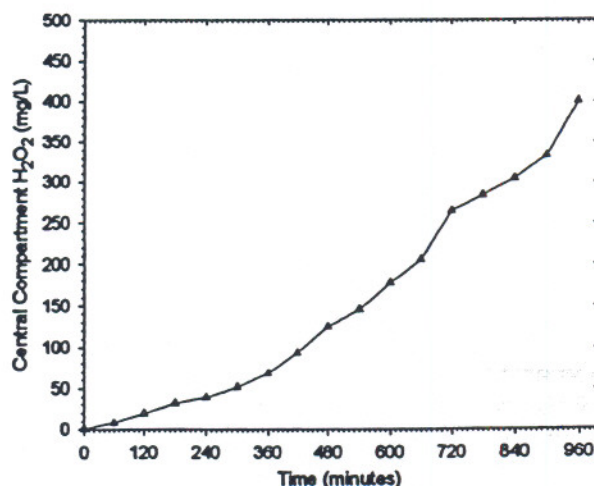


Figure 7. H_2O_2 Production in Central Compartment, EC2.

The relationship between applied voltage and peroxide production was studied over the range between 0.6 - 1.0 V at an O_2 flow rate of 350mL/min. The EC2 cell was

operated at each potential for three hours. At the midpoint of the experiment the cell was turned off overnight. Upon restart, the voltage was decreased at three hour intervals. Operating currents were 80mA at 0.6V, 120mA at 0.8V and 220mA at 1.0V. A steady increase in the concentration of HO_2^- was observed in the cathode compartment at potentiostat settings of 0.6 and 0.8V, while decomposition was evident at 1.0V. Evidently, the efficiency of peroxide electrogeneration decreased due to competition from parasitic cathode reactions at 1.0V. Simultaneous measurement of HO_2^- migration through the anion exchange membrane into the central compartment indicated transport of the product HO_2^- into the central chamber increased as HO_2^- concentration increased in the catholyte. The best transfer rates occurred at 0.6V. This behavior indicates the great importance of the $[\text{HO}_2^-]/[\text{OH}^-]$ ratio in voltage driven electrodialysis.

This experiment confirmed the validity of the 0.6V applied operating potential. Elimination of contact resistance in EC2 resulted in an increase in cell current by a factor of 5-10 reaching between 400-1,000mA. Under these higher current conditions, much higher levels of $\sim 12,000$ mg/L of HO_2^- were produced in the cathode chamber. Responding to the higher concentration gradient, transport across the anion exchange membrane was also dramatically improved, resulting in the production of $\sim 6,600$ mg/L of H_2O_2 into the central compartment. These results are shown in Figure 8.

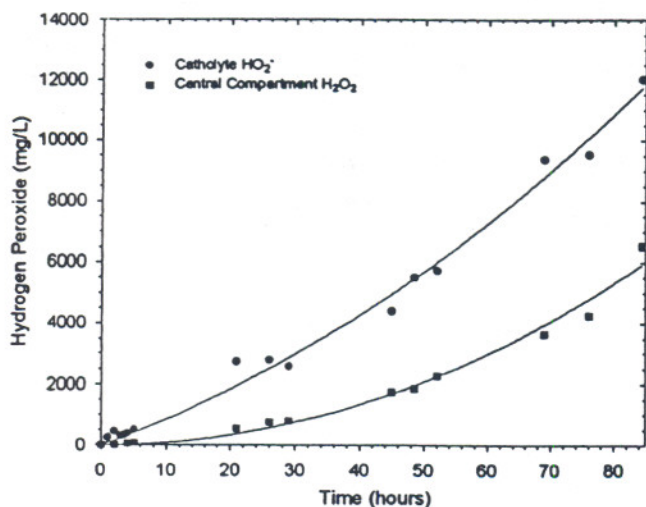


Figure 8. Hydrogen Peroxide Generation in.

H_2O_2 Separation by Pervaporation. Deionized water containing 5,000mg/L of H_2O_2 was recirculated through the shell side of the LLEM at a constant 16mL/min. On the tube side of the LLEM, DI water fed in a single pass at flow rates between 0.10-0.24mL/min. Total volume of the recirculating solution was 100mL. A similar set of experiments was performed using a recirculating solution of 5,000mg/L H_2O_2 in 0.5 M H_2SO_4 on the shell side. A comparison between the two is illustrated in Figure 9 in terms of contact time for the DI water stream. In the case of the acid containing H_2O_2 feed solution, significant transfer of water across the membrane

from the DI stream into the acid stream occurs due to the osmotic pressure between the two streams. In another experiment, a 2L reservoir of 10,000mg/L H_2O_2 in 0.5 M H_2SO_4 was recirculated at 20mL/min on the shell side of the LLEM and the tube side of the LLEM was fed DI water at a flow rate of 0.39mL/min. Over the course of 72 hours, a ten percent increase in volume of the recirculated acid solution was observed. During this pervaporation run, 1.6L of 2700mg/L H_2O_2 solution was collected on the fiber bundle side of the LLEM. These results demonstrate transfer and delivery of H_2O_2 to a second aqueous stream.

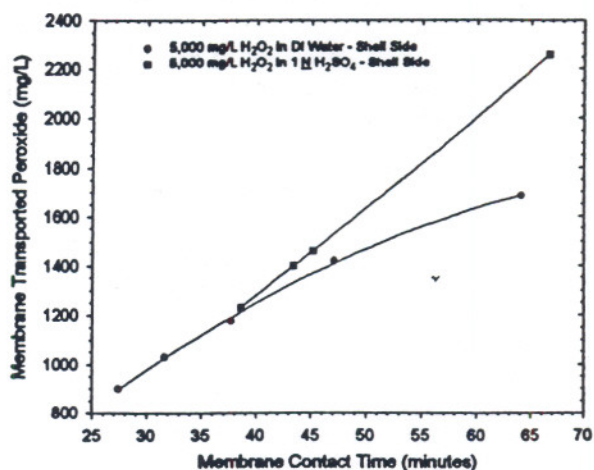


Figure 9. Peroxide Transfer by Pervaporation

Comparison of Aqueous Phase Catalytic Oxidation using O_2 and H_2O_2 as Oxidants. Catalysts used to demonstrate enhanced oxidation by H_2O_2 were designed to utilize dissolved O_2 at moderate temperatures (100-140°C). The noble metal sites on these catalysts promote H_2O_2 decomposition which reduces effectiveness at promoting H_2O_2 as a free radical source. Nevertheless, enhanced aqueous phase catalytic oxidation afforded by the use of H_2O_2 result in lower oxidation temperatures, more complete oxidation, and higher conversion of problematic compounds. In order to demonstrate this behavior, several different catalytic oxidation experiments were carried out. Among these were challenges of high concentrations of urea and oxidation of high concentrations of acetic acid at moderate temperatures. These organic contaminants are known to resist oxidation and represent an endpoint to other oxidation technologies.¹⁶⁻²²

Urea is a problematic organic contaminant primarily because of the formation of NH_3 as an intermediate. Since NH_3 strongly binds with noble metals, its presence reduces the number of oxidation sites available and decreases oxidation activity. In order to demonstrate the effectiveness of H_2O_2 assisted catalytic oxidation, two 11.3 mL reactors filled with 1 % Pt on 2.0mm Al_2O_3 balls (from Shimadzu) were challenged by urea (247mg/L or 49.4 mg/L as C) at a moderate reactor temperature of 100°C using O_2 and H_2O_2 , respectively. A comparison of the two oxidants for Total Organic Carbon (TOC) reduction is shown in Figure 10. The reactor using H_2O_2 is more efficient at equivalent flow rates. As the flow rates decrease, the superiority of H_2O_2 over O_2 increases. The strong dependence of oxidation on contact

time (i.e. flow rate, space velocity, or space time) is a reflection of the effect of unoxidized NH_3 on urea oxidation. When the reactor's temperature was raised to 120°C , urea was nearly completely oxidized in both reactors with TOC levels below 500 ppb. This behavior reflects the capacity of catalytic reactors to mineralize organic contaminants at high temperatures in the absence of competing reactions.

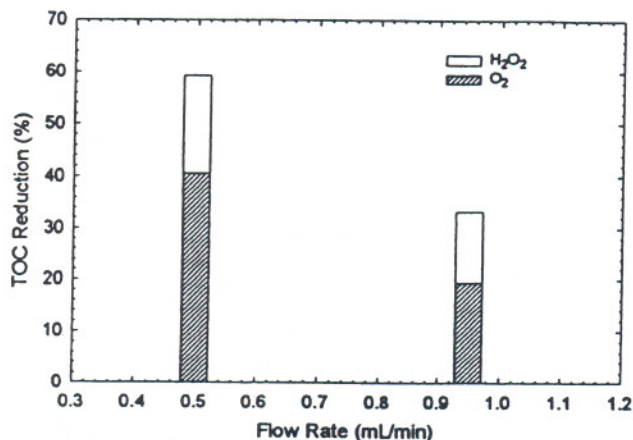


Figure 10: Urea Oxidation at 100°C with H_2O_2 and O_2 .

The complete oxidation of a highly contaminated waste stream is a primary objective for a H_2O_2 based catalytic oxidation system. To test H_2O_2 based catalytic oxidation capacity, a reactor operating at 120°C was challenged with a 500mg/L (TOC=200mg/L) acetic acid solution. The system was pressurized to ensure single phase operation, and a 25% stoichiometric excess of H_2O_2 was added to the influent. The effluent TOC as a function of space time (contact time) and the resulting pseudo first order decay curve are shown in Figure 11. At longer space times, nearly complete mineralization was achieved. The effluent TOCs dependence upon contact time is typical of plug flow catalytic oxidation reactors.¹⁰⁻¹⁵ These data convincingly supports the use of

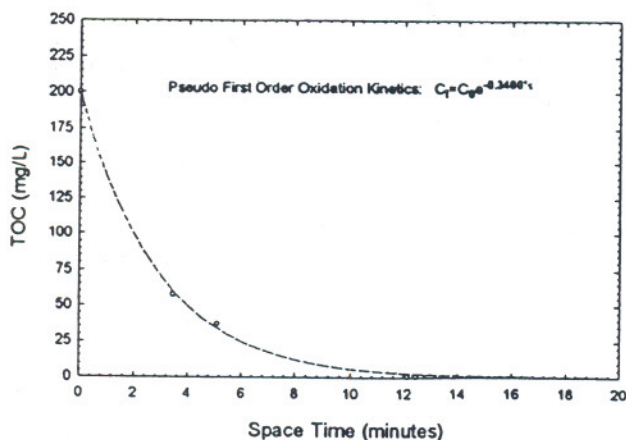


Figure 11: Pseudo First Order Oxidation Kinetics for a 500 mg/L Acetic Acid Challenge at 120°C

H_2O_2 to boost aqueous phase catalytic oxidation rates on highly contaminated waste water. Both the reactivity of H_2O_2 and its solubility contribute to this enhancement.

Biocidal Activity of H_2O_2 Solutions on Planktonic and Biofilm Microbial Activity.

Laboratory deionized water was used as the source for planktonic microorganisms primarily *Pseudomonas pickettii*. Addition of a stock 30% H_2O_2 solution to deionized water containing 8.84×10^5 Colony Forming Units (CFU)/mL was used to produce microbially contaminated samples containing 30,000, 10,000, 3000, 300, and 30mg/L H_2O_2 . Samples were removed from each flask at designated time intervals, and diluted to 10^{-1} , 10^{-2} , and 10^{-3} prior to plating on R2A Agar. The deionized water's initial microbial concentration was determined using a 10^{-4} dilution.

Following addition of H_2O_2 to the deionized water samples, all microbial activity was eliminated within 15 minutes at all H_2O_2 concentrations in excess of 30mg/L. This mixture reduced the microbial concentration gradually through the first 60 minutes. No bacteria were detected in the 120 minute sample. Results for this sample are shown in Figure 12. The effectiveness of H_2O_2 on planktonic microbial forms is rapid and complete with H_2O_2 concentrations of 300mg/L or more. At 30mg/L, the microbial death curve is atypical. From time zero through 60 minutes the bacterial population reduces slowly. At some point between 60 and 120 minutes, the population was eradicated. Clearly, low concentrations of H_2O_2 will eliminate the planktonic microorganisms found in deionized water.

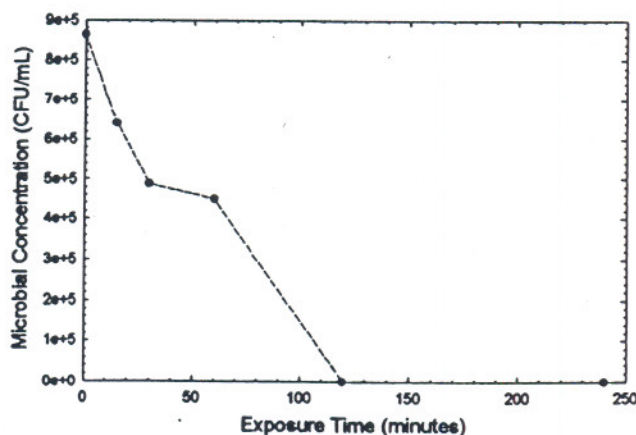


Figure 12: Microbial Activity for Planktonic Microorganisms Exposed to 30 ppm H_2O_2

Solutions of 30,000, 10,000, 3000, 300, and 30mg/L H_2O_2 were prepared by serial dilution of the stock 30% H_2O_2 solution. Slides were removed from the biofilm growing chamber and flushed with sterile buffered water to remove any free form bacteria, and then placed in 80mL of each of the H_2O_2 solutions. Each slide was periodically agitated to prevent bubble formation. After the designated time period, slides were removed from the H_2O_2 solution and thoroughly flushed with sterile unbuffered water to remove residual H_2O_2 . Each biofilm was then aseptically removed into a 100mL sample of sterile buffered water. The solution containing the removed biofilm was then diluted by factors of 10^{-1} , 10^{-2} , 10^{-3} , and 10^{-4} . Each dilution and the original sample were plated on R2A Agar and incubated at 20°C . The

CFU/mL was then determined for each H_2O_2 concentration at different exposure intervals. The untreated biofilm possessed an initial microbial concentration of 2.48×10^7 CFU/mL. The exposure data as a function of time is presented in Figures 13 and 14.

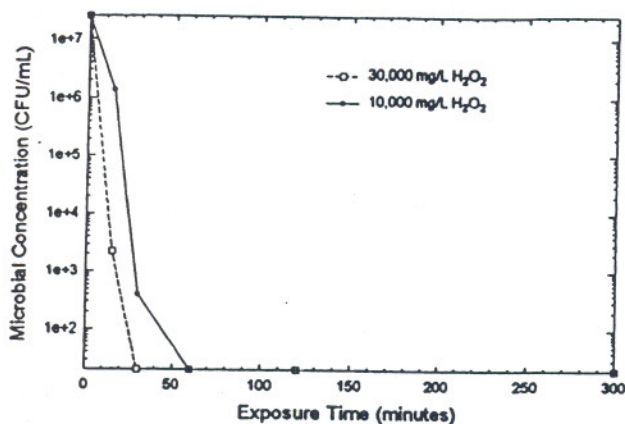


Figure 13: Biofilms Exposed to 30,000 and 10,000mg/L H_2O_2 .

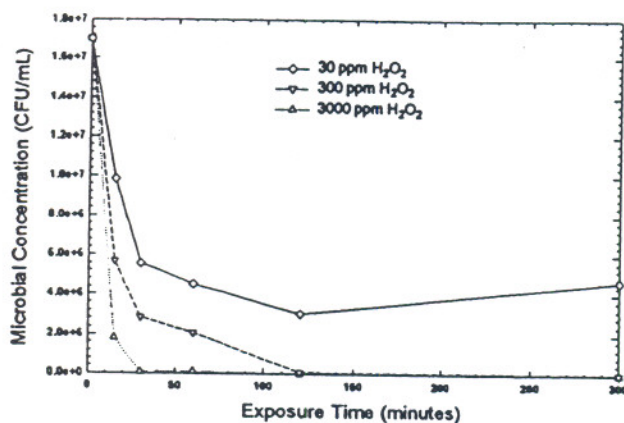


Figure 14: Biofilms Exposed to 3,000, 300, and 30mg/L H_2O_2 .

These data indicate that H_2O_2 is a very effective biocide even at low concentration. The 10,000mg/L (1%) solution reduced the 10^7 microbial concentration to zero between 30 and 60 minute. The 30,000mg/L (3%) solution accomplished the same results between 15 and 30 minutes. The 3000mg/L (0.3%) H_2O_2 solution eradicated the bacterial population in the biofilm between 180 and 300 minutes. The 300 and 30mg/L H_2O_2 concentrations did not eliminate the biofilm in the time frame of the test. However, the 300mg/L H_2O_2 level reduced the bacterial numbers significantly in 300 minutes.

CONCLUSIONS

The electrochemical generation of H_2O_2 , followed by its separation and delivery to a second aqueous stream for on-demand use as a disinfectant or oxidant has been

demonstrated. Using an iridium oxide dimensionally stable anode and a high surface area carbon felt cathode held at a potential of 0.6V relative to a Ag/AgCl reference, peroxide anion (HO_2^-) concentrations of 12,000 mg/L have been produced by electro-reduction of O_2 in the cathode chamber. Electrodialytic transfer of these ions across an anion exchange membrane from the catholyte into an acidic recirculating central compartment has been shown to produce H_2O_2 concentrations greater than 6,500mg/L. The central stream's acidity and charge balance are maintained by H^+ generation at the anode, and subsequent transfer across the cation membrane which separates the anolyte from the central compartment. The H_2O_2 in the H_2SO_4 containing central compartment is then transferred to a neutral influent stream by vapor phase transport across a microporous polypropylene membrane. Pervaporation across the LLEM has been shown to deliver an average of 2,700mg/L of H_2O_2 for a seventy-two hour period of continuous flow from a 10,000mg/L H_2O_2 source.

Improvements in the performance of aqueous phase catalytic oxidation reactors resulting from the use of H_2O_2 as oxidant were also demonstrated. When compared to elemental oxygen at equal stoichiometric concentrations, H_2O_2 was found to promote increased urea destruction rates at equivalent temperatures and space times. This demonstration indicates the enhanced oxidation afforded by H_2O_2 as compared to O_2 . In addition, the use of H_2O_2 for aqueous phase catalytic oxidation of high concentrations of acetic acid has been demonstrated at 120°C. The potential for oxidation temperatures below 100°C is a second distinct advantage of H_2O_2 as an oxidant. Another significant advantage of H_2O_2 was demonstrated by mineralization of 500mg/L of acetic acid (TOC=200 mg/L), a concentration for which the use of O_2 would be impractical owing to the required reactor operating pressure.

The effectiveness of H_2O_2 as an antimicrobial agent for application to biofilms and free form bacteria has been clearly demonstrated. The use of H_2O_2 solutions for disinfection and as a sterilant aboard spacecraft is an ideal match between the absence of chemical residues and high antimicrobial activity.²³ Although current plans are to deploy pre-packaged wipes containing 3% H_2O_2 for the disinfection of surfaces aboard space station, these wipes will have a limited life due to H_2O_2 decomposition. An on-demand H_2O_2 generator obviates these concerns, eliminates the need for resupply, and permits more aggressive microbial control measures to be taken. *In situ* generation of H_2O_2 extends its potential uses to situations where larger quantities are needed.

ACKNOWLEDGEMENTS

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