RESEARCH AND DEVELOPMENT OF AN ELECTROCHEMICAL BIOCIDE

LIFE SYSTEMS, INCORPORATED

PREPARED FOR
ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND

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RESEARCH AND DEVELOPMENT OF AN ELECTROCHEMICAL BIOCIDE

FINAL REPORT

by

G. G. See, C. A. Bodo
and K. K. Kacholia

October, 1975

Prepared Under Contract No. DAMD17-74-C-4102

by

Life Systems, Inc.
Cleveland, Ohio 44122

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The development and preliminary characterization of an electrolytic technique for destruction of microorganisms in potable and waste water were successfully completed. The technique has been termed the "Electrochemical Biocide" process and employs low level cyclic voltages at chemically inert electrodes to pass an alternating current through the process water.

The program was directed toward (a) expanding the design of the electrochemical biocide reactor, (b) determining the engineering parameters which affect process effectiveness and efficiency and establishing hypotheses for the microorganism kill mechanism(s), and (c) preparing recommendations for scaling the process to both United States Army Medical Research and Development Command (USAMRDC) and the National Aeronautics and Space Administration (NASA) requirements.

The report describes the experimental hardware, the methodology and microorganism kill results with three bacteria: (Escherichia coli, Pseudomonas aeruginosa and Klebsiella pneumoniae), two viruses (Polio I and Coxsacki B), one yeast (Saccharomyces cerevisiae), and the normal flora of microorganisms found in domestic raw settled sewage. A literature search was conducted on prior research and development efforts related to the electrolytic disinfection of water and waste water. The objective was to attain a thorough understanding of any previous efforts and to summarize the state of-the-art of the electrolytic process for the destruction of microorganisms.

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FOREWORD

The work described herein was conducted by Life Systems, Inc. during the period, July 1974 through August 1975, under Contract DAMD17-74-C-4102. The Program Manager was Gary G. See. The program included a subcontract with the University of Virginia and consultants, J. Carrell Morris and Vincent P. Olivieri, from Harvard University and John Hopkins University, respectively. The personnel contributing to the program and their area(s) of responsibility are outlined below.

Personnel	Area(s) of Responsibility
G. See	Program Management, Reactor and Test Support Accessories Design and Microorganism Kill Mechanism(s) Hypothesis, Systems Evaluation and Scaleup
C. Bodo, PhD	Program Testing, Microorganism Kill Mechanism(s) Hypothesis and Literature Review
F. Schubert	Systems Design
J. Powell	Control and Monitor Instrumentation Design
R. Davenport, PhD	Electrochemistry, Test Water and Electrode Selection
K. Kacholia	Reactor Design and Microorganism Kill Mechanism(s) Hypothesis, Systems Evaluation and Scaleup
T. Steenson	Program Testing
J. Maver	Test Support Accessories and Reactor Fabrication
G. Little	Test Support Accessories and Reactor Fabrication
C. Parker, PhD (Univ. of Virginia)	Virus Testing, Literature Review and Microorganism Kill Mechanism(s) Hypothesis
J. Morris, PhD (Harvard University)	Microorganism Kill Mechanism(s) Hypothesis
V. Olivieri, ScD (Johns Hopkins)	Microorganism Kill Mechanism(s) Hypothesis

The contract's Technical Monitor was Lt. Col. Leroy H. Reuter, Chief, Sanitary Engineering Research Branch, Environmental Protection Research and Development Command, Fort Detrick, Maryland 21701.

The authors wish to acknowledge the technical contributions and program guidance offered by Lt. Col. Leroy H. Reuter and Captain John P. Glennon.

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SUMMARY

The development and preliminary characterization of an electrolytic technique for destruction of microorganisms in potable and waste water were successfully completed. The technique has been termed the "Electrochemical Biocide" process and employs low level cyclic voltages at chemically inert electrodes to pass an alternating current through the process water.

The program was directed toward (a) expanding the design of the electrochemical biocide reactor, (b) determining the engineering parameters which affect process effectiveness and efficiency and establishing hypotheses for the microorganism kill mechanism(s), and (c) preparing recommendations for scaling the process to both United States Army Medical Research and Development Command (USAMRDC) and the National Aeronautics and Space Administration (NASA) requirements.

The report describes the experimental hardware, the methodology and microorganism kill results with three bacteria: (Escherichia coli, Pseudomonas aeruginosa and Klebsiella pneumoniae), two viruses (Polio I and Coxsacki B), one yeast (Saccharomyces cerevisiae), and the normal flora of microorganisms found in domestic raw settled sewage. A literature search was conducted on prior research and development efforts related to the electrolytic disinfection of water and waste water. The objective was to attain a thorough understanding of any previous efforts and to summarize the state-of-the-art of the electrolytic process for the destruction of microorganisms.

The test hardware for the Electrochemical Biocide process consisted of the Electrochemical Biocide Reactor and the Test Support Accessories (TSA). Batch, plug-flow and constant flow stirred-tank reactor designs were considered. The parallel plate plug-flow reactor type was evaluated to be the optimum design for the current, exploratory and process feasibility stage in the research and development cycle. Evaluation and selection criteria were established for the selection of electrode type and material. Solid plate graphite electrodes were found to be the most cost effective. Other non-noble metal electrode materials considered were titanium, 316 stainless steel, lead and palladium. The major considerations in the design of the electrochemical biocide reactor flow compartment were: (a) entrance and edge flow effects, (b) single pass residence time, and (c) perturbations in the reactor flow characteristics due to sampling for microbiological bioassay.

The primary functions of the TSA were to allow operating flexibility and consistent quantitative determination of the effects of critical engineering parameters on process effectiveness and efficiency.

Test water was pumped through the electrochemical biocide reactor and exposed to different electrical signals. Instrumentation was designed to control and monitor the frequency, waveform, amplitude, duty cycle, and current and voltage levels of the applied signal.

The baseline or near optimum conditions for microorganism kill were found primarily using the one-variable-at-a-time method. This method is recommended when a concept is at the initial exploratory stage of development, and when as many as a dozen or more variables are expected to influence the effectiveness or efficiency of the process. The technique was used to eliminate variables that seemed to be of minor importance and to establish the more critical ones.

Control experiments (no power) were run for each power experiment under identical conditions. Control experiments insured that no outside influences or experimental errors which would enhance microorganism kill were introduced into the experimental results. The results present the effects of critical operating parameters on microorganism kill. The critical parameters include the applied cyclic voltage (4 to 19V), the resulting current density (10 to 55 mA/cm^2), waveform of applied electrical signal (sine, triangular, rectangular), frequency of applied waveform (0.5 Hz to 1.5 Hz), process water flow rate (100 to 600 cc/min), pH (5 to 9), turbidity (0 to 50 NTU), process water chemical content (with and without sodium chloride (NaCl)), process water conductivity (120 to 3000 μmho/cm), reactor exposure time (0 to 6 min), and flow regime (laminar and turbulent).

Five- to six-log cycle kills at 10 mA/cm^2 were achieved with no NaCl in the test water. The reactor configurations used to achieve these performance levels are covered sequentially as they were initiated during the experimental activities. The development of experimental accessories prior to experimentation, and any modification of experimental accessories during experimental activities of the program, are also covered.

Preliminary recommendations on scaling the process for the USAMRDC and the NASA requirements are included. Conservative engineering estimates of an Electrochemical Biocide process suited for disinfection of 10^6 gallons of raw settled sewage per day are also described. Raw settled sewage was treated in the Electrochemical Biocide because it was readily obtained and contained a desirable concentration of microorganisms.

INTRODUCTION

A variety of water disinfecting techniques exist based upon:

1. Chemical agents such as chlorine, bromine, iodine, silver ion, and ozone
2. Gamma and ultraviolet radiation
3. Heat
4. Electrolytic

The first disinfection technique is based upon adding chemicals to the water. The latter three techniques are based upon adding energy to the water.

Recently, increased emphasis has been given to improving the state-of-the-art in water and waste water disinfection. Three major problem areas have caused this activity:

1. Advances in microbiological technology indicate that present disinfection practices do not adequately reduce water-born virus concentration.[1]

2. The use of chlorine and other halogen disinfectants have been shown to produce potentially toxic compounds in process waters.[2,3]

3. The challenge to conserve water resources by recycling and reuse results in a more direct route from the byproduct water to the consumer, compounding the first two concerns.[4]

This program reviews development of the Electrochemical Biocide process, a specific form of electrolytic disinfection that may result in improvement over past water disinfectant processes and alleviate the aforementioned problem areas.

Figure 1 is a schematic showing the relationship between electrochemical biocide components. The Electrochemical Biocide process consists of an electrochemical reactor and control instrumentation. The latter consists of a power conversion unit and an AC waveform generator.

Program and Report Scope

To accomplish the program objectives, the program was divided into the following five technical tasks with contractor-supporting management and documentation tasks. The specific objectives of the five tasks were to:

1. Design, develop, fabricate and assemble components of an electrochemical biocide system for indiscriminate inactivation of all types of microorganisms in water while avoiding electrode fouling

2. Design, develop, fabricate, assemble, functionally check-out and calibrate Test Support Accessories (TSA) for testing, consisting of test apparatus, contaminated water supply and water analysis and sampling equipment

3. Establish and implement a mini-product assurance program to assure that hardware reproducibility, appropriate testing procedures and safety are incorporated

4. Perform testing to establish the quantitative effects of key engineering parameters

5. Provide supporting technology studies to incorporate prior literature and establish hypotheses for the mechanism of microorganism destruction or inactivation

(1) References cited in parentheses are listed on Page 103.

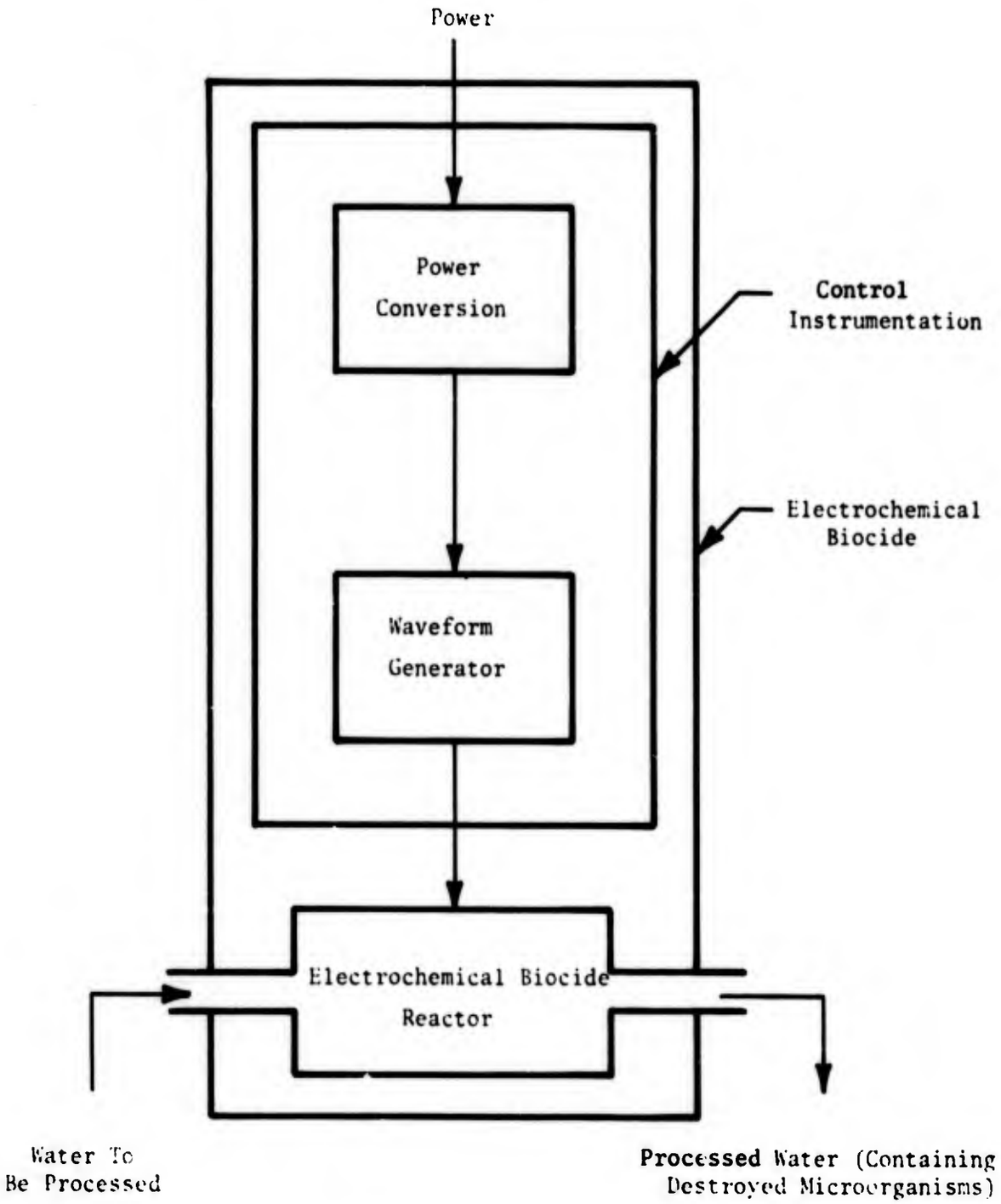


FIGURE 1 ELECTROCHEMICAL BIOCIDE SCHEMATIC

The report first concerns itself with a review of prior efforts to establish a technical base for electrolytic destruction of microorganisms. The next section addresses the design and development of the Mark I electrochemical biocide reactor. Following this section, the design and development of the TSA are discussed. The experimental program, with experimental results on viruses and microorganisms is then presented. This is followed by a discussion on system evaluations of the Electrochemical Biocide process and the microorganism kill mechanisms. The report concludes with the Conclusions and Recommendations section.

LITERATURE REVIEW OF ELECTROLYTIC DISINFECTION OF WATER AND WASTE WATER

This section presents a state-of-the-art literature review of electrolytic disinfection of water and waste water. Review of the literature suggests that the reported work on electrolytic disinfection has centered around the development of the process and the hypotheses for the microorganism kill mechanisms. The review will be discussed under those two headings.

The terms electrolytic and electrolysis, pertaining to the disinfection of water and waste water, have been used interchangeably to mean the oxidation or reduction of molecules and/or organisms present in the process water stream. The term electrolytic will be used in this review.

The electrolytic disinfection process involves oxidation or reduction processes which occur as a result of applying a constant or alternating voltage across the electrodes. This results in the passage of a direct current (DC) or an alternating current (AC) through the process stream between the reactor electrodes.

The primary objective of the review was to cover the development of electrolytic methods not employing the generation of any biocidal chlorine species for disinfection.

Related technical and patent literature was obtained by searching the Engineering Index under related topic headings, and having a National Technical Information Service (NTIS) search made for information in the area of electrolytic water disinfection. National Aeronautics and Space Administration and Defense Documentation Center (DDC) literature searches were done under the topics "Biocides for Water Treatment" and "Water Biocides," respectively. Broad word descriptors were used in the NASA and DDC computer searches to minimize the possibility of excluding from the search, pertinent literature with vague reference descriptors. A card catalogue search for books related to electrolytic water disinfection was also conducted under twenty related topics. These topics are listed in Table 1.

Process Development

Two types of electrodes have been employed predominantly in the electrolytic disinfection of water and waste water. These are the consumable electrodes (e.g. iron, aluminum) and the relatively inert electrodes (e.g. carbon, platinum, lead).

TABLE 1 CARD CATALOG SEARCH TOPICS

Bactericides

Biochemical Engineering

Biochemistry

Biocides

Biological Apparatus and Supplies

Disinfectants

Disinfection

Electrical Sterilizers

Electrochemistry

Electrochemistry - Industrial

Electrolysis

Electrophysiology

Germicides

Pollution and Pollution Control Equipment

Purification

Sewage Treatment

Sterilization

Water Pollution

Water Purification

Water Treatment

The earliest reported application of electrolytic waste water treatment was in a patent issued to William Webster in 1889.[5] Consumable iron electrodes were used to electrolyze sea water at a potential of about 10V. Addition of salt or sea water was specified if insufficient chlorides were present for adequate chlorine generation.

Electrolytic waste water treatment processes were quite popular during the first three decades of the nineteenth century. According to Kuhn,[6] two approaches were adapted. In the first approach, waste water was electrolyzed with only the addition of lime as it entered the plant. The second concept incorporated the electrolysis of sodium chloride (NaCl) to generate hypochlorite which served to disinfect the sewage. Both these concepts employed DC to electrolyze the waste water.

Plants employing the Landreth process (lime addition) were built in the United States as early as 1911.[7] A rectangular box contained vertical steel plates spaced about one-half inch apart and surrounded by rotating paddles used to mix the solution in contact with the electrodes. The plates were alternately connected to the negative and positive terminals of a DC power source. Power requirements were determined by the conductivity of the waste water and the condition of the electrodes. Lime was added to the waste water prior to electrolytic treatment to increase its conductivity and to retard electrode erosion at a higher pH. These plants were abandoned by 1930 primarily due to high operating costs.

Although electrolytic methods for treating waste water have appeared in the patent literature since the thirties, little development has been done on large scale systems.[5]

Wei and Heinke[8] reviewed the commercial and scientific development of electrolysis of human and industrial sewage through 1973. The review includes processes which are dependent on the generation or addition of chlorine or hypochlorite to achieve disinfection in the treated water. Wei and Heinke conclude that there is a conspicuous absence of any valuable reports on experimental studies of bacterial kill as an indicator of bactericidal effectiveness of the electrolytic disinfection process.

In the last decade two groups in Europe[5,7,8] have been actively working on the electrolytic disinfection of waste water. These processes, however, rely on mixing the waste water with sea water prior to electrolytic treatment to generate hypochlorite.

There is little literature presenting experimental studies of microbial kill as an indicator of microbiocidal effectiveness of electrolytic disinfection.

Kuhn[6] presents a curve plotting survival time of coliforms in sea water, electrolyzed by a DC process, but gives no detailed information about the conditions of the experiments or the manner in which the assays were conducted. There was a four-log cycle reduction in percent of surviving coliforms after a contact time of twenty minutes.

Miller and Knipe[5] present standard plate count data on coliforms which indicate that after 14,400 coulombs (180 min of power) had been passed through the reactor, the initial count of coliform organisms (1.3×10^6 organisms/ml had been reduced substantially (2.4×10^2 organisms/ml). The five cathodes and four anodes had a total DC of 2 amperes. Raw secondary effluent was electrolyzed in this experiment.

Hiler and Lyle[9] mixed one gallon of municipal sewage effluent with 150 gallons of a test clay suspension to give a most probable number of between 800 and 1000 coliforms/100 ml of suspension. This suspension was then used to test the disinfecting properties of an electrode grid model reactor utilizing a DC power source.

Many processes which employ DC power have been patented for the electrolytic treatment of aqueous media.[10-15] Inoue[11] specifies that a high frequency AC be superimposed on the DC in order to reduce the work function and cause a promotion in electron transfer at the electrode interface. Some of these processes[14-17] have provisions for reversing the polarity periodically to prevent a residual buildup of materials on the electrodes. The process suggested by Treharne[12] was proposed as either an AC or DC method for controlling polluting algae at reactor current densities not higher than 0.054 mA/cm^2. When AC current was employed, cleansing of the electrodes occurred.

Stoner[18] presents some data on the reduction of T4 and polio virus virions in water samples exposed to an AC process. This process used comparatively low current densities and AC potentials. The process specified that the peak voltage during the anodic phase is less than that at which vigorous electrolytic oxygen is generated, and during the cathodic phase, the peak voltage is greater than that at which electrolytic hydrogen is generated. The generation of hydrogen would defoul the electrode surface during the cathodic phase. Accordingly, it is stated, the potentials should not exceed ±5V, and preferably not be greater than ±2V. The minimum potential which can be used is 200 mV. The voltage was cycled between ±1.0 and ±1.5V relative to a saturated calomel electrode. The current frequency stated was from 0.1 cycle/sec to 10 cycles/sec. Optimum current density range between electrodes was established from 1 to 20 mA/cm^2 and preferably 1 to 5 mA/cm^2 at which range oxygen generation is sporadic.

Some results were expressed as an average number of plaque forming units (PFU) while the results of other experiments were expressed as percent survival ratio based on the initial virus concentrations. The initial virus concentrations were not always stated. The experiments were carried out with carbon rod electrodes (2 to 3 cm^2 area) and carbon cloth electrodes (100 cm^2 area) in stirred batch reactors (glass and polyethylene beakers). Stirring speeds between 300 and 1350 rpm were used. Stoner concludes that the virus inactivation rate constant is strongly dependent on the stirring speed and suggests that the transfer of viruses to the electrode surface is the rate-determining step.

The interpretation of Stoner's data on the T4 virus must be considered with caution. Hershey and Chase[19] report that shearing forces imparted by a semi-micro-size Waring Blender were sufficient to separate the majority (approximately 80%) of empty T2 phage particles from the host bacteria which they

infected. Shearing forces may also play a part in disaggregating virus particles of complex symmetry and large size into their component parts.

An experiment with Escherichia coli was conducted by Stoner[18] with a voltage of ±2.0V impressed across the electrodes. No initial concentration of Escherichia coli for the experiment was reported and results were expressed as percent survival ratio of Escherichia coli based on initial concentrations. The results with low starting concentrations of disease flukes (Platyhelminthes) utilizing flow-through and batch reactors are also reported.

Russian scientists have reported data on the disinfection of drinking water. Lovtsevich and Sergunina[20] have studied the disinfection of drinking water containing enteroviruses. In their experiments, disinfection was primarily achieved by the electrolytic products (active chlorine species) of common salt.

Kunina treated drinking water[21] and drinking water innoculated with Escherichia coli[22] to result in an initial concentration of 20 cells of Escherichia coli/liter. After a DC electrolytic treatment, 0.2 ml samples were spread on Endo Agar plates and the bactericidal effect was determined by the number of colonies which appeared in the dish. When a DC of 20 amperes or more was placed across the five electrodes, no colonies of Escherichia coli appeared on the plates. The electrodes were 5 ml apart and connected in parallel.

Hallum and Youngner[23] have measured the rates of inactivation of influenza, newcastle disease, polio, vaccinia, and adeno viruses. These viruses were inactivated by oxidizing them at controlled DC potentials of 1.1 to 1.8V. A phosphate buffered saline feed was used. The amount of NaCl in the buffered solution was not explicitly stated.

Paul, Chari and Bhattacharyya[24] killed algae with AC varying from 3 to 6 amperes resulting from potentials of 85 to 195V. The gap between steel electrodes was adjusted from 6.5 to 30 ml. The presence of NaCl in the test solution was not discussed.

In summary, the electrolytic disinfection of water and waste water has been examined on a large scale. Most processes have used DC and more recent efforts have focused on the generation of hypochlorite as the disinfecting process.

Patented processes for the treatment of waste water and water have consisted of DC and AC processes and combinations of these processes.[25,26] None of these individual processes have been tested extensively and precisely enough to prove their effectiveness on disinfecting water or waste water containing virus, bacteria, protozoa and fungi, as well as the more resistent spore forms of some of these microorganisms. However, all the pertinent data accumulated from prior efforts was used in determining the parameters to be controlled and monitored in the current research with the Electrochemical Biocide.

In general, alternating current processes are more favorable, both for large scale and smaller applications of water and waste water treatment because of limited electrode fouling in these processes. Processes using low current densities have been reported. These advances make the electrolytic process potentially competitive with the traditional disinfection processes.

Microorganism Kill Mechanisms

Any chemical agent or a process which destroys organisms must, in some way, have interfered with the life processes of that organism.[27]

Specifically, how an organism is inactivated or destroyed by electrolytic treatment is a difficult question to answer. More than one mechanism may be responsible for destroying a microorganism. Moreover, the mechanism(s) may differ for different kinds of microorganisms (e.g. eucaryotic and procaryotic types).

Chemical reactions take place at both the cathode and the anode. Cathode reactions in water or waste water result chiefly in the evolution of hydrogen gas formed from the decomposition of water and some reductions. The anode reactions are more important, since oxidations take place at the anode by four major means of interest:[28]

1. Oxidation of chloride to chlorine
2. Formation of highly oxidative materials such as ozone, nascent oxygen, and peroxides
3. Direct oxidation of molecules or organisms at the anode
4. Electrolysis of water to give gaseous oxygen

Electrolytic disinfection methods which depend on the generation of free chlorine or hypochlorite are adequately covered in the references cited above. References to the last three of the above organism kill mechanism(s) are discussed below.

If the primary mechanism for inactivating or killing organisms is through contact with an oxidative species like ozone or peroxides, a direct contact by the microorganisms with the surface of the anode would not be necessary for its oxidation. Unfortunately, if one could assume that organisms are killed without ever contacting the electrodes, the conclusion that an oxidizing agent is responsible could still not be made, since the microorganism may be killed by the influence of the electric field.

Myers[16] refers to bacteria "vibrating" to death during the operation of his process. Perhaps, under certain conditions, the electrolytic potential acting on the organism can cause enough structural damage to either inactivate or destroy it without coming in contact with an oxidizing agent or with the anode.

The direct oxidation of microorganism by migrating to the anode is a third possibility. Actual adsorption onto the anode may or may not be necessary for this direct oxidation to take place.

Electrosorption experiments with organic molecules have been conducted by Gileadi[29,30] and Heiland, Gileadi and Bockris.[31] Electrosorption studies with fibrinogen on platinum[32] and fibrinogen on germanium[33] indicate that the amount of fibrinogen adsorbed varied with electrical potential. These experiments were conducted at low protein concentrations. Duic, Srinivasan and Sawyer[34] have studied the electrochemical behavior of prothrombin and thrombin, as well as fibrinogen.[35]

Hallum and Youngner[23] indicated that the loss of infectivity of various viruses they tested was due to oxidation of the viruses at the surface of the working electrode. Contact of the viruses with the electrode was necessary for the inactivation to occur. Because viruses inactivated by this method retained hemaglutination, enzymatic, and antigenic activity, it is likely that loss of infectivity was associated with alterations of the nucleic acid of the virus particle.

The conditions mentioned in many of the electrolytic processes reviewed have peak voltages less than that at which appreciable amounts of oxygen would be generated. The generation of molecular or gaseous oxygen would probably not have a significant oxidative effect on most microorganisms.[28]

In summary, a vague picture of the microorganism kill mechanism exists. The electrolytic process has been shown to be effective in the absence of NaCl in the process feed. Hence, oxidation by chlorine or other active chlorine species is not likely to be the major kill mechanism. Further microbiological studies are needed to elucidate the microorganism kill mechanism.

ELECTROCHEMICAL BIOCIDE PROCESS EXPERIMENTAL HARDWARE

The experimental hardware for the Electrochemical Biocide process consists of the Electrochemical Biocide Reactor and the TSA.

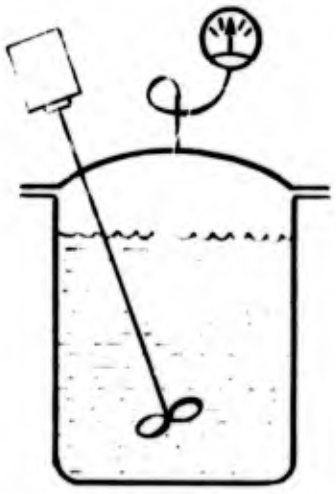
Electrochemical Biocide Reactor

The heart of the Electrochemical Biocide process is the Electrochemical Biocide Reactor. Batch, plug-flow and constant flow stirred-tank reactor designs were considered. A variety of electrode types, configurations, and materials were evaluated. Critical engineering calculations were made on the reactor flow compartment size and configuration. Another major consideration was to build flexibility into the reactor design. This allowed modifying the original design with minimal effort and cost, incorporating changes deemed necessary to allow a better understanding of the process and improving process efficiency and effectiveness.

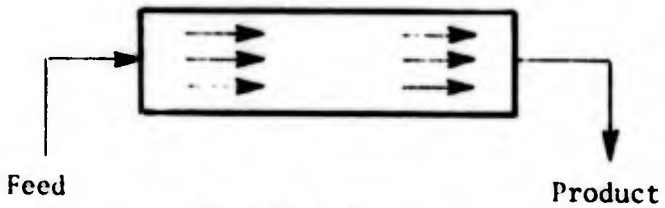
Selection of the Electrochemical Biocide Reactor Type

Three types of ideal reactors are typically used in exploratory engineering studies on reactor process characterizations. These are shown schematically in Figure 2. The characteristics of these reactor types are described in detail in general references on chemical reaction engineering.[36,37]

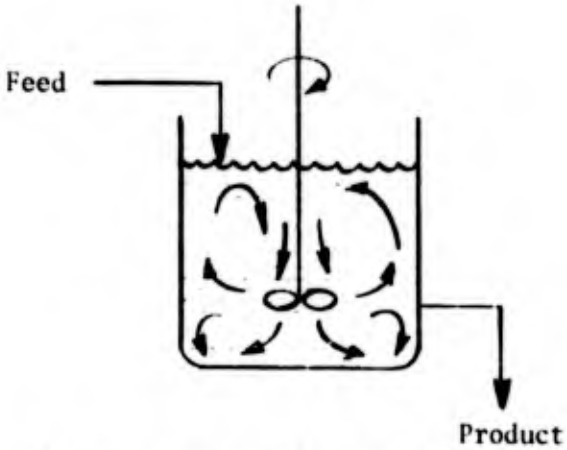
The batch reactor is simply a container to hold the contents while they are processed. All that is to be determined is the extent of microorganism reduction at various times. The batch reactor is a relatively simple device adaptable to small-scale laboratory setups. It needs little auxiliary equipment or instrumentation. However, the applicability of the batch reactor to the electrochemical biocide concept is limited for the following reasons:



Batch Reactor



Plug-Flow Reactor



Constant Flow Stirred-Tank Reactor

FIGURE 2 THREE TYPES OF IDEAL REACTORS

1. The voltage drop across electrodes, necessary to achieve a constant current density, increases proportionally to the electrode separation. Low conductivity process water feeds (0 to 3000 μmhos/cm) would require that, for reasonable voltage drops across the electrodes, separation must not be greater than 4 to 8 cm (1.6 to 3.1 in). At high voltages, electrolysis of water occurs and the formation of gas bubbles at the electrodes tends to mask or slow down the electrochemical biocidal effect.

2. From prior efforts data, it is suggested that in batch reactors, the Electrochemical Biocide process is dependent on the stirring rate. High stirring speeds are needed for acceptable microorganism reduction rates. As emphasized above, in the Electrochemical Biocide process, the maximum separation between the electrodes should not exceed 8 cm (3.1 in). High speed mixers with a stirrer blade diameter of less than 8 cm (3.1 in) are commercially available and can provide the necessary turbulence in small (1 to 5 gal reactor capacity) electrochemical biocide batch reactors. However, in larger systems (20 to 5000 gal reactor capacity) stirrers limited to a stirrer blade diameter of less than 8 cm would be impractical. Hence, any electrochemical biocide concept based on stirrers would have no potential for scale-up. Obtaining exploratory and empirical information for scale-up in a stirred batch reactor would, therefore, be of insignificant value. Further, such data would be complicated by possible microorganism kills due to stirring and imperfect correlation of turbulence and the resulting mass transfer of microorganisms to the electrode surfaces in a stirred batch reactor when extrapolated to a plug-flow Electrochemical Biocide Reactor design.

3. The batch reactor requires non-continuous operation. For scaled operation, this is expensive, time consuming and requires storage facilities for the process fluid.

The mixed flow reactor is a flexible system but is more difficult to analyze than the batch or plug-flow reactor.[36,37] The mixed-flow reactor also suffers from the limitations inherent in a stirred reactor system. However, the mixed-flow reactors offer continuous processing of the water or waste stream.

The plug-flow reactor has the flexibility of the mixed flow reactor without any of its limitations. Effective turbulence can be obtained by using high process fluid velocities and/or turbulence promotors. The plug-flow reactor also lends itself to bipolar electrode arrangements for process scale-up. This flexibility is discussed later. The plug-flow reactor offers continuous processing of process fluid with possible recirculation. It requires minimal process fluid storage to dampen influent flow fluctuations. The plug-flow reactor data also lends itself to simple kinetic modeling.[36,37] This reactor type was, therefore, selected for the development and preliminary characterization of the Electrochemical Biocide process.

Electrochemical Biocide Plug-Flow Reactor Design Considerations

The following discussion outlines the engineering evaluations which were made on the plug-flow electrochemical biocide reactor design:

1. Evaluation and selection of electrode type, geometries and material
2. Evaluation of the electrochemical biocide flow compartment

Evaluation and Selection of Electrode Type, Geometries and Material. The following discusses the different electrode types, geometries and materials considered in the development of the Electrochemical Biocide process. The following criteria were established:

1. The electrode material must have biocidal activity when an alternating current is applied to it
2. The electrode material must not corrode
3. The electrode material must be of low cost
4. The electrode material should minimize power consumption
5. Structural requirements necessary for serviceable electrodes should be minimized

Selection of the Electrodes. Electrodes are available in solid sheets, porous plaques and screens, predominantly in parallel plates, tubular, and porous plug-flow geometries.

Parallel plate reactors, with either porous plaques or solid sheet electrodes, were used predominantly in prior electrolytic disinfection studies. The parallel plate electrode geometry is simple in its design and has the most readily reproducible electrode arrangement. It is advantageous to use a simple electrode geometry when a process is in its early (exploratory) stages of development and when as many as a dozen or more parameters are expected to influence the efficiency or effectiveness of the process. This allows flexibility for incorporation of changes in the reactor design deemed necessary for more efficient or effective process operation. Also, a parallel plate reactor lends itself to simple kinetic modeling and would permit correlation of the current data with prior effort in electrolytic disinfection.

One of the limitations of the parallel flow reactor is that, to achieve effective mass transfer of the microorganisms to the electrode surface, high process fluid velocity with turbulence promotors are needed. Without high fluid velocities and turbulence promotors, very low microorganism kills may result.

One consequence of high fluid velocities is that long reactor paths are needed for two- to six-minute residence times. Another is pumping power loss due to high pressure drops.

The greatest advantage of the porous flow-through electrode reactors is that effective contact of the microorganisms with the electrodes occurs even at low process fluid velocities. Hence, high microorganism kill rates are expected to result at low velocities. One serious limitation with the flow-through reactors is the possibility of plugging of the porous electrodes by process water suspended

solids. The flow-through electrode reactors were eliminated from consideration under the current program because of the possible plugging problem. However, they do merit investigation in the future.

The literature review on prior efforts indicates that only platinum, stainless steel, porous graphite, and graphite cloth electrode materials have been used in the electrolytic disinfection process reactors to date. Platinum was found to be less effective in destroying microorganisms and, therefore, was eliminated from further consideration. Stainless steel electrodes were effective in killing microorganisms but corroded in use. The type of stainless steel tried is not known. Porous graphite and graphite cloth electrodes were biocidal and no signs of corrosion were observed.

Other noble metals like gold and palladium were considered under the current program as alternatives to platinum. Gold dissolves in the presence of chloride ions (Cl^-) when potentiostated at positive potentials. A process based on consumable gold electrodes would be too uneconomical to warrant further investigation. Therefore, palladium was chosen as the noble metal candidate for evaluation.

Cyclic voltammograms were obtained using rotating disk electrodes made of palladium, titanium, lead, 316 stainless steel, and porous tooling graphite. This study made it possible to predict the approximate electrochemical biocide cell voltages that would be obtained with each electrode material. The electrolytes used were 0.01M potassium nitrate (KNO_3) and 0.01M potassium chloride (KCl). The KCl solution was used to determine the effect of the presence of Cl^- on electrode behavior. Both air-saturated and deaerated solutions were studied. Cyclic voltammograms for porous graphite and polished titanium electrodes in 0.01M KNO_3 electrolyte are illustrated in Figure 3.

The voltammograms of the palladium and the stainless steel electrodes exhibit peaks due to surface-controlled electrochemical processes. The anodic peaks (peaks having positive currents) are due to oxidation of species on the electrode surface. These peaks sometimes indicate formation of metal oxides on the surface and the possibility of electrode dissolution. Cathodic peaks (peaks having negative currents) result from the reduction of surface species, such as metal oxide coatings. The voltammograms of palladium and stainless steel show the possibility of electrode dissolution. Further studies are necessary to verify this phenomenon.

The sizeable hysteresis in the voltammograms of the porous graphite results from the large surface area of the electrode. Little surface activity is present except for the hysteresis due to the charging current; hence, no electrode dissolution should occur.

The titanium electrode had little surface activity and high hydrogen and oxygen overvoltages. The oxygen overvoltage increased on successive scans. Therefore, the actual Electrochemical Biocide Reactor voltage with titanium electrodes may be somewhat higher than the titanium voltage limit shown in Table 2.

The lead electrode was oxidized at negative potentials. In the KCl electrolyte, lead chloride ($PbCl_2$) formed on the electrode surface. In the KNO_3 solution,

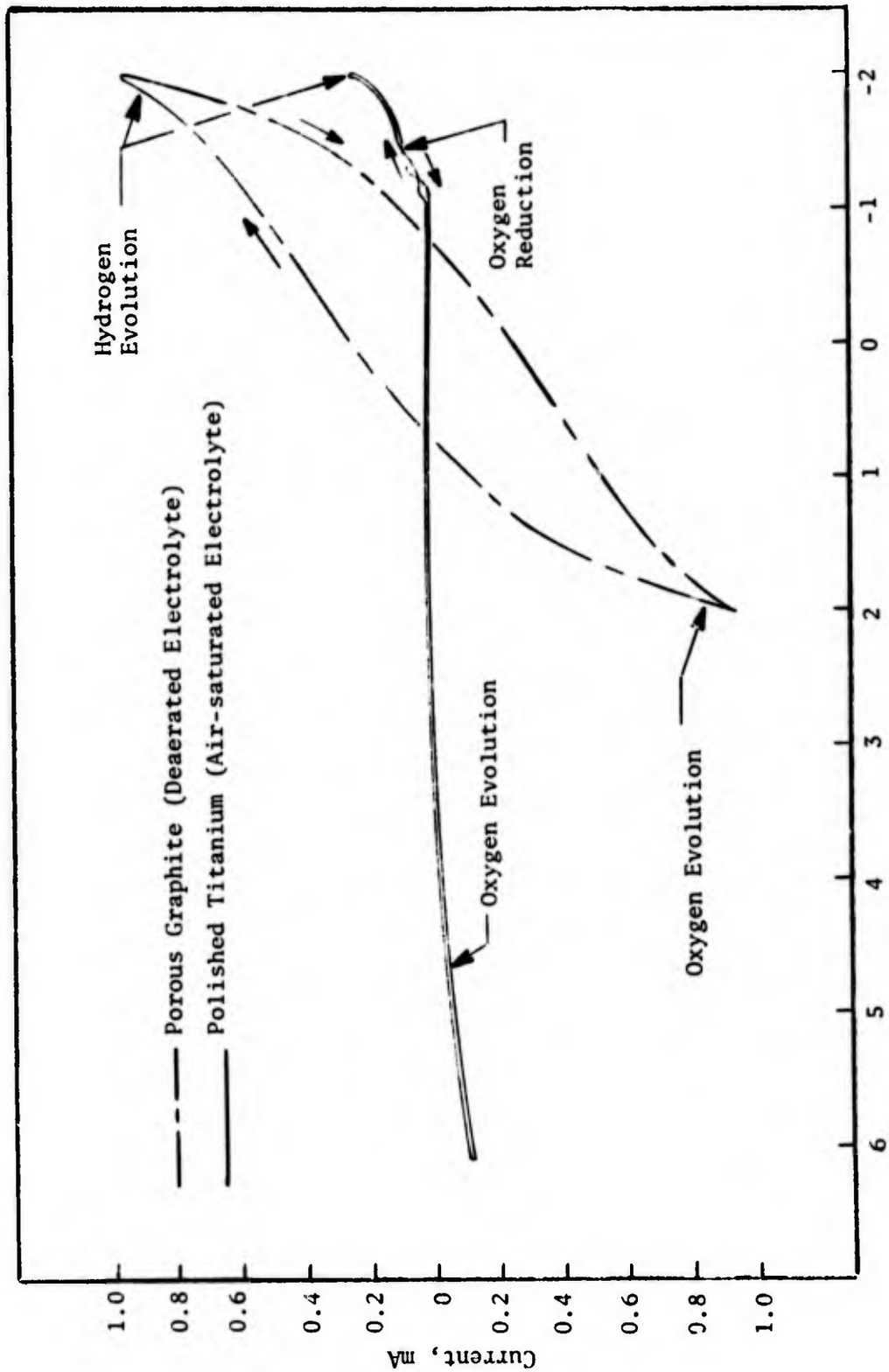


FIGURE 3 VOLTAMMOGRAMS FOR GRAPHITE AND TITANIUM ELECTRODES

TABLE 2 VOLTAGE LIMITS OF ELECTRODES AT 0.60 mA/cm^2

Electrode Material	Anodic Limit[a]		Cathodic Limit[a]	
	0.01M Potassium Nitrate Electrolyte			
	Air-Saturated	Deaerated	Air-Saturated	Deaerated
316 Stainless	1.35	1.31	-0.89	-1.36
Palladium	1.25	-0.05	-0.35	-0.38
Graphite	0.89	0.80	-0 30	-0.47
Lead	-0.36	-0.33	-0.83	-1.20
Titanium	5.67	5.18	-1.37	-1.63
	0.01M Potassium Chloride Electrolyte			
316 Stainless	1.30	1.26	-0.90	-1.40
Palladium	1.26	-0.09	-0.35	-0.97
Graphite	0.61	0.61	-0.46	-0.60
Lead	-0.31	-0.32	-0.78	-0.82
Titanium	4.70	5.12	-1.51	-1.74

(a) Volts versus saturated calomel electrode.

the electrolyte became slightly turbid with time and repeated scans, indicating dissolution of the electrode.

The power consumption of the Electrochemical Biocide Reactor is given by the product of the reactor current times the voltage difference between the electrodes. Normally, the potential difference between the electrodes is considered to be the difference between the potentials of hydrogen evolution at one electrode and oxygen evolution at the other electrode.

Other reactions can occur which depolarize the electrodes. One such reaction is the oxygen reduction at the cathode. The reduction of oxides on the electrode surface, or oxidation of the surface to produce these oxides, may also occur. The latter was observed in the case of the palladium electrode. From the voltammograms, the voltage limits of each electrode were measured for a current density of 0.60 mA/cm^2. This was the highest current density delivered by the instrument. In order to obtain these values, charging currents from the positive-going scan were averaged with the current from the negative-going scan. The voltage limits are shown in Table 2. The expected voltage differences required to run the Electrochemical Biocide Reactor at a current density of 0.60 mA/cm^2 with the various materials is shown in Table 3.

In general, saturation of the electrolyte with air slightly reduces the voltage requirements except in the case of palladium. The voltage limits of palladium are unusual because of the surface oxidations and reductions taking place. At larger current densities this unusual behavior would not be observed. Chloride has little effect on the voltage limits of the electrodes except in the case of lead and palladium. In the case of lead, the difference is small. In the case of palladium, the presence of Cl^- would seem to have a greater effect. However, the difference results from effects of the surface reactions and not from the potentials of the electrolysis reactions. The difference Cl^- exerts on the voltage limits of the palladium electrode may be negligible since the electrochemical biocide reactor is expected to operate at high current densities.

Table 4 lists the projected power consumption of the Electrochemical Biocide Reactor for each electrode material. The power consumption is given by the product of the reactor voltages in Table 3 and the electrode currents, resulting in the current density of 0.60 mA/cm^2. The results in Table 4 indicate that there is little difference in the projected power consumption between electrode materials. These values are for a current density of 0.60 mA/cm^2. However, at higher current densities, the titanium electrodes would require greater power due to large hydrogen and oxygen overvoltages.

Another characteristic important to the choice of electrode materials is the resistance to corrosion. Noble metals are normally resistant to corrosion when DC signals are applied to them.[38] However, platinum and palladium blacken and form rough surfaces when AC is applied to them. An AC signal superimposed on a DC signal causes platinum to dissolve in acid and alkaline solutions if an oxidizing agent such as oxygen is present in the solution. No dissolution occurs when only a DC signal is applied.[39] Lead and lead-silver alloys have been used as anodes with DC signals. However, the application of an AC signal dissolves lead.[40]

TABLE 3 PROJECTED ELECTROCHEMICAL BIOCIDE REACTOR VOLTAGES AT 0.60 mA/cm^2

Electrode Material	Cell Voltage, V			
	0.01M KNO_3 Electrolyte		0.01M KCl Electrolyte	
	Air-Saturated	Deaerated	Air-Saturated	Deaerated
316 Stainless	2.24	2.67	2.20	2.66
Palladium	1.60	0.33	1.61	0.88
Graphite	1.19	1.27	1.07	1.21
Lead	0.47	0.87	0.47	0.50
Titanium	7.04	6.81	6.21	6.86

TABLE 4 PROJECTED REACTOR POWER CONSUMPTION AT 0.60 mA/cm^2

Electrode Material	Power Consumption, mW			
	0.01M KNO_3 Electrolyte		0.01M KCl Electrolyte	
	Air-Saturated	Deaerated	Air-Saturated	Deaerated
316 Stainless	0.42	0.51	0.42	0.50
Palladium	0.43	0.090	0.44	0.24
Graphite	0.32	0.34	0.29	0.33
Lead	0.28	0.52	0.28	0.30
Titanium	0.33	0.33	0.30	0.33

The dissolution of the electrode may be important from the point of view of injecting toxic ions into the water. This is especially true in the case of lead. Lead electrodes should not be used since they corrode and release lead ions in the water. Similarly, stainless steel may corrode in the Electrochemical Biocide Reactor and result in the dissolution of chromium ions in the process stream.

Titanium is normally covered with a strong oxide film. Hydrofluoric acid (HF) corrodes titanium in the absence of oxygen.[41] Data on corrosion of titanium electrodes under AC operation was not found. Therefore, titanium may merit further investigation into its corrosion characteristics.

Porous graphite and graphite cloth electrodes have been used in electrochemical biocide reactors without corrosion. In DC operation, the graphite electrodes are known to produce hydrogen peroxide from the reduction of oxygen. However, spot tests have indicated that detectable amounts of hydrogen peroxide are not produced during AC operation. Therefore, graphite has an obvious advantage over other electrode materials in the processing of potable or waste water.

Consumption of electrode materials increases the process operating costs. As shown above, stainless steel, palladium and lead dissolve in the process stream and would require frequent replacement. Titanium may be compatible and porous graphite has been shown to be compatible in the Electrochemical Biocide process. The cost of 7.6 x 15.2 cm (3 x 6 in) electrodes (the size selected for the Electrochemical Biocide Test Reactor) is shown in Table 5. At the current market price, the cost of a palladium electrode would be $883.00. For economic reasons, palladium electrodes would have to be supported on some low cost matrix when used in the Electrochemical Biocide process. These electrodes would still be much more expensive than graphite electrode. The other electrode materials would be cost effective in a particular application only if they had a distinct advantage over graphite.

Stainless steel and titanium could be used as self-supporting electrodes. These materials are available as porous plaques and could be used in a high surface area form. Lead is too soft to be durable in a thin, light form. Therefore, lead must either be alloyed or used with some structural support.

Graphite must be used in thick plates for structural strength or supported on a metallic current collector. The use of a current collector is also necessary for good current distribution across the face of the electrodes.

In summary, lead electrodes are not favorable because of their high cost and probable corrosion in use. Stainless steel and lead also corrode and may release toxic ions in the process stream. This corrosion and production of toxic species eliminates the above materials from further consideration.

Graphite is the cheapest, is biocidally active, has a high surface area and does not corrode. For these reasons, porous graphite was used for research and development of the Electrochemical Biocide process. A lightweight metallic titanium current collector was used to obtain good current density distribution.

TABLE 5 COST OF ELECTROCHEMICAL BIOCIDE REACTOR ELECTRODES[a]

Electrode Material	Cost[b]
Palladium	883.00
Lead	0.37
316 Stainless Steel	0.58
Titanium	2.85
Graphite[c]	0.06

(a) Electrode size, cm (In): 7.6 x 15.2 x 0.13 thick (3 x 6 x 0.05 thick)
(b) Cost estimation made in November, 1974
(c) Graphite electrode size, cm (In): 7.6 x 15.2 x 0.31 thick (3 x 6 x 0.125 thick)

The biocidal activity of titanium and its resistance to corrosion in the Electrochemical Biocide process is unknown. However, if titanium were biocidal and resistant to corrosion, the use of titanium could lead to a compact and lightweight reactor suited for space application. This indicates that titanium electrodes deserve further consideration and investigation for use in the Electrochemical Biocide process.

In conclusion, parallel porous plaques of graphite, supported by metallic titanium current collectors are the most cost effective electrodes and were used in the Electrochemical Biocide Reactor.

Evaluation of the Electrochemical Biocide Flow Compartment. The major considerations in the design of the electrochemical biocide flow compartment were: (a) entrance and edge flow effects, (b) exposure time, and (c) the microbiological bioassay sample size.

Entrance and Edge Flow Effects. For process flow conditions which do not change along the axis of flow, mass transfer is a function of fluid velocity. However, due to entrance and edge flow effects, a buildup of boundary layer occurs. This phenomenon is illustrated in Figure 4. The boundary layer forms on the inside surface and occupies a larger amount of the flow area for increasing values of x, the distance downstream from the reactor compartment entrance. At some value of x, the boundary layer fills the flow area. The velocity profile will not change downstream from this point, and the flow is said to be fully developed. The distance downstream from the reactor compartment entrance to where flow becomes fully developed is called the entrance length, L_e. The fluid velocity outside the boundary layer increases with x, as is required to satisfy continuity. The velocity at the center of the pipe finally reaches a value of $2V_\infty$ for fully developed laminar flow. The entrance length required for a fully developed velocity profile to form in laminar flow has been expressed by Langhaar[42] according to:

$$\frac{L_e}{D} = 0.575\ Re \qquad (1)$$

where

D = equivalent diameter of the flow compartment

Re = Reynolds number

This relation, derived analytically, has been found to agree well with the experiment. The flow compartment and the reactor length were sized such that the entrance length was no more than 10% (for the process fluid flow range between 100 and 700 ml/min) of the reactor flow compartment length. Hence, the flow characteristics within the reactor were designed to be laminar (without a turbulator) to simplify scale-up calculations.

Single-Pass Exposure Time. The electrochemical biocide flow compartment was sized such that the microorganisms in the process feed would be exposed to at least one complete electrical cycle during a single-pass in the desired process feed flow range (100 to 700 ml/min).

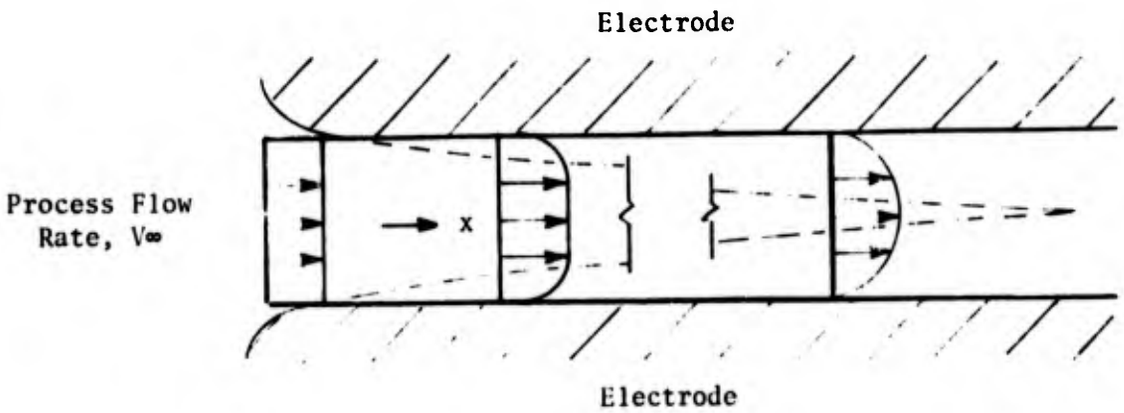


FIGURE 4 BOUNDARY LAYER BUILDUP IN THE ELECTROCHEMICAL BIOCIDE REACTOR FLOW COMPARTMENT

The Microbiological Bioassay Sample Size. The characterization of the plug-flow reactor is achieved by assaying the microorganism concentration reduction with time. The standard power plate method[43] was selected for the assaying technique, and required a minimum sample size of 0.6 mil. It was conservatively established that a sample size larger than 10% of the flow compartment volume would upset the process and/or flow characteristics in the reactor. A flow compartment volume greater than 6 ml was, therefore, required to minimize perturbations on reactor flow and, consequently, performance characteristics. A flow compartment of 7.6 x 15.2 x 0.08 cm (3 x 6 x 0.003 in) was designed to satisfy the above requirements and had a volume of 8.85 ml.

Design of Electrochemical Reactor. The heart of the Electrochemical Biocide process is the reactor through which the process water flows while an AC is impressed across the reactor electrodes. This section discusses the development of the Life Systems, Inc. (LSI) Mark I plug-flow reactor and the modifications to the original design which resulted from the experimental activities.

Mark I Reactor. Figure 5 is a schematic of the Electrochemical Biocide Reactor. It consisted of an electrochemical reactor made of two carbon electrodes between which process water flowed. The essential parts of the reactor were the parallel, flat plate carbon electrodes which were supported by expanded titanium sheets backed by titanium current collectors with the resulting composite housed in plastic endplates. The endplates and carbon electrodes were separated by a plastic spacer and held in place by stainless steel bolts using Viton A O-rings for sealing.

The internal water flow path was established by the configuration of the polysulfone spacer. It provided for an even process water flow distribution across the electrodes. The titanium current collectors and expanded sheet provided for even current distribution to the electrode surfaces.

The reactor design characteristics and materials of construction are shown in Table 6. The baseline configuration of the Mark I Reactor had an electrode spacing of 0.08 cm (0.03 in). The electrode separation could be varied utilizing different thicknesses of the polysulfone spacer.

Figure 6 is a photograph of the disassembled Mark I Reactor. It indicates the water inlet and outlet manifolds, process water flow cavity, O-ring sealing technique and expanded titanium configuration.

Figure 7 is a photograph of the assembled reactor. It indicates the inlet and outlet septums where water samples were taken for microbiological analysis. It also shows the location of thermocouples utilized to monitor the temperature of the water into and out of the reactor. The reactor size was given in Table 6.

The process water enters at the right of the assembly (Figure 7), passing into the internal manifold and then flows between the carbon electrodes through the cavity generated by the spacer and exits through the manifold on the left.

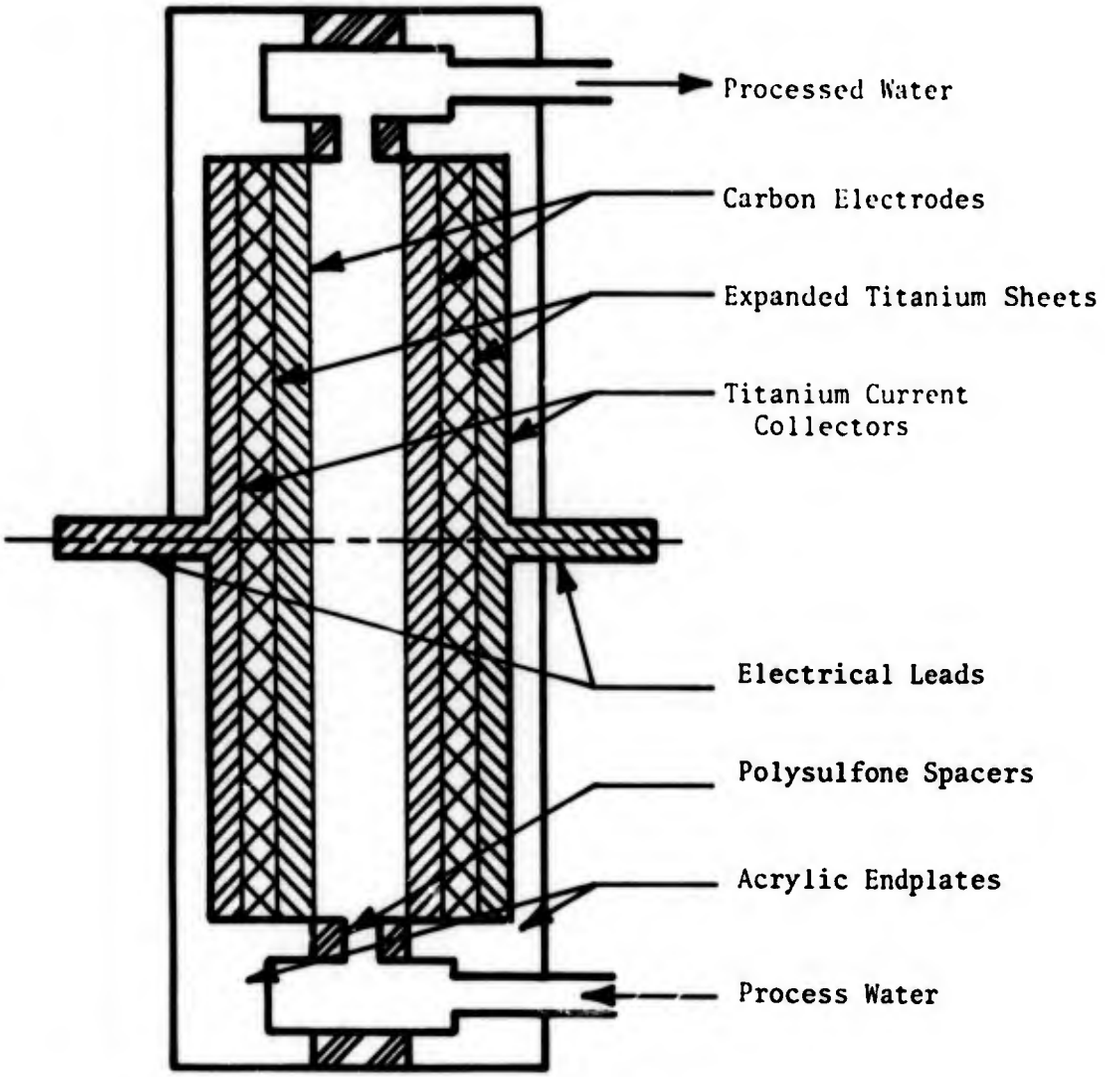


FIGURE 5 ELECTROCHEMICAL BIOCIDE REACTOR SCHEMATIC (TOP VIEW)

TABLE 6 REACTOR DESIGN CHARACTERISTICS AND MATERIALS

Characteristics	Description
Overall Size, cm (In)	22.86 x 13.97 x 5.21 (9 x 5.5 x 2.03)
Electrode Active Area, cm^2 (In^2)	106 (16.43)
Electrode Spacing, cm (In)	0.08 (0.03)
Flow Cavity Volume, cm^3 (In^3)	7.2 (0.44)
Flow Cavity Cross Sectional Area, cm^2 (In^2)	0.579 (0.09)
Manifold Volume, cm^3 (In^3)	37.54 (2.29)
Manifold Cross Sectional Area, cm^2 (In^2)	4.23 (0.666)
Electrode/Current Collector Area, cm^2 (In^2)	115.55 (17.91)

Components	Materials
Housing	Acrylic
Current Collector	Titanium
Expanded Sheet	Titanium
Electrode	Carbon
Electrode Spacer	Polysulfone
Fittings/Thermocouple Sheath	Stainless Steel
Septum	Tri-Layered Rubber
O-Ring	Viton A

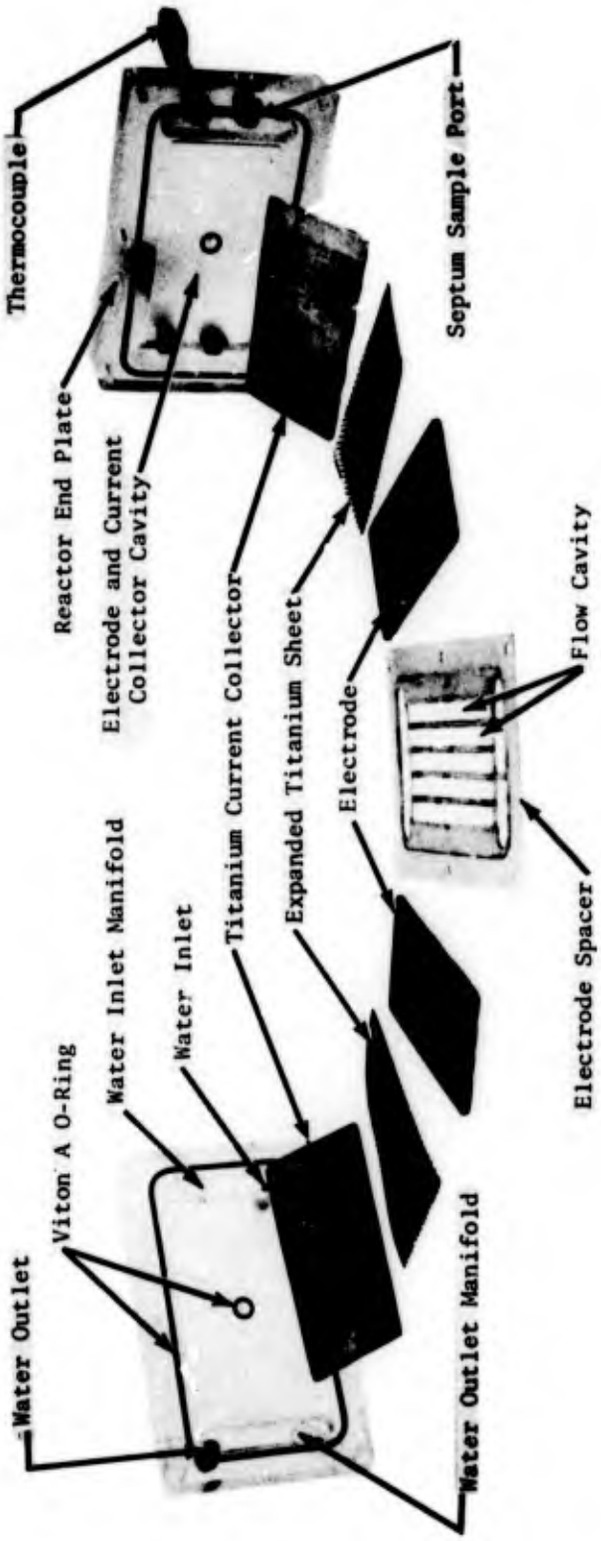


FIGURE 6 DISASSEMBLED ELECTROCHEMICAL BIOCIDE REACTOR (MARK I-1)

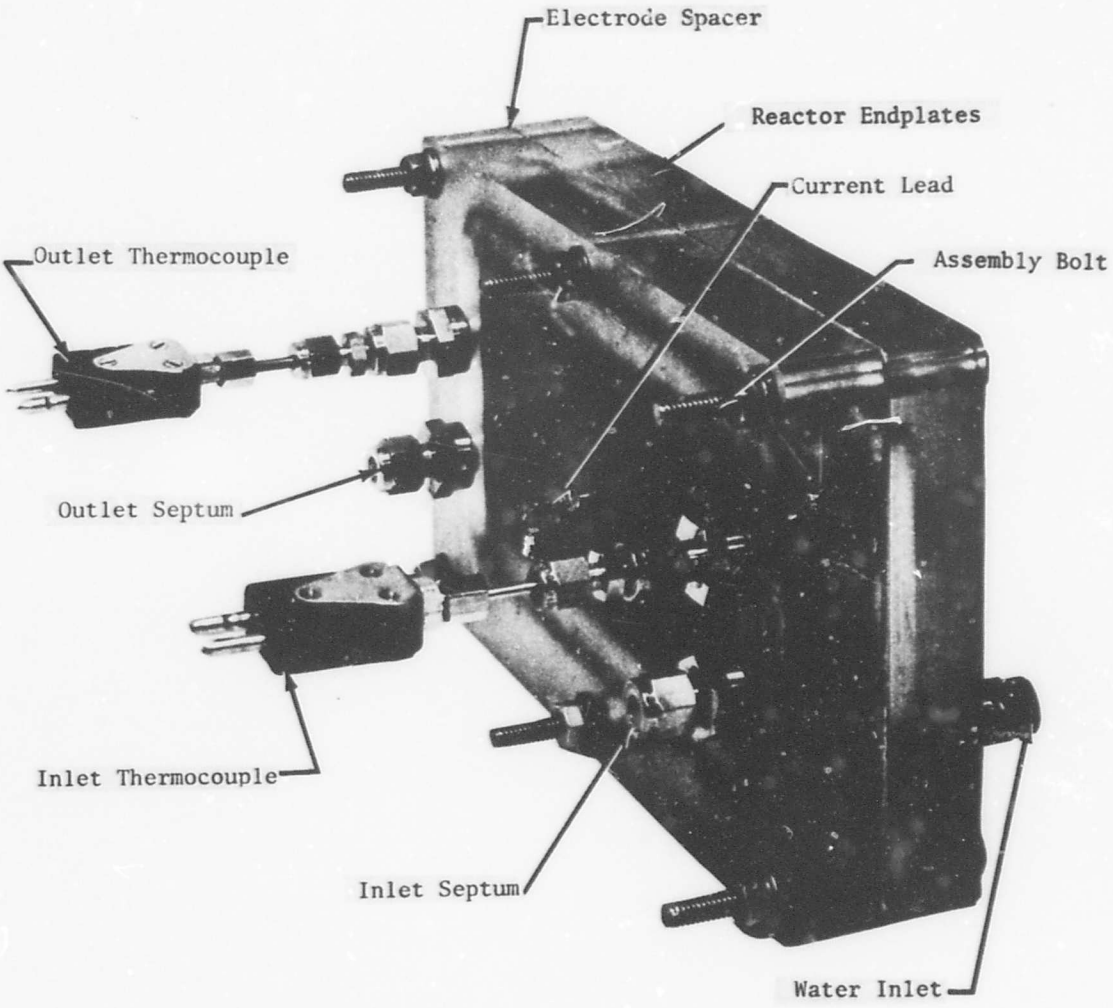


FIGURE 7 ASSEMBLED ELECTROCHEMICAL BIOCIDE REACTOR (MARK I-1)

Electrical contact between the leads, the titanium current collectors, and carbon electrodes are achieved by a compressive force exerted through the bolt load and plastic spacer to the carbon electrodes and titanium current collectors.

Test Support Accessories

This section of the report is subdivided into the following three sections:

1. Mechanical Accessories - this section discusses the materials, mechanical components, and schematics of the test stand for the Electrochemical Biocide Reactor

2. Electrical Accessories - the power supplies, amplifiers, waveform generator and electrical control and monitor instrumentation are discussed

3. Test water - the provision for a source of sterile distilled water is described. The selection of the chemicals added to formulate the test water are listed. The specific microorganisms that were used in the Electrochemical Biocide process development and characterization are discussed

Mechanical Accessories

The primary function of the experimental apparatus was to allow operating flexibility and consistent quantitative determination of the effect of key engineering parameters on the process effectiveness and efficiency. Figure 8 is a simplified experimental apparatus block diagram. Test water was pumped through the Electrochemical Biocide Reactor with AC power imposed across it. The AC signal was obtained through the waveform generator. Under the current program, the experimental apparatus was operated in two different modes. These were:

1. Open-loop recycle mode to a small reservoir with the Mark I Reactor
2. Recycle mode in a closed loop with the Mark I Reactor

Materials. The experimental apparatus was fabricated with materials compatiblee with the process. During process operation these materials did not produce any biocide species or serve as organism "sinks." All internal wetted surfaces, with the exception of the reactor (noted previously) and the flow control flowmeter, were fabricated with stainless steel. The flowmeter-wetted components consisted of glass tubing, a brass flow controller housing, and a Delrin diaphragm.

Mechanical Components. The detailed electrochemical biocide experimental apparatus schematic is shown in Figure 9. It includes all the necessary controls needed to vary the process parameters essential for establishing the Electrochemical Biocide process technology base. It provided flexibility for single pass and recirculating mode operation.

The recycle loop was included in the experimental apparatus to:

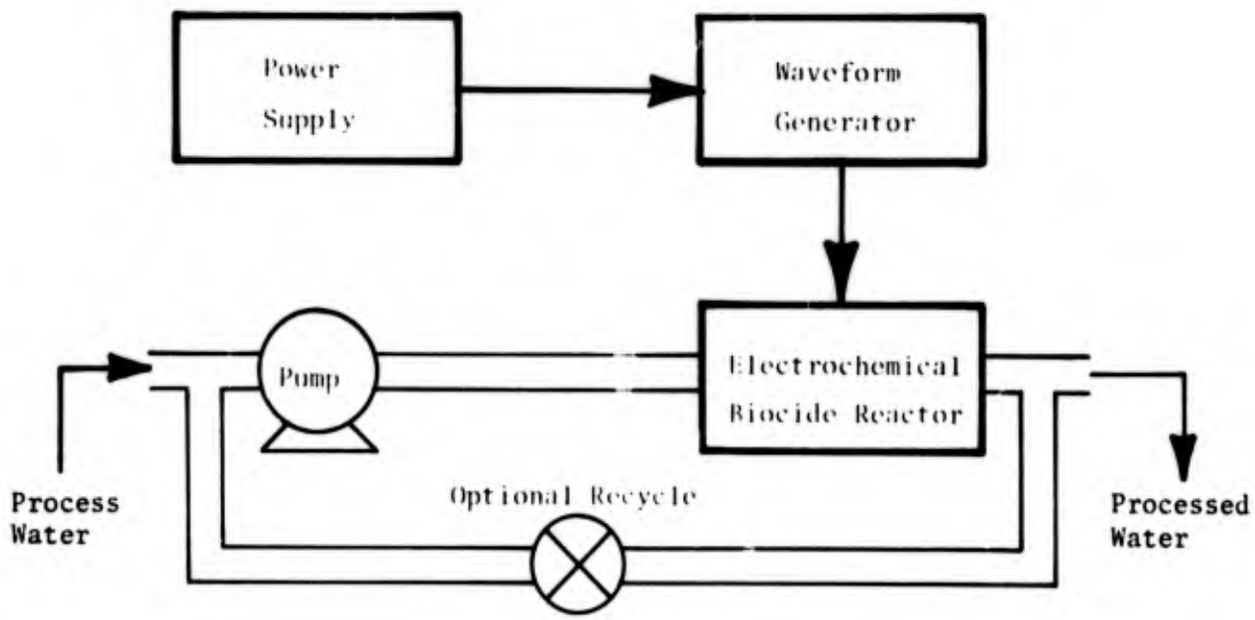


FIGURE 8 SIMPLIFIED ELECTROCHEMICAL BIOCIDE TEST STAND BLOCK DIAGRAM

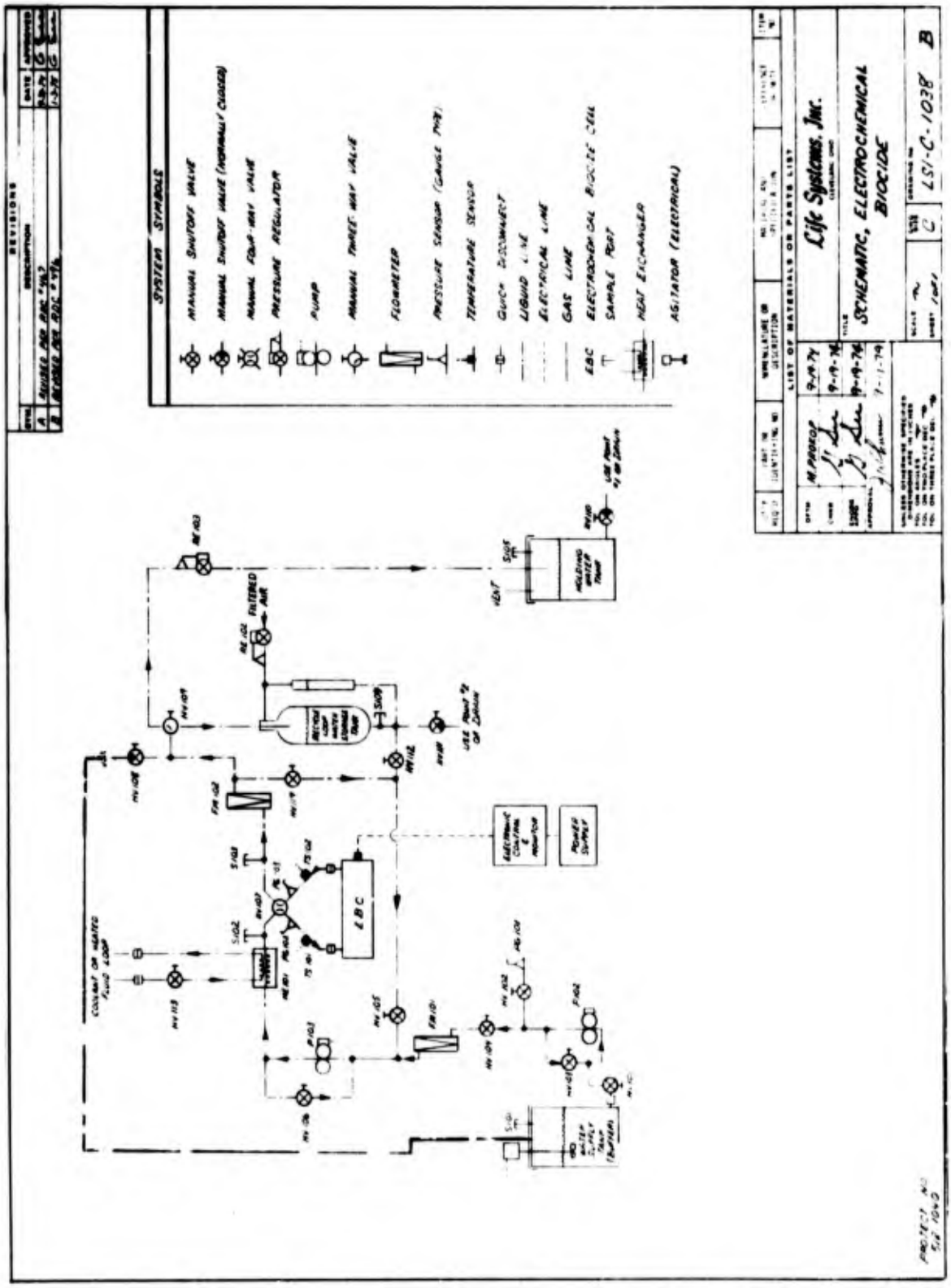


FIGURE 9 ELECTROCHEMICAL BIOCIDE TEST STAND SCHEMATIC

1. Allow variable process water exposure time with a single, fixed geometry reactor, independent of flow rate

2. Allow recirculation of process water through the Mark I Reactor with or without time delay

3. Allow for variation of process water temperature from 288 to 328K (50 to 131F)

4. Allow simulation of NASA's Space Shuttle Water System flows[44]

Figure 10 is a photograph of the experimental apparatus showing the mounted Electrochemical Biocide Reactor. The photograph shows the water supply reservoir and supply mixer, and the water supply and recycle pumps.

Figure 11 is a photograph of the experimental apparatus control panel. The control panel provides regulation of the process stream flow parameters.

Process water enters from the four-liter (one-gallon), stirred supply tank through the supply pump (P102) and supply regulating flowmeter (FM101) into a recycle loop containing the Mark I Reactor, recycle loop flowmeter (FM102) and recycle loop pump (P103). Process water could pass directly from the supply water reservoir through the Mark I Reactor to the holding tank or it could be recycled through HV114 or the recycle loop storage tank. The recycle loop storage tank provided a variable holding time between passes through the reactor. The process water could recirculate indefinitely or for a defined period of time by controlling the water supply flow rate (FM101 and RE103).

The water supply reservoir was covered and the entire system sealed from outside contamination. Samples were withdrawn with a sterile syringe from the closed system through the septums (S102).

Constant speed supply and variable speed recycled gear micropumps were used to move the test water through the reactor and experimental apparatus. A maximum flow rate of 600 cc/min (9.5 gal/hr) was used to allow a single pass reactor exposure time sufficient for one complete electrical cycle at the baseline electrical operating frequency (1 Hz).

$$T_E = \frac{T}{\frac{V_{RL}}{V_R} + 1} \qquad (2)$$

where

T_E = exposure time, min

T = real elapsed time, min

V_{RL} = volume of the recycle loop, cm^3 (in^3)

V_R = active volume of the reactor, cm^3 (in^3)

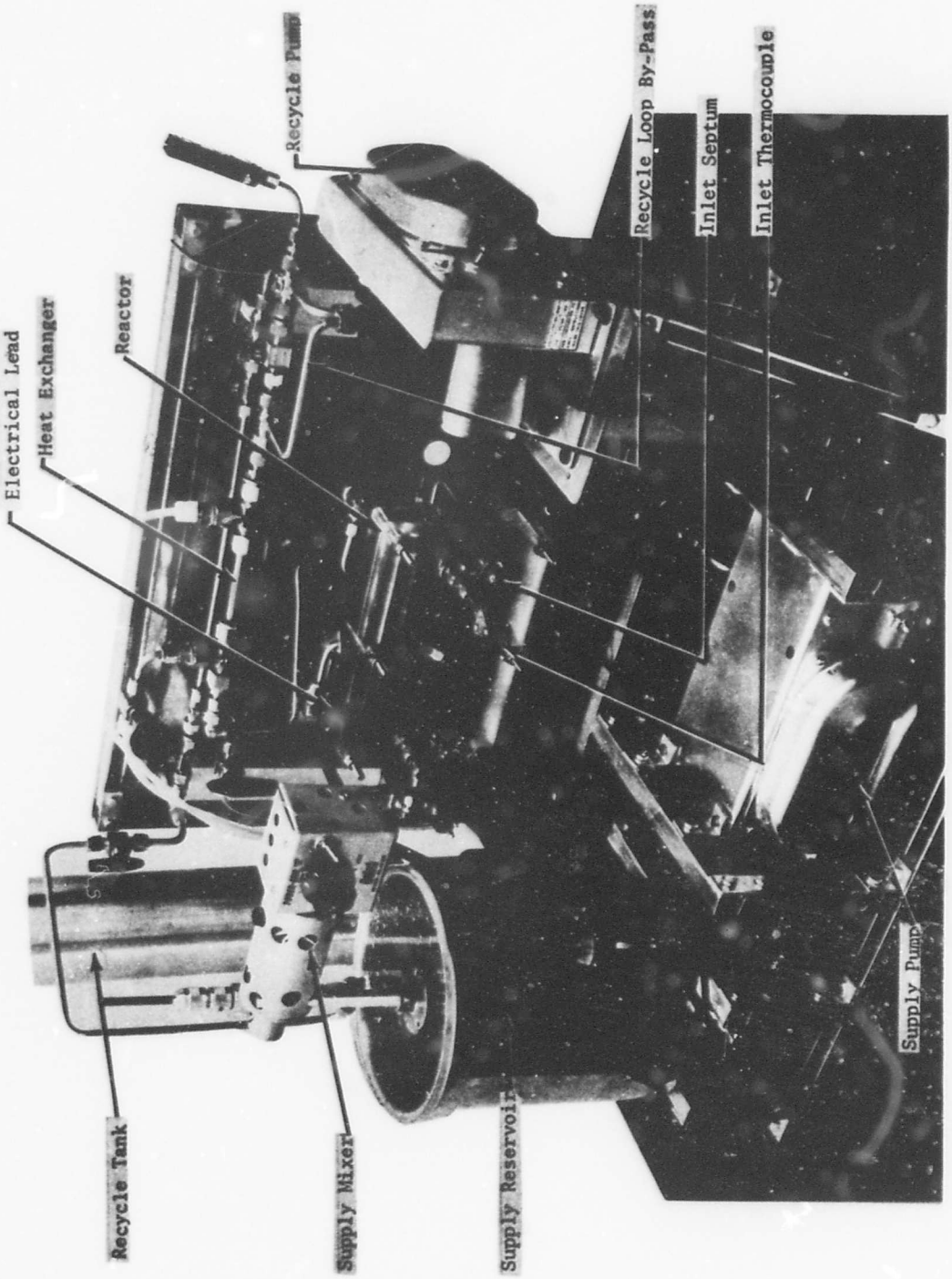


FIGURE 10 TEST STAND WITH MOUNTED ELECTROCHEMICAL BIOCIDE REACTOR

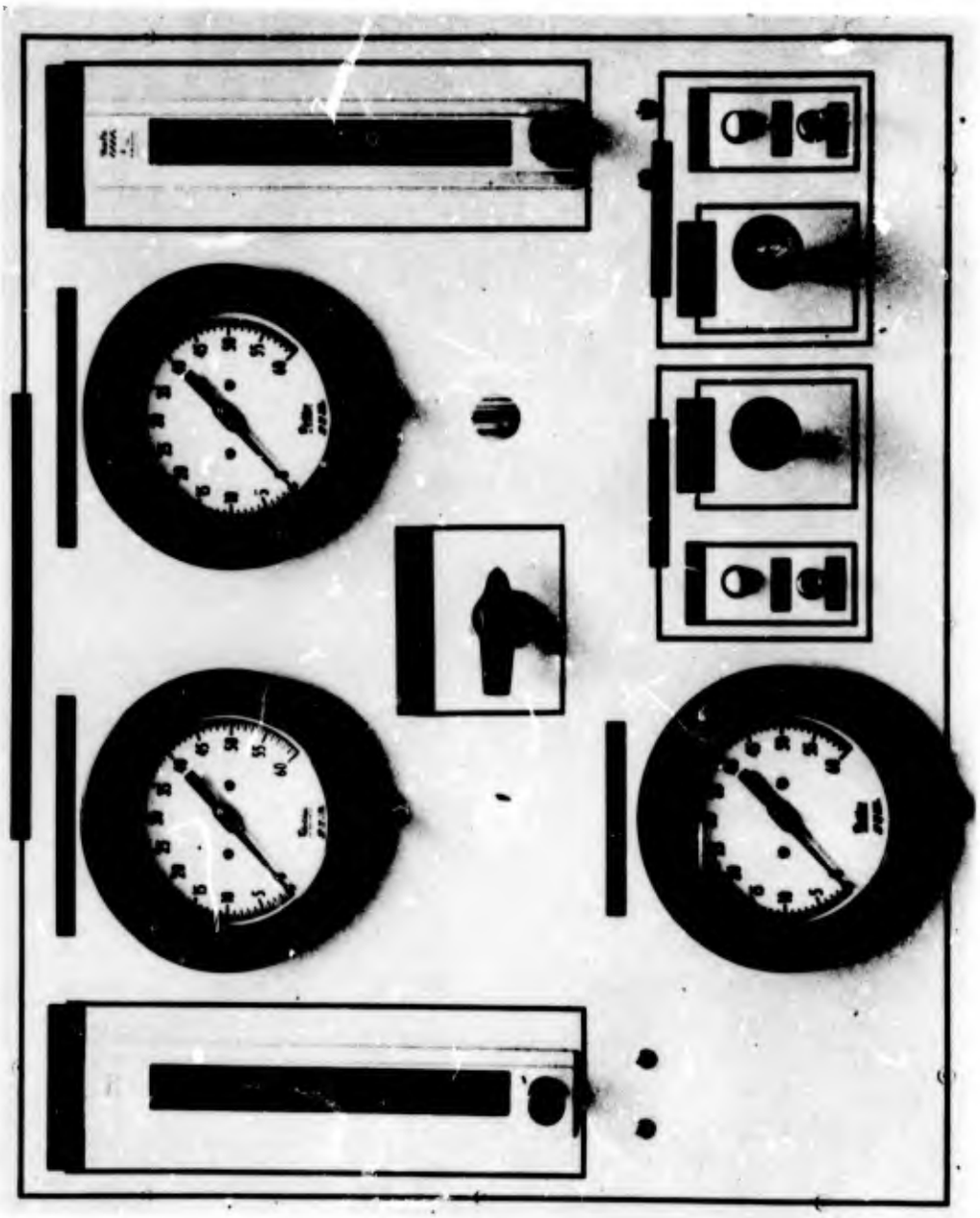


FIGURE 11 ELECTROCHEMICAL BIOCIDE TEST STAND PLUMBING CONTROL PANEL

The experimental apparatus had a 177 cm^3 (10.4 in^3) recycle loop volume (excluding the recycle storage tank) and an active reactor volume (baseline condition) of 7.2 cm^3 (0.44 in^3). Therefore, Equation 2 becomes:

$$T_E = \frac{T}{25.6} \quad (3)$$

Electrical Accessories

The instrumentation for the program was designed to control and monitor all pertinent electronic parameters. These were:

1. Frequency of applied signal
2. Waveform of applied signal
3. Amplitude of applied signal
4. Duty cycle of applied signal (relates to operating power)
5. Input current and voltage

Figure 12 is a block diagram of the control/monitor instrumentation utilized on the program. The electrochemical biocide could be operated in either a voltage- or a current-controlled mode with the reactor's voltage or current signal, respectively, fed back to the predriver amplifier. In the voltage control mode, the potential difference across the cell electrodes was held constant, independent of process water conductivity. In the current control mode, the reactor current was held constant, again independent of process water conductivity. This control mode flexibility is provided to determine whether the biocidal effect is current or voltage related.

The waveform was produced by a function generator integrated circuit with supporting circuits to vary amplitude, frequency and duty cycle.

Figure 13 is a photograph of the control and monitor instrumentation enclosure front panel. Analog parameters were provided for temperature readout of reactor inlet and outlet process water. The Electrochemical Biocide process operating conditions were established by selecting the desired operating mode, frequency range and level, waveform, amplitude and duty cycle. The true root mean square (RMS) current or voltage for the set conditions were displayed on the digital readout meter.

The digital, true RMS readout was chosen to give a real power cell consumption value under the different waveform and duty cycle conditions. Power was calculated from the RMS values of voltage and current:

$$P = I_{RMS} \cdot V_{RMS} \quad (4)$$

Peak and average values could easily be calculated from the RMS readings for the particular waveform. The power supply voltage and current level capability were based on the anticipated range of process water conductivity and current density levels for the maximum 120 cm^2 (18.6 in^2) active electrode area. The power supply could deliver 10 amps at 15V.

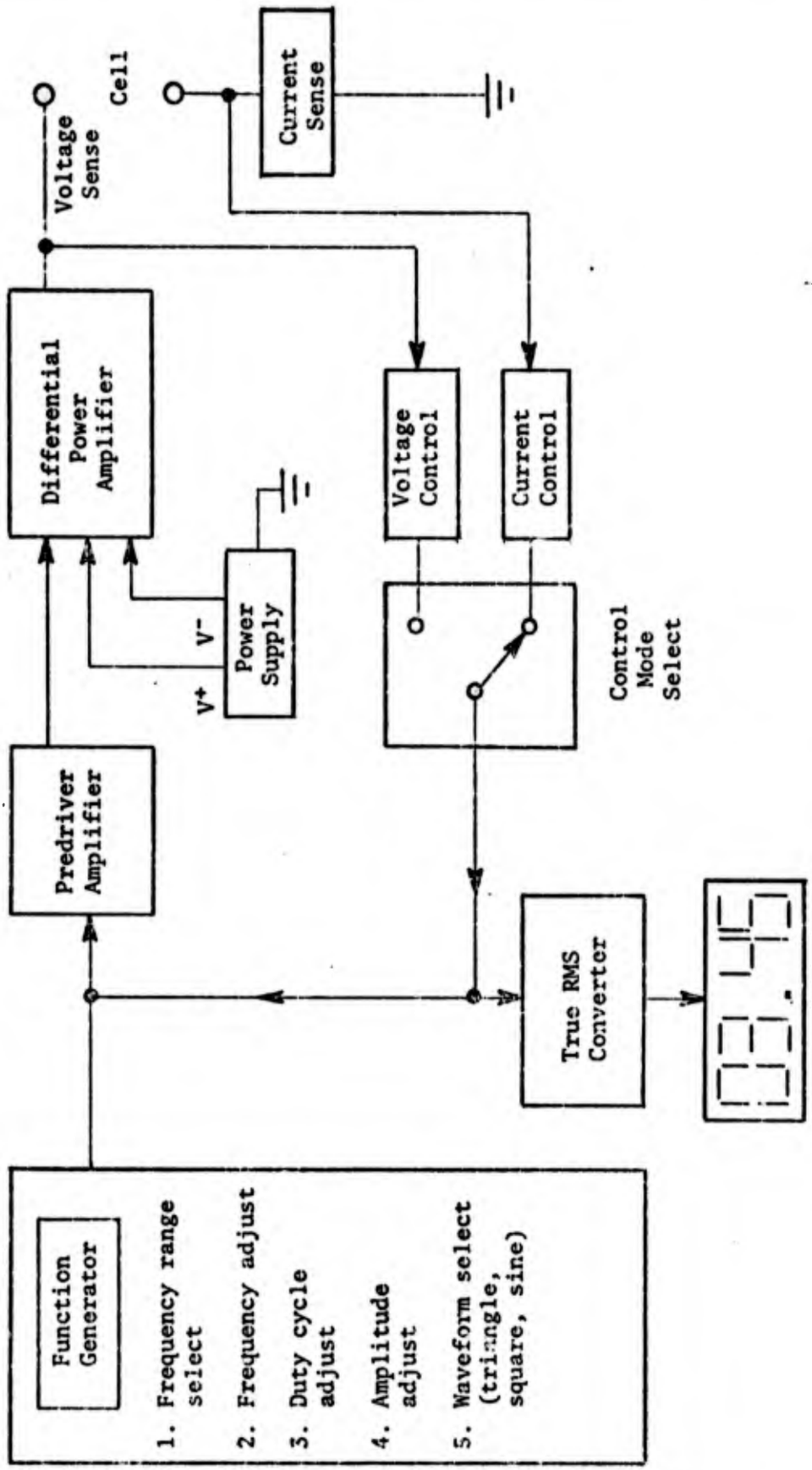


FIGURE 12 CONTROL AND MONITOR INSTRUMENTATION BLOCK DIAGRAM

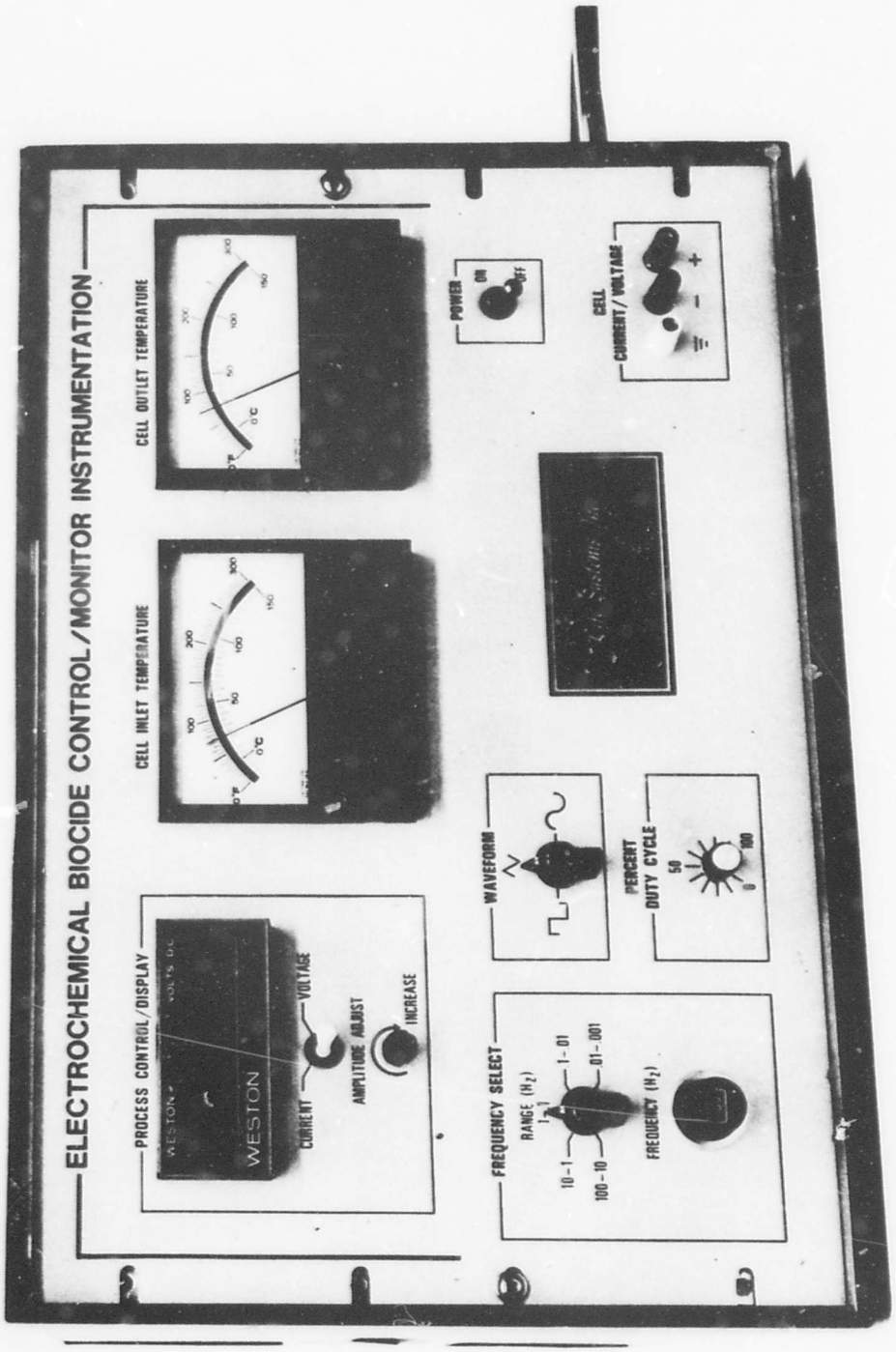


FIGURE 13 ELECTROCHEMICAL BIOCIDE TEST STAND CONTROL AND MONITOR INSTRUMENTATION PANEL

Test Water

This subsection describes the source of sterile distilled water used for testing the Electrochemical Biocide process. The chemical constituents of the test water and the procedure for preparing this water are discussed. Finally, the test water innoculated with the various test microorganisms are described.

Source of Sterile Distilled Water. A source of distilled water was provided by an all-glass Corning Megapure three-liter still. The apparatus distilled demineralized water producing pyrogen-free water with a resistance of 0.7MΩ. The water was collected and stored in a Pyrex collection bottle. To insure sterility of the collected, distilled water, all water used in the Electrochemical Biocide process was steam sterilized prior to use. The sterilized distilled water was tested for any bactericidal properties[43] with negative results.

Chemical Constituents of Test Water. Two test waters were designed and used under the current program. The first test water was designed to be buffered and resulted in high conductivity and the second test water was unbuffered with a low conductivity. The chemical constituents of the buffered test water and the procedure for preparing this water are described in Table 7. Experiments were also conducted with 100 and 500 mg/l NaCl added to the buffered test water. Program testing required that at least two of the following be present as chemical contaminants in the buffered test water: cadmium, chromium (hexavalent), copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, selenium, silver and ammonium ions. Magnesium and potassium were selected and program testing indicated these ions do not interfere with the electrochemical disinfection process.

The buffered test water included sodium, magnesium, potassium, chloride, sulphate and phosphate ions and dissolved oxygen. In addition, the added mono and dipotassium hydrogen phosphate salts gave this water good buffering capacity at a pH close to neutrality. The conductivity of this water was 2180.0 μmhos/cm. When 100 mg/l NaCl was added, the conductivity increased to 2385.0 μmhos/cm.

The unbuffered test water was designed to study the effect of lower conductivity water on process efficiency and effectiveness. This water was prepared by adding 42 mg/l KH_2PO_4 and 50 mg/l $NaNO_3$ to distilled water. In some experiments, 100 mg/l NaCl was added to this low conductivity test water to enhance the microorganism kill rate. The addition of 100 mg/l NaCl was recorded in the results. The conductivity of this water without NaCl was 120.0 μmho/cm. With the addition of 100 mg/l NaCl, the conductivity increased to 327.5 μmho/cm.

Microbiological Constituents of Test Water. A selection of multiple test microorganisms and types was made to show the overall effectiveness of the process. Three bacteria, Escherichia coli, (ATCC strain No. 11229), Pseudomonas aeruginosa, (ATCC strain No. 10145), and Klebsiella penumoniae, (ATCC strain No. 23357), two viruses, Polio WI-2 and Coxsacki B, and one yeast, Saccharomyces cerevisiae were selected for investigation.

Factors involved in the organism selection included:

TABLE 7 CHEMICAL CONSTITUENTS OF THE ELECTROCHEMICAL BIOCIDE BUFFERED TEST WATER

Compound	Gm/Liter (10X Solution)		Working Solution	Ion	Ppm in Working Solution
Na_2SO_4	1.562	Autoclave Solution A	For every liter (1000 ml)	Na^+	50
$MgSO_4 \cdot 7H_2O$	12.324		100 ml Solution A	Mg^+	1.2×10^2
				SO_4^{-2}	5.9×10^2
K_2HPO_4	8.719	Combine to required pH (5, 7 or 9) then Autoclave = Solution B	100 ml Solution B	K^+ (pH 7.0) (a)	3.9×10^2
KH_2PO_4	13.609		800 ml Distilled Water	PO_4^{-3} (pH 7.0) (a)	7.0×10^2

(a) At pH 5.0 and 9.0, concentration of PO_4^{-3} is different (concentration of K^+ does not differ)

ppm PO_4^{-3} at pH 5.0 = 4.8×10^2

ppm PO_4^{-3} at pH 9.0 = 9.5×10^2

1. Selection of test organisms that would likely present contamination problems in water reuse systems

2. Selection of organisms that are representative of a wide variety of human pathogens

3. Selection of test organisms that have been studied with other disinfection processes so that comparisons could be made

Although not ideal, Escherichia coli was selected as the indicator organism for determining baseline experimental conditions. Extensive data already exists with this microorganism exposed to other disinfecting processes and, therefore, allows the electrochemical biocide to be compared to these processes.

The Pseudomonas species are a common bacterial contaminant in the environment. Pseudomonas aeruginosa represents a likely bacterial species that could contaminate a water reuse treatment system. Klebsiella pneumoniae was selected as a pathogenic organism. It has been increasingly detected in domestic waste waters and its heavy polysacchride capsule layer could offer additional protection from disinfection, representing a worst-case bacterial contaminant.

Animal viruses, Polio I and Coxsacki B, were selected for investigation over the more convenient bacteriophage to avoid the significant differences in virion morphologies and thus be more representative of human pathogens.

The single yeast, Saccharomyces cerevisiae, was selected to provide comparative data on these organisms. This is a primary concern when a water reuse system is to be utilized in a closed-loop environment such as during manned spaceflights.

Dissolved Oxygen. The higher conductivity buffered test water (Table 7), containing 100 mg/l NaCl and 10^6 Escherichia coli/ml, had 7.6 mg/l dissolved oxygen.

EXPERIMENTAL PROGRAM

The experimental procedures and results are sectioned into the following major areas:

1. Experimental Operating Procedures
2. Baseline Experimental Conditions
3. Checkout Experiments
4. Parametric Experimental Results
   (a) Electronic parameter experimental results
   (b) Reactor and test water parameter experimental results
   (c) Microorganism experimental results
5. Post-Test Component Analysis

Experimental Operating Procedures

The operating sequence of the experimental apparatus is defined in Table 8. Prior to experimentation, the supply reservoir was autoclaved and the experimental

TABLE 8 EXPERIMENTAL APPARATUS OPERATING SEQUENCE

New Organism/Experimental Phase

1. Autoclave supply reservoir and all removable test apparatus elements

2. Purge test apparatus

   a. Hot 338K (150F) distilled water flush (15 Min, 900 cc/Min (14.3×10^{-3} Gal/Hr))
   b. Drain

3. Add buffer to supply reservoir

4. Inoculate supply reservoir with organism (record time)

5. Flood test apparatus with test water

   a. Start pumps (P102, P103)
   b. Open HV104, HV105, HV114 (recycle operation)
   c. Bleed air through HV108 and RE103
   d. Close HV108, RE103, and HV104 (recycle operation)
   e. Stop supply pump P102

Continuous Testing

6. Gas electrodes (3 Min, 10V, square wave, 1 Hz, 100% duty cycle)

7. Drain

8. Start supply reservoir mixer

9. Flood test apparatus with test water from reservoir and recycle for three minutes

10. Drain

11. Flood test apparatus with test water from reservoir

12. Take initial sample (S102) (record time)

13. Turn power on (record time)

14. Complete experiment/time out

15. Take final sample (record time)

16. Turn power off

apparatus flushed with hot distilled water for 15 minutes. The supply reservoir containing buffered test water was then inoculated with 10 ml of the suspension of the experimental bacteria for every liter of buffer to give an initial concentration of approximately 10^6 organisms/ml. For the viral testing, 2 ml of the stock viral suspension was added to 198 ml of test solution. The reactor electrodes were cleaned prior to each experiment by pregassing. This step consisted of turning the power on in the voltage control mode with a square waveform at 10 to 12V and 100% duty cycle. Gassing was allowed to continue for three minutes. The experimental apparatus was then drained and flushed with buffered test water containing microorganisms (or viruses). The buffer containing microorganisms (or viruses) was then circulated through the test apparatus and Steps 12 to 16 of the experimental apparatus operating sequence in Table 8 were completed. The experimental operating procedures for Saccharomyces cerevisiae, were identical to those for the bacterial testing with the exception that the initial concentration of Saccharomyces cerevisiae in the reservoir was approximately 2×10^3 organisms/ml.

All glassware used in the experimental work was borosilicate and was rinsed in distilled water and autoclaved prior to use. All chemicals used were Fisher reagent grade or higher. Samples were withdrawn through tri-layered rubber septa by means of sterile, disposable 1 ml tuberculin syringes fitted with sterile 21 gauge 3.8 cm (1.5 in) needles to insure sampling from within the reactor process water flow stream. Septa were aseptically changed for each experiment.

Preparation of Bacteria

Bacteria were grown on nutrient agar slants for 16 to 22 hours at 308K (95F) and removed from the slant surface by means of a pipet containing 1 ml of buffered test water. The suspension was pipetted into a 99 ml dilution blank which provided the inoculant for the supply reservoir.

Preparation of Yeast

Saccharomyces cerevisiae was grown on Malt Agar for 22 hours. The remainder of the procedure was identical to the preparation of bacteria above.

Preparation of Viruses

Stock viruses were grown in the following 2% culture media with Hank's Balanced Salts Solution (BSS):

77.3 ml	Distilled deionized sterile water
10.0 ml	Minimum essential medium (MEM) (10X) or 10.0 ml Basal Medium (Eagle) plus 1 ml Glutamine
2.0 ml	Fetal calf serum
6.5 ml	Lactalbumin hydrolysate
1.5 ml	Antibiotic antimycotic mixture

1.0 ml	Anti-Pleuropneumonia-like organisms (PPLO) (or 0.25 ml Tetracycline)
1.8-3.0 ml	$NaHCO_3$ (7.5%)
100 ppm	Myostatin

The final media in which the stock viruses were stored consisted of the remaining fraction of a saline solution rinse plus 1.2 ml of Hank's BSS plus 14 ml of the 2% media. The saline solution rinse solution consisted of 0.85 gm NaCl per 100 ml distilled, deionized, sterile water (this was the storage solution for the viruses and was added to the test water in the virus experiments). The stock viruses were frozen at 203K (-94F) until needed in the experiments.

The buffalo green monkey (BGM) continuous cell line was cultured to grow both the polio virus and the coxsacki virus. The cell line was obtained from Hem Research, Inc., Rockville, Maryland. Except for the initial test with the polio virus, all cells were shipped in No. 20 flasks and culture tubes ready for use requiring only feeding and assaying. The procedure for handling BGM cells is shown in Table 9.

The media used for the BGM cells was the previously described 2% media and the following 10% media:

76.2 ml	Distilled deionized sterile water
10.0 ml	Hank's 199 (10X)
10.0 ml	Fetal calf serum
1.5 ml	Antibiotic-antimycotic mixture
1.0 ml	Anti-PPLO (or 0.25 ml Tetracycline)
1.8-3.0 ml	$NaHCO_3$ (7.5%)

The BGM cells were maintained in a carbon dioxide incubator and analyses were made in accordance with the information published by Dahling, Berg and Berman.[45] The overlay media used in the Plaque Forming Technique was as follows:

41.5 ml	2X MEM with Hank's salts, Eagle's with Glutamine
1.0 ml	Nonessential amino acids
2.0 ml	Fetal calf serum
3.0 ml	$NaHCO_3$ (7.5%)
1.0 ml	$MgCl_2 \cdot 6H_2O$ (1%)
1.5 ml	Neutral red (0.1%)

TABLE 9 PROCEDURE FOR HANDLING BGM CELLS

1. BGM cells received, placed in CO_2 incubator overnight.
2. Cells removed from incubator, Media in flasks (or tubes) is poured off and fresh 2% Media is added.
3. Cells placed back in incubator.
4. Flasks (or tubes) are checked each day for growth and possible contamination.
5. When cell sheet appears to be a confluent, thick monolayer, the cells are trypsinized.
6. Flasks (or tubes) are then placed back in incubator.
7. Flasks are removed from incubator the following day. The 10% Media is poured off and replaced with 2% Media and placed back in incubator.

1.0 ml	Sterile whole milk
1.5 ml	Antibiotic antimycotic mixture
1.0 ml	Anti-PPLO (or 0.25 ml Tetracycline)
50.0 ml	Agar, purified (1.8%) melted
100 ppm	Myostatin

Bacteria and Yeast Sampling and Assay Procedures

One ml samples were removed from the outlet septum (S-102) of the reactor or the reservoir when using the open-loop test apparatus operating mode before applying power and at the predetermined sampling times. Bacteria were assayed by the standard plate count procedure.[43] Standard dilutions were employed and all dilutions of samples were plated in triplicate. Plates were counted after 48 hours of incubation at 308K (95F). Saccharomyces cerevisiae was plated in triplicate both on Malt Agar and Potato Dextrose Agar and counted after 96 hours of incubation at 303K (90F).

One experiment, using Escherichia coli as the test organism, employed millipore filtration of 1 ml samples (first added to 99 ml dilution blanks) as the assaying technique. The filters were placed on broth pads saturated with 2 ml MF-Endobroth. The petri dishes were closed, inverted and incubated at 310.5K (99.5F) for 24 hours.

This experiment was conducted to verify the microorganism counts obtained using the standard plate count procedure. The Escherichia coli kill rates obtained were similar to that obtained in earlier experiments using the standard plate count assaying procedure.[43] Approximately four-log order kills resulted in a little over three minutes exposure time.

Viral Sampling and Assay Procedures

Virus determinations were made using the Test Tube Tissue Culture Technique (Endpoint Method) and the Plaque Assay Technique. The polio virus was determined by the Plaque Assay Technique and reported as plaque-forming units per ml (PFU per ml). The procedure for Plaque Assay Technique is shown in Table 10. The coxsacki virus was determined by the Endpoint Method and reported as most probable number per ml (MPN per ml). The procedures for the Endpoint Method is given in Table 11.

Control Experiments

Control experiments were run for each power experiment. Two exceptions were experiments with (a) unbuffered test water with 100 mg/l NaCl, and (b) buffered test water with 500 mg/l NaCl discussed under the Effects of Sodium Chloride Section.

TABLE 10 PROCEDURE FOR PLAQUE ASSAY TECHNIQUE

1. Dilute stock virus:

   a. Rapid thaw stock (310K (98.6F) water bath)
   b. Add 2 ml stock to 198 ml test water
   c. Mix well
   d. Remove 10 ml virus solution; place in holding vessel (holding samples taken from this)
   e. Take 1 ml sample using sterile syringe

2. Run virus solution in reactor test.

3. Remove samples (1.0 ml volumes) at designated time intervals with sterile syringe.

4. Filter samples with membrane filter to remove bacteria and put samples into sterile vials.

5. To prepare dilution tubes (24 hours in advance), add 1.8 ml Hanks' BSS IX to each tube.

6. Dilute 0.2 ml sample from vial into dilution tube.

7. Mix well.

8. Serial dilution step using 0.2 ml from each dilution.

9. Prepare cell cultures (24 to 48 hour monolayer):

   a. Pour off media
   b. Wash with saline and pour off
   c. Add Hanks' BSS IX (0.9 ml/flask)

10. Add 0.1 ml of dilution to flask; mix over cell sheet.

11. Incubate at 310K (98.6F) for two hours.

12. Add 15 ml/flask of overlay media; allow to harden at room temperature.

13. Invert and incubate at 310K (98.6F).

14. Examine and count plaques on days 3, 4 and 5.

TABLE 11 PROCEDURE FOR ENDPOINT
(TEST TUBE TISSUE CULTURE) METHOD

1. Dilute stock virus:

   a. Rapid thaw stock (310K (98.6F) water bath)
   b. Add 2 ml stock to 198 ml test water
   c. Mix well
   d. Remove 10 ml virus solution; place in holding vessel (holding samples taken from this)
   e. Take 1 ml sample using sterile syringe

2. Run virus solution in reactor test.

3. Remove samples (1.0 ml volumes) at designated time intervals with sterile syringe.

4. Filter samples with membrane filter to remove bacteria and put samples into sterile vials.

5. To prepare dilution tubes (24 hours in advance), add 1.8 ml Hanks' BSS IX to each tube.

6. Dilute 0.2 ml sample from vial into dilution tube.

7. Mix well.

8. Serial dilution step using 0.2 ml from each dilution.

9. Prepare cell cultures in tubes (24 to 48 hour monolayer):

   a. Pour off media
   b. Wash with saline and pour off
   c. Add Hanks' BSS IX (0.9 ml/tube)

10. Add 0.1 ml of dilution to tube; mix over cell sheet.

11. Incubate at 310K (98.6F) for two hours.

12. Add 2.5 ml/tube of 2% media.

13. Place in incubator at 310K (98.6F).

14. Examine cell sheet under the microscope on days 3, 4 and 5 for destruction of cell sheet and determine degree of cell sheet destruction.

TABLE 12 MEASURED AND CONTROLLED PARAMETERS

Parameter	Levels/Range Studied	Baseline
• Turbidity, JTU	5 to 50	None
• Temperature, K (F)	283 to 327 (50 to 130)	297 (75)
Pressure, kN/m^2 (Psig)	0 to 308 (0 to 30)	136 (5)
• pH	5 to 9	7
• Chemical Content	Buffered and unbuffered test water with and without 100 gm/l NaCl	Unbuffered test water without 100 mg/l NaCl
Microorganism Concentration	10^4/ml to 10^6/ml	10^6/ml
• Microorganism Type	E. coli, P. aeruginosa, K. pneumoniae, Polio I, Coxsacki B, Saccharomyces	E. Coli
Process Electrical Control	Current - Voltage	Voltage
• Voltage, V	2 to 12	12
Current Density, mA/cm^2 (ASF)	10 to 53.8 (10 to 50)	10 (10)
• Waveform	Sine, Square, Triangular	Square
Duty Cycle, %	40 to 100	100
• Flow Compartment		
Electrode Spacing, cm (in)	0.08 to 0.127 (0.03 to 0.05)	0.08 (0.03)
Turbulator	With and without Nylon Screen	With Nylon Screen
Reactor Resident Time, Min	1 to 5	4
• Flow Rate, cc/Min (Gal/Hr)	100 to 600 (1.58 to 9.51)	350 (5.55)
• Flow Regime	Laminar - Turbulent	Turbulent
Flow Path	Once Through - Recycle	Recycle

• These parameters are independently varied.

Control experiments for the bacteria and yeast experiments were run separately under identical conditions to the power experiments, except that no power was applied to the reactor.

The virus experiments were run with the viruses held in a vessel containing the test solution for the duration of the power experiments (shelf control) and with the no-power controls run in sequence with the power experiment. The no-power controls were run sequentially with the power experiments because of the difficulty in handling and assaying the viruses.

Baseline Experimental Conditions

The parameters that were measured and controlled as a part of the experimental program are summarized in Table 12. The data indicates both the level or ranges studied and the value of the parameter considered as baseline.

Eighteen process parameters were monitored during the course of the experimental activities, and ten parameters independently varied. The parameters independently varied under the experimental program are marked with a dot in the extreme left column in Table 12.

The range over which the critical parameters were varied were suggested in part by results obtained under prior research and development efforts on the Electrochemical Biocide process.

Checkout Experiments

Figure 14 shows the electrical performance characteristics of the Mark I-1 Reactor under varying AC and DC densities. When operated in the DC mode, measurements were taken at two minute intervals. The reactor's performance was measured with one electrode having positive polarity and then repeated with the same electrode having negative polarity. No significance was attached to the slight difference in electrode performance obtained by interchanging polarity. From Figure 14 it is evident that under the AC operating anode, the Mark I Reactor behaves like an ohmic resistance device. This implies that the electrochemical polarization effects are either constant or zero and do not vary significantly with the impressed voltage and current density.

Parametric Experimental Results

The experimental phase summary for the electrochemical biocide development is flow-charted in Figure 15. The experimental results generated under Phase I were conducted with a Mark I Reactor which did not have an internal flow compartment turbulator. With this flow compartment configuration, and *Escherichia coli*, a maximum microorganism reduction of 99.5% (10^6 organisms/ml to 5×10^3 organisms/ml) in four minutes of exposure time was achieved with the buffered test water containing (100 mg/l) NaCl (See Figure 16, No Turbulator Experiment). Under this phase of the experimental activities, the process operating parametric levels were determined to be 5V which resulted in a 40 mA/cm^2 current density (above 5V gassing in the reactor was observed which masked the kinetic data), square electrical waveform, 0.5 Hz frequency, and 100 ml/min (1.6 gal/hour) process water flow rate. Process water pH and temperature (5 to 9 and 283K (50F) to 317.4K (112F), respectively) were shown not to have an influence on the

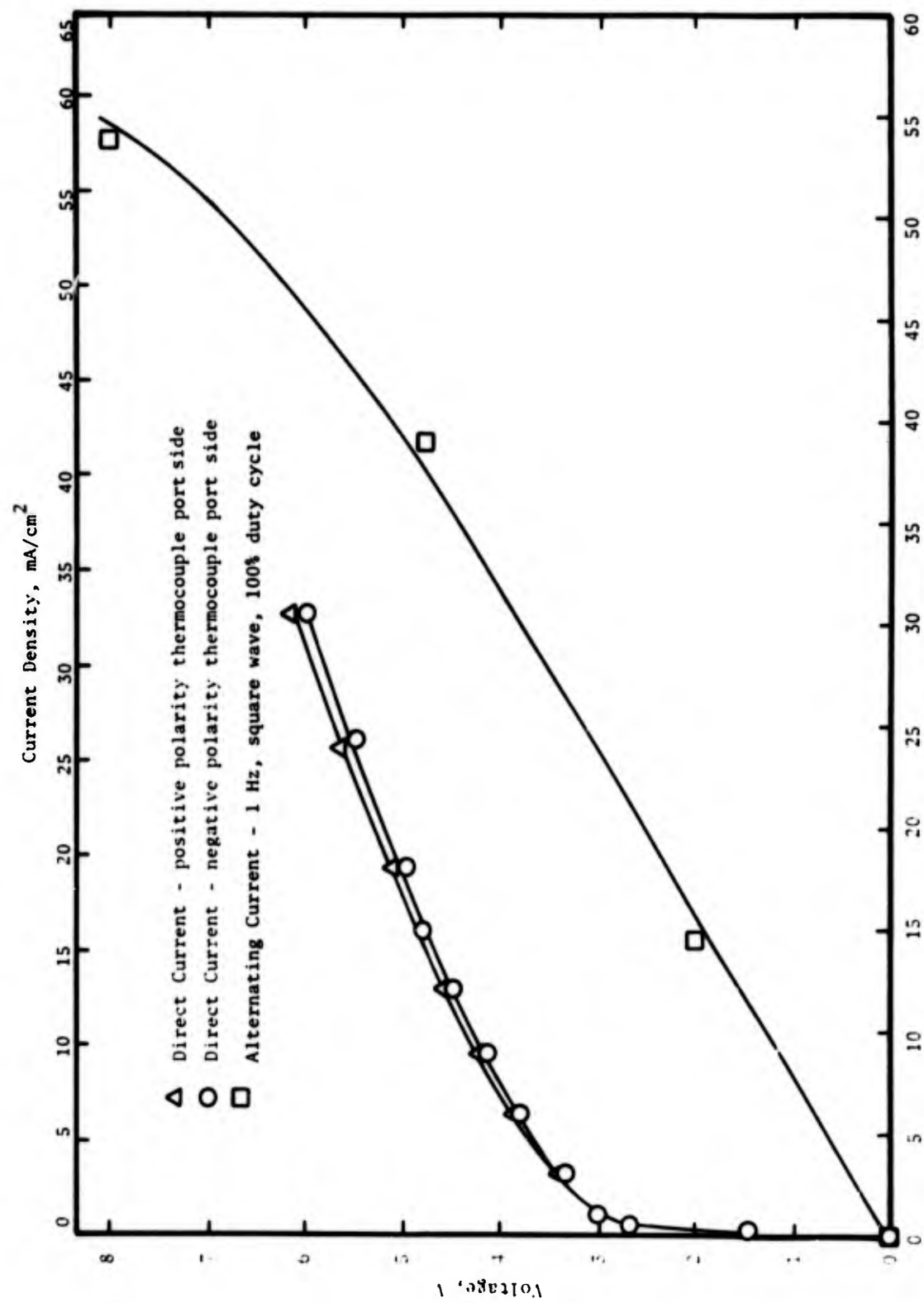


FIGURE 14 AC AND DC REACTOR PERFORMANCE CHARACTERISTICS

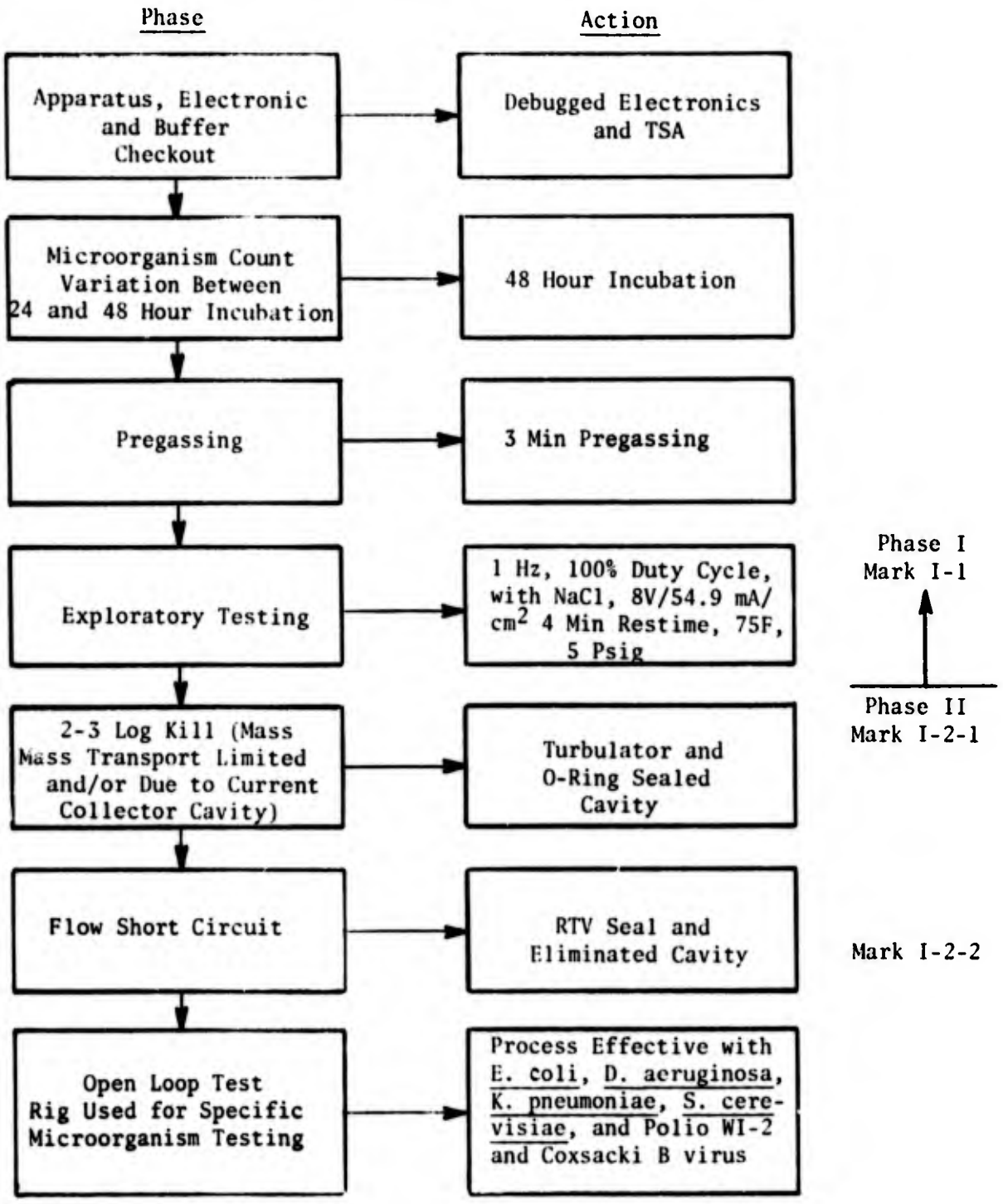


FIGURE 15 EXPERIMENTAL PHASE SUMMARY

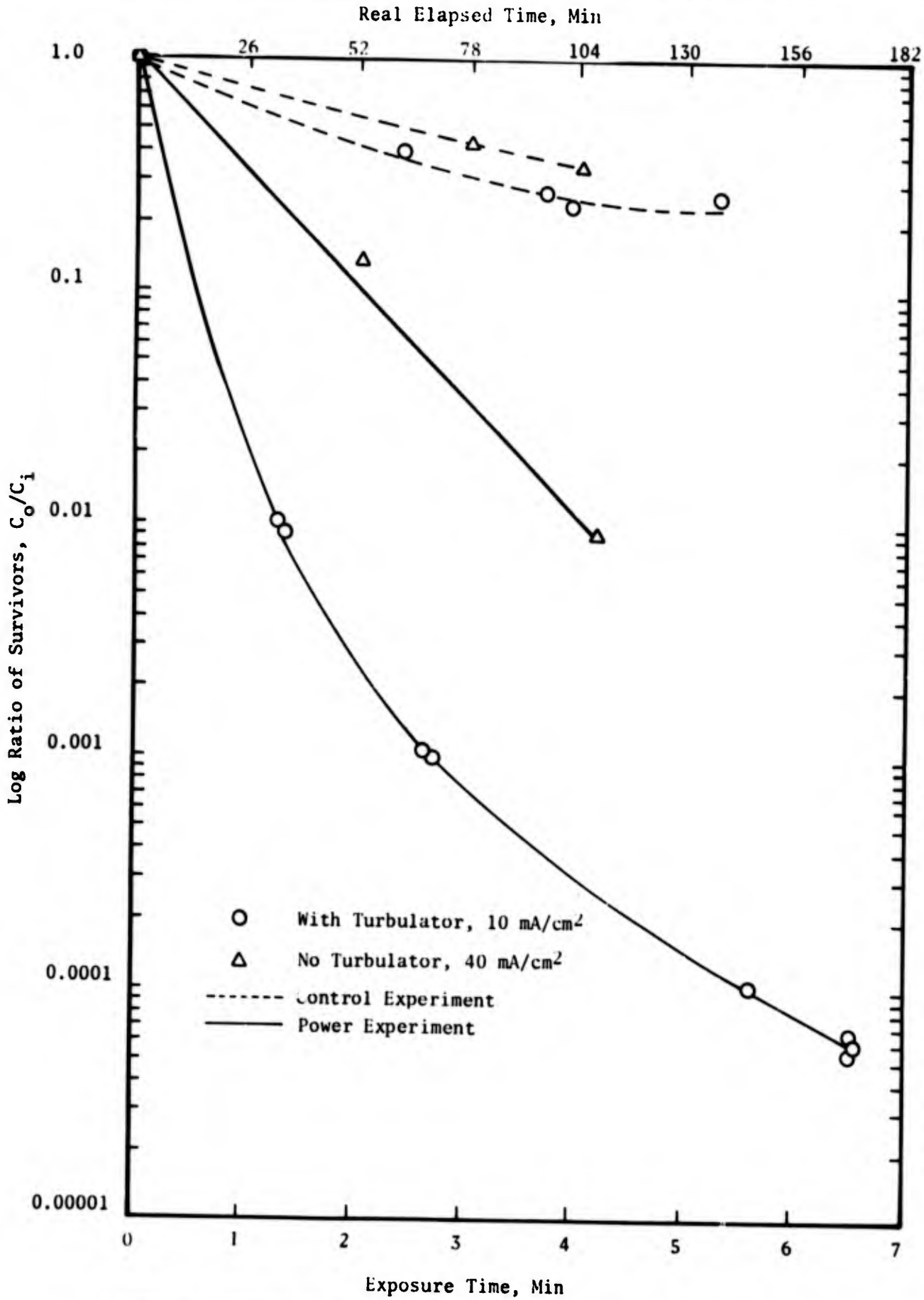


FIGURE 16 EFFECT OF FLOW COMPARTMENT TURBULATOR AT BASELINE CONDITIONS

process efficiency. The presence of NaCl in the buffered test water was shown not essential for effective destruction of Escherichia coli.

In the second experimental phase, the Mark I Reactor flow compartment was modified and updated to incorporate a screen turbulator to evaluate the effects of mass-transport on the process efficiency. The turbulator greatly enhanced the process efficiency. Experimental data comparing the results with and without a flow compartment turbulator are shown in Figure 16. The results show the process to be more effective in destroying microorganisms with the turbulator at one-fourth the current density and 80% of the power. The specific power requirements with the turbulator and unbuffered test water were 89W-hr/gal/log organism reduction.

When the reactor turbulator was added to the flow compartment, three other alterations were made to the Mark I Reactor which may have further enhanced the efficiency of the process. These alterations were:

1. Elimination of the expanded titanium sheet current collector cavity (which potentially served as a reservoir for the high initial microorganism concentration feed)

2. Elimination of a partial flow path short circuit between the inlet and exit manifolds via the O-ring seal cavity (allowing bypass of the active flow compartments within the reactor)

3. Open-loop recycle operation of the test stand apparatus to allow the escape of gas bubbles. Gas formed in the reactor was observed to build up in the process water stream in the closed recycle loop operation. This severely affected the kill efficiency of the Electrochemical Biocide process

Unless otherwise indicated, the experiments presented in the following sections were run at baseline conditions with the exception of the experimental parameter being varied. The baseline conditions were described in Table 12.

Control Experiments

The reduction of viable microorganisms in control experiments can be attributed to dying of microorganisms in the test water (osmotic shock, etc.), entrapment of organisms in the mechanical dead ends of the test apparatus, such as pressure gauges and some adsorption onto components of the test apparatus such as the carbon electrodes.

Although not an objective of the present program, it was determined that test solutions, with increasing amounts of NaCl, had lower reductions of viable microorganisms in the control experiments. This may have been due to a more favorable osmotic environment for the microorganisms (especially in the unbuffered test water) or less likely competition for adsorption onto the electrodes between microorganisms and chloride and sodium ions.

Controls for the microorganism experiments in the latter testing had lower reductions of viable microorganisms with the exception of the experiment with Pseudomonas aeruginosa where the unbuffered test water seemed to be an unfavorable environment for the test organism.

More drastic reductions in controls in earlier experiments may have been due to the more complex reactor configuration with more microorganism traps such as the current collector cavities.

Virus control data represented nominal reductions in infective phage, with the exception of the Coxsackie B shelf control given in the Results Section.

Electronic Parameter Experimental Results. The effects of voltage level, waveform and frequency were studied and are shown in Figures 17, 18, and 19, respectively. These experiments were conducted under Phase I testing. Experimental conditions were not set at baseline and are listed in the figures. The results of exposing Escherichia coli to OV (control), 2V, 5V, 8V, and 10V are presented in Figure 17. Increased kill resulted from the increased voltage levels up to 8V. At 10V the Electrochemical Biocide process was not as effective. An increase in temperature was observed at the 10V level due to the increased power passed through the reactor.

The results of studying square, triangular, and sine waveforms are shown in Figure 18. All were run at 5V RMS, 1 Hz, and 100% duty cycle. The results showed no appreciable difference in the log ratio of survivors at the two-minute and four-minute exposure times for the three waveforms. The square waveform was the most efficient in destroying the Escherichia coli.

The results for frequency levels of 0.5, 1.0, and 1.5 Hz with the square waveform are shown in Figure 19. The 0.5 Hz frequency was the most efficient in killing the Escherichia coli. The process became more efficient as the waveform frequency approached DC. The best level of operation was concluded to be with the square waveform at 5V and 0.5 Hz frequency. Additional testing will have to be conducted in order to define the most effective operating frequency for the destruction of the microorganisms without allowing the electrodes to foul.

Since the testing disclosed no appreciable differences in the log ratios of survivors for the three waveforms, and only moderate differences between frequency changes, a simplified electronic power supply with no waveform generation may be considered for future application of the Electrochemical Biocide.

Pregassing the electrodes before the start of the experiment resulted in a slight increase in microorganism kill. Increased kills were observed for both experimental control and power experiments as illustrated in Figure 20. Apparently, pregassing renews the slightly fouled electrode surface, resulting in the higher microorganism kills.

Reactor and Test Water Parameter Experimental Results. This subsection discusses the effects of process water temperature, pH, turbidity, flow rate and NaCl content on the Electrochemical Biocide process, microorganism kill effectiveness and efficiency.

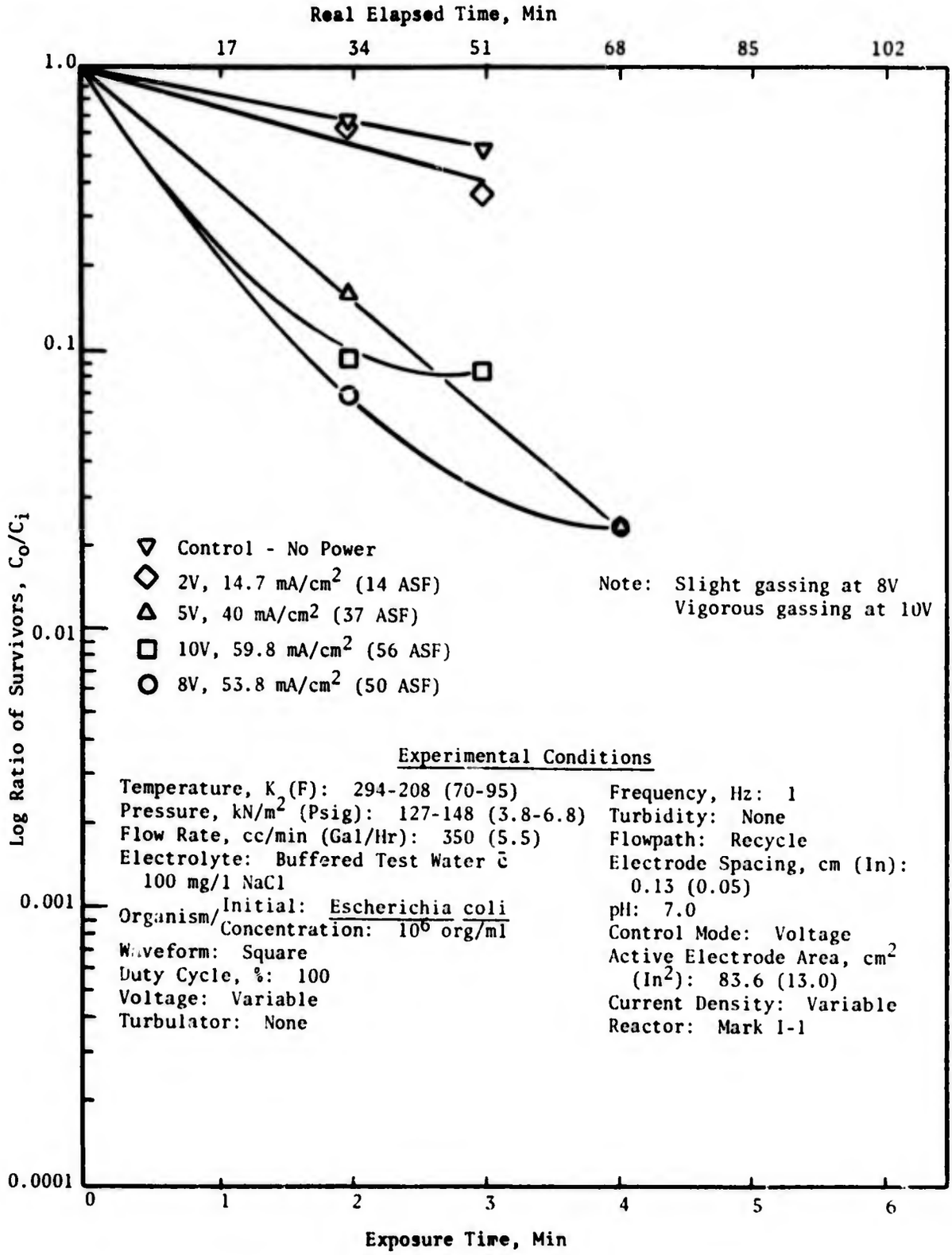


FIGURE 17 MICROORGANISM SURVIVAL VERSUS VOLTAGE

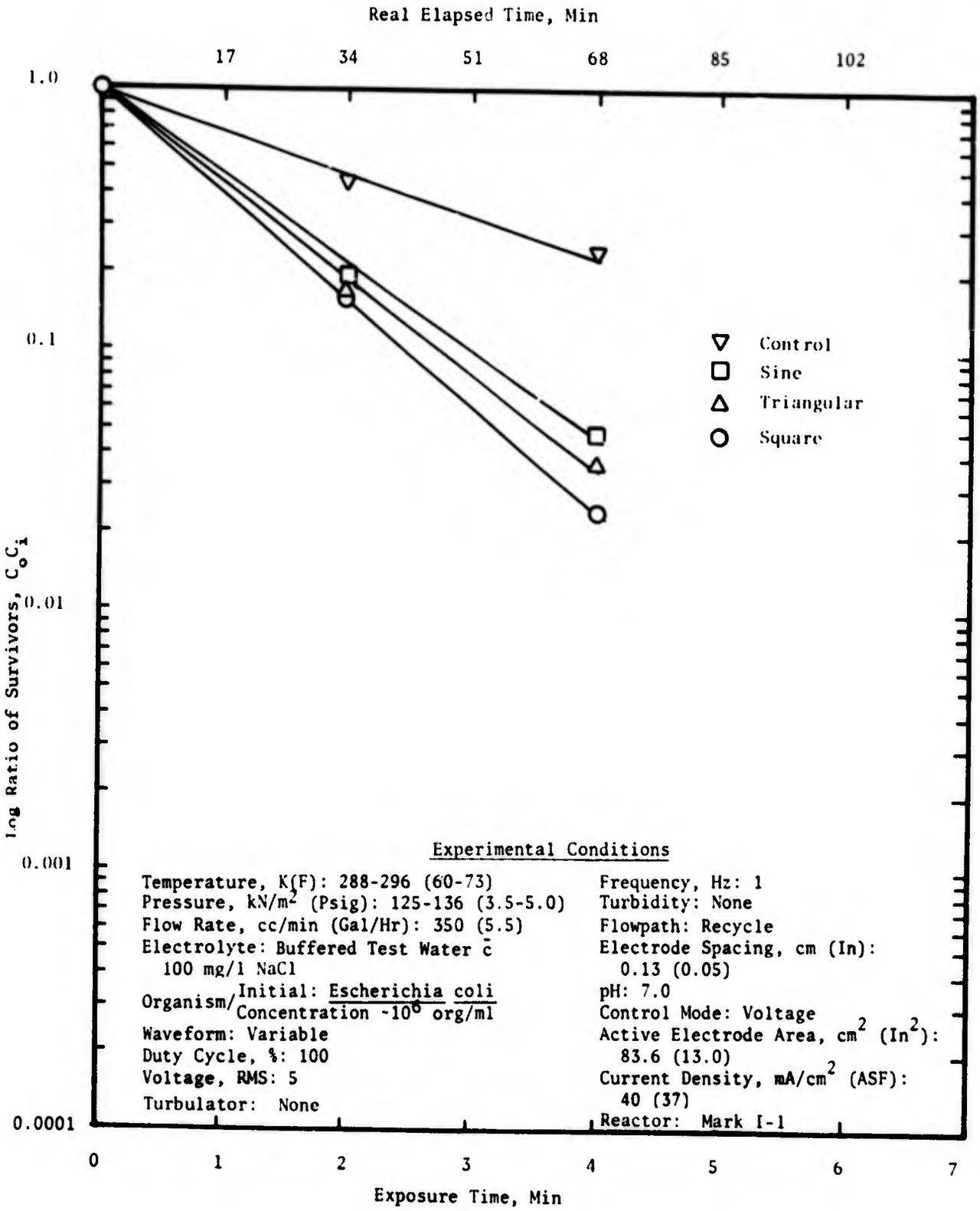


FIGURE 18 MICROORGANISM SURVIVAL VERSUS WAVEFORM

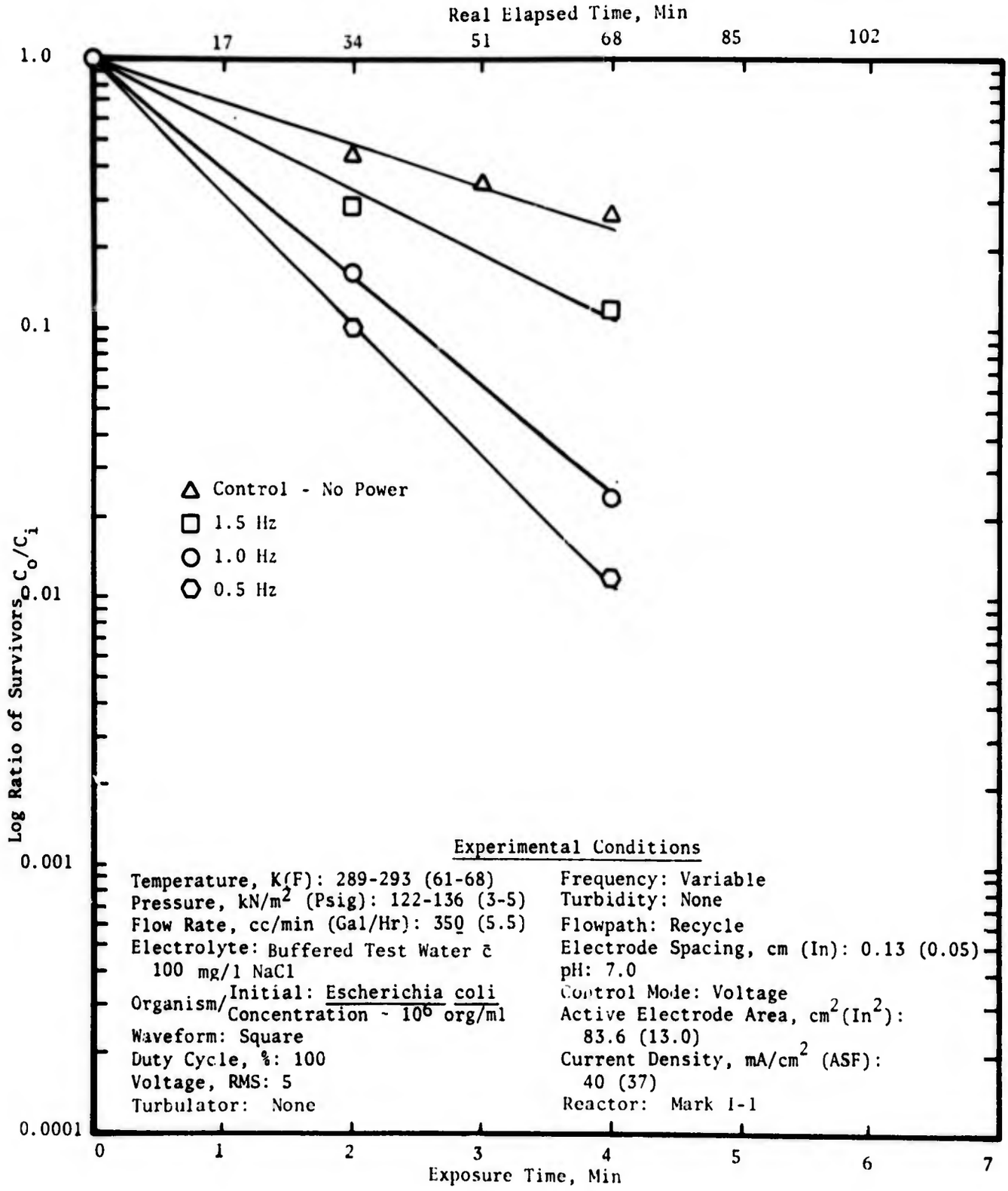


FIGURE 19 MICROORGANISM SURVIVAL VERSUS FREQUENCY

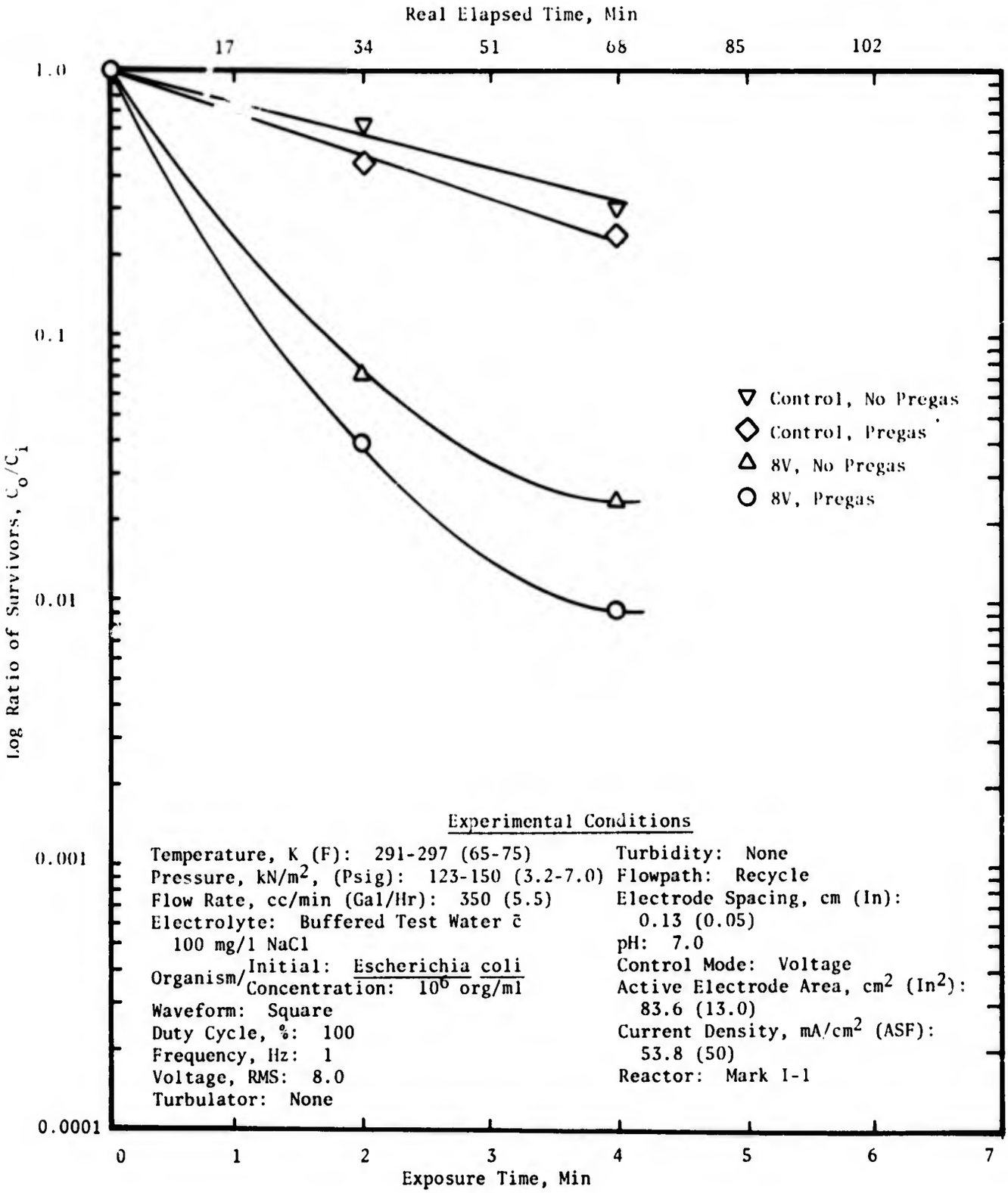


FIGURE 20 MICROORGANISM SURVIVAL VERSUS ELECTRODE PREGAS

Temperature. Escherichia coli kills observed when the Electrochemical Biocide Reactor was run with the process water at temperatures of 283 to 286K (50 to 55.4F), 293 to 296K (68 to 73.4F) and 314 to 317K (105.8 to 111.2F) are presented in Figure 21. The results show no appreciable difference in kill at 283 to 286K (50 to 55.4F) and 293 to 296K. (68 to 73.4F). A higher kill rate was observed at 314 to 317K (105.8 to 111.2F). However, the control experiment run at this temperature reveals that most of the increased kill could be attributed to the thermal effects rather than the electrochemical biocidal effects.

pH. Escherichia coli kills observed when the Electrochemical Biocide Reactor was run with the process water pH's of 5, 7 and 9 are illustrated in Figure 22. At a residence time of four minutes, the results of the power experiments showed no appreciable differences in final kill. The control experiment at pH 9 showed a much higher Escherichia coli kill rate. The smaller difference between the control and experimental results at pH 9 could in part be attributed to the unfavorable equilibrium of the biocidal HOCl species generated from the NaCl present in the electrolyte. At pH 9, the equilibrium for the reaction, $HOCl \; H^+ + OCl^-$, is far to the right. The OCl^- specie predominates at this pH and is thought to be a much poorer disinfecting agent compared to HOCl.[45,47]

Turbidity. The effect of turbidity on the survival rate of Escherichia coli with the experimental conditions are illustrated in Figure 23. The data showed that the microorganism kill rate is significantly affected by the turbidity. The reduction in microorgansim kill rate may be explained by: (a) the tendency of the turbidity to foul the electrodes, causing reduced kill, and (b) the protective shielding offered to the microorganisms by the suspended solids.

The turbidity experiments were conducted at a separate laboratory on a PA reactor series. The PA reactor series were parallel plate plug-flow reactors similar to the Mark I Reactor. These reactors use carbon electrodes which also form the reactor body (housing). The electrical connections were made directly to the electrodes. The two electrode plates support a spacer that separated the connected channels cut into the inner surface of the two carbon plates. The test water flowed through these channels. The design characteristics for the PA reactors are listed in Table 13. The overall reactor size was 3.81 cm (1.5 in) thick, 10.2 cm (4 in) wide and 57.2 cm (22.5 in) long. The reactors contain seven channels that provide a total channel length of 400.1 cm (157.5 in). Each channel was 57.2 cm (22.5 in) long and 0.8 cm (0.3 in) wide. The reactor housing was coated with epoxy to prevent leakage and reactor degradation.

Electrode Spacing. The effects of electrode spacing for the PA series of reactors are illustrated in Figure 24. The test conditions are also listed in the figure. In these experiments, the test water velocity through the reactors was held relatively constant. The highest kill rate was observed for the PA-I reactor which had the smallest electrode spacing (0.17 cm (0.7 in)). The smallest possible electrode spacing (at which arcing between electrodes does not occur) has not been determined. Process efficiency may well be increased by a narrower spacing than 0.17 cm (0.07 in). This will be studied in future testing.

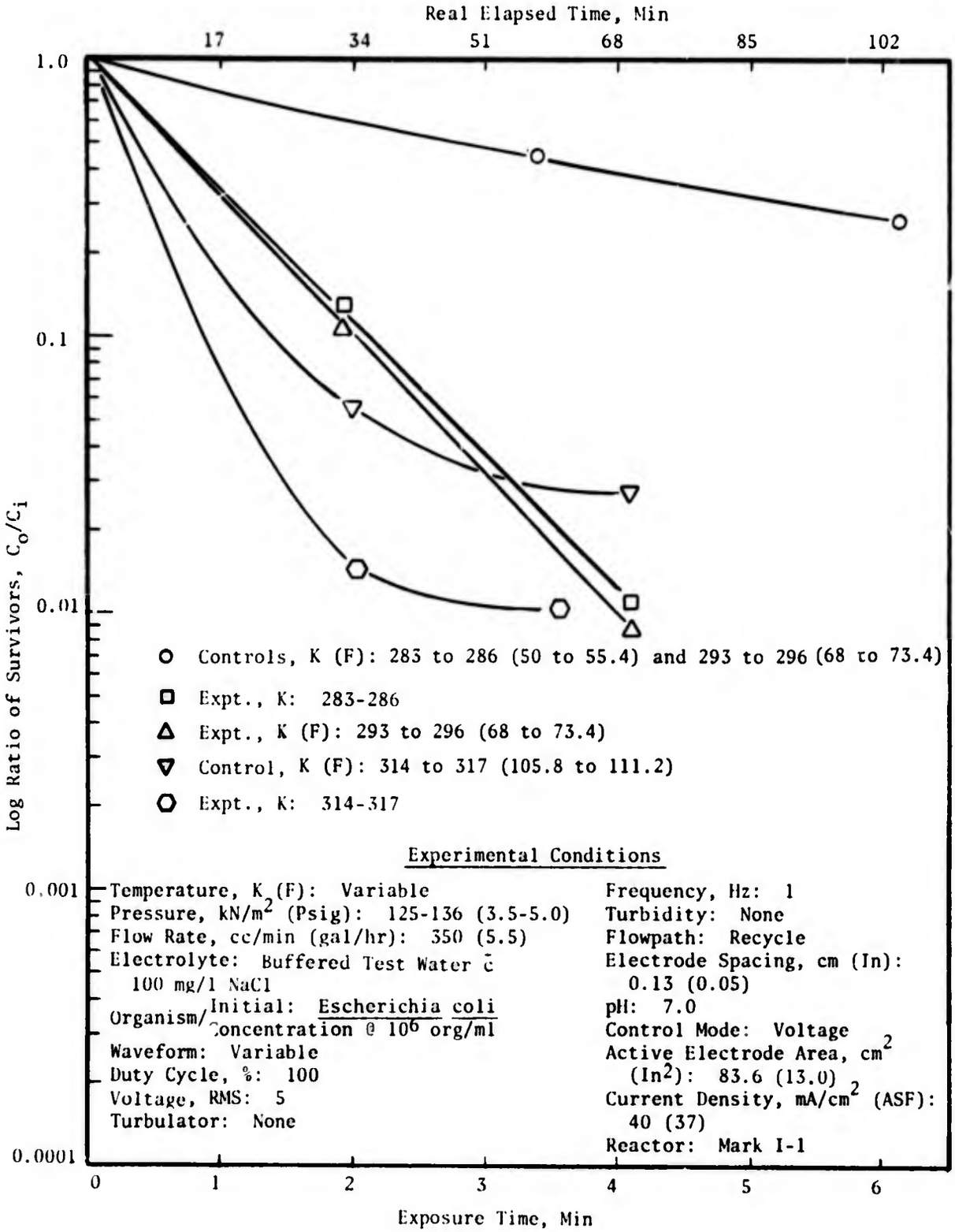


FIGURE 21 MICROORGANISM SURVIVAL VERSUS TEMPERATURE

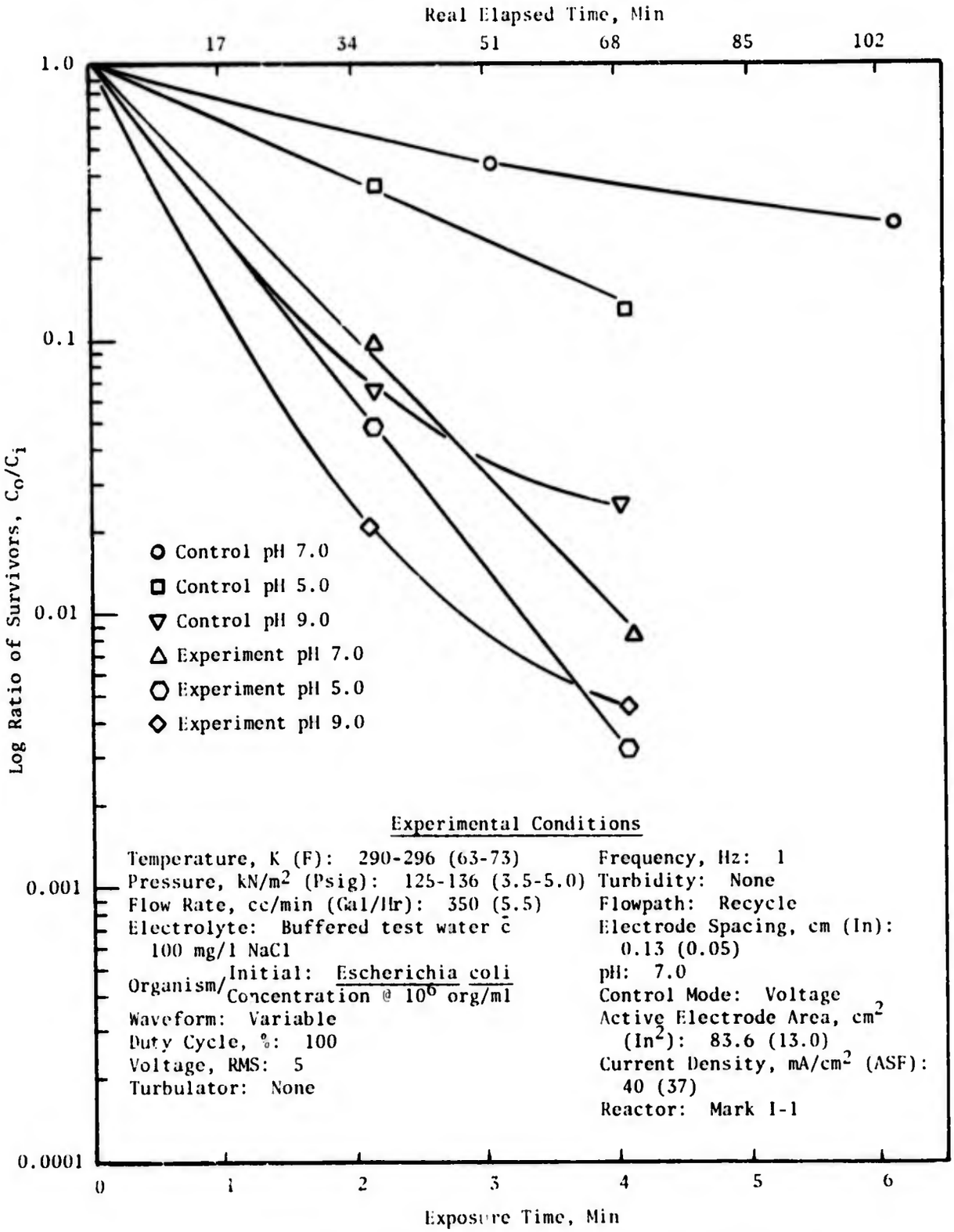


FIGURE 22 MICROORGANISM SURVIVAL VERSUS pH

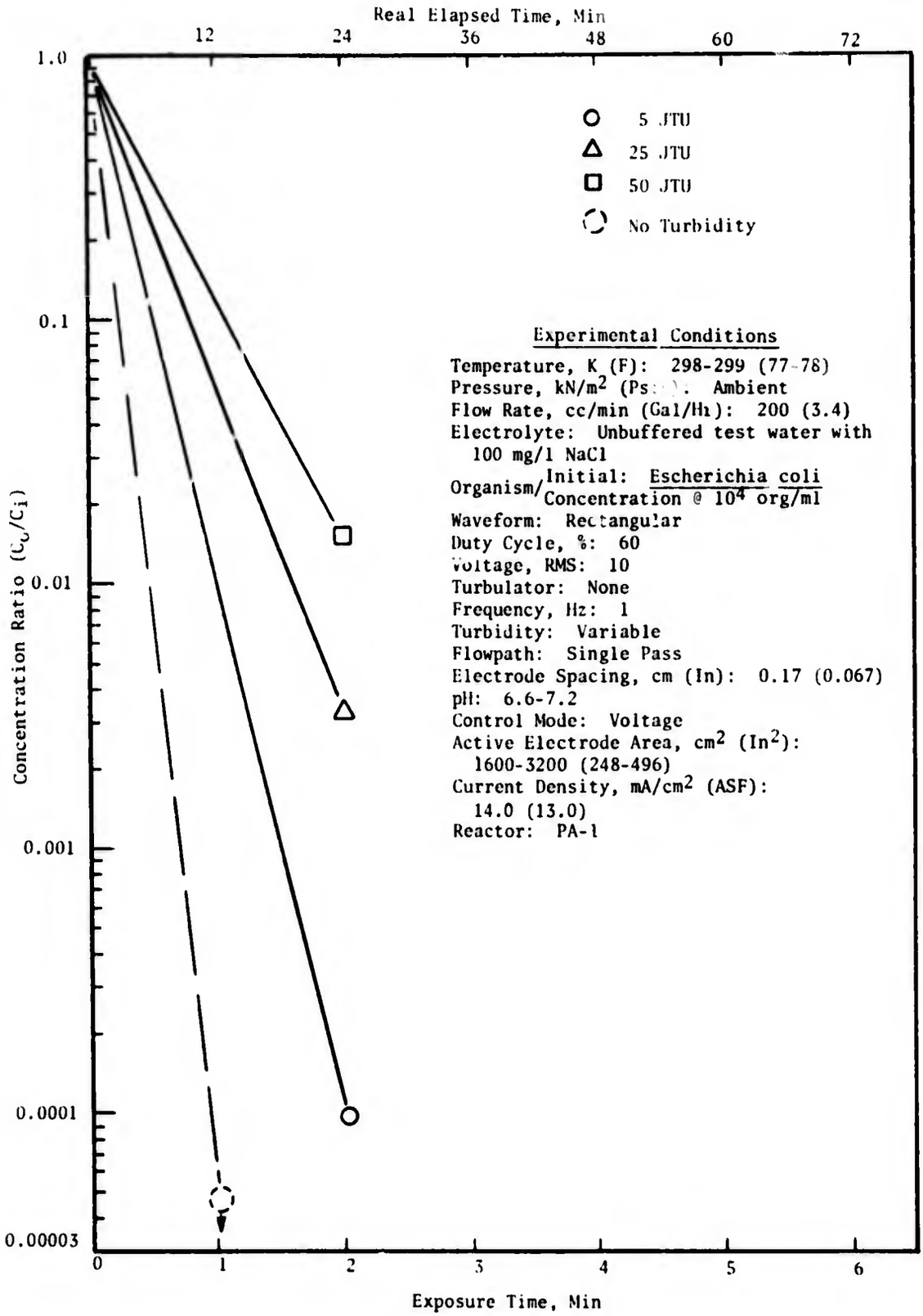


FIGURE 23 EFFECTS OF TURBIDITY ON MICROORGANISM KILL

TABLE 13 PA REACTOR SERIES DESIGN CHARACTERISTICS

	1974 Reactor Plug Flow		
	PA-1	PA-2	PA-3
Volume, cm^3	53.8	98.1	161.3
Active Electrode Area, cm^2	400	400	400
Electrode Spacing, cm	0.17	0.31	0.51
Overal Dimensions, cm	15 x 61	15 x 61	15 x 61

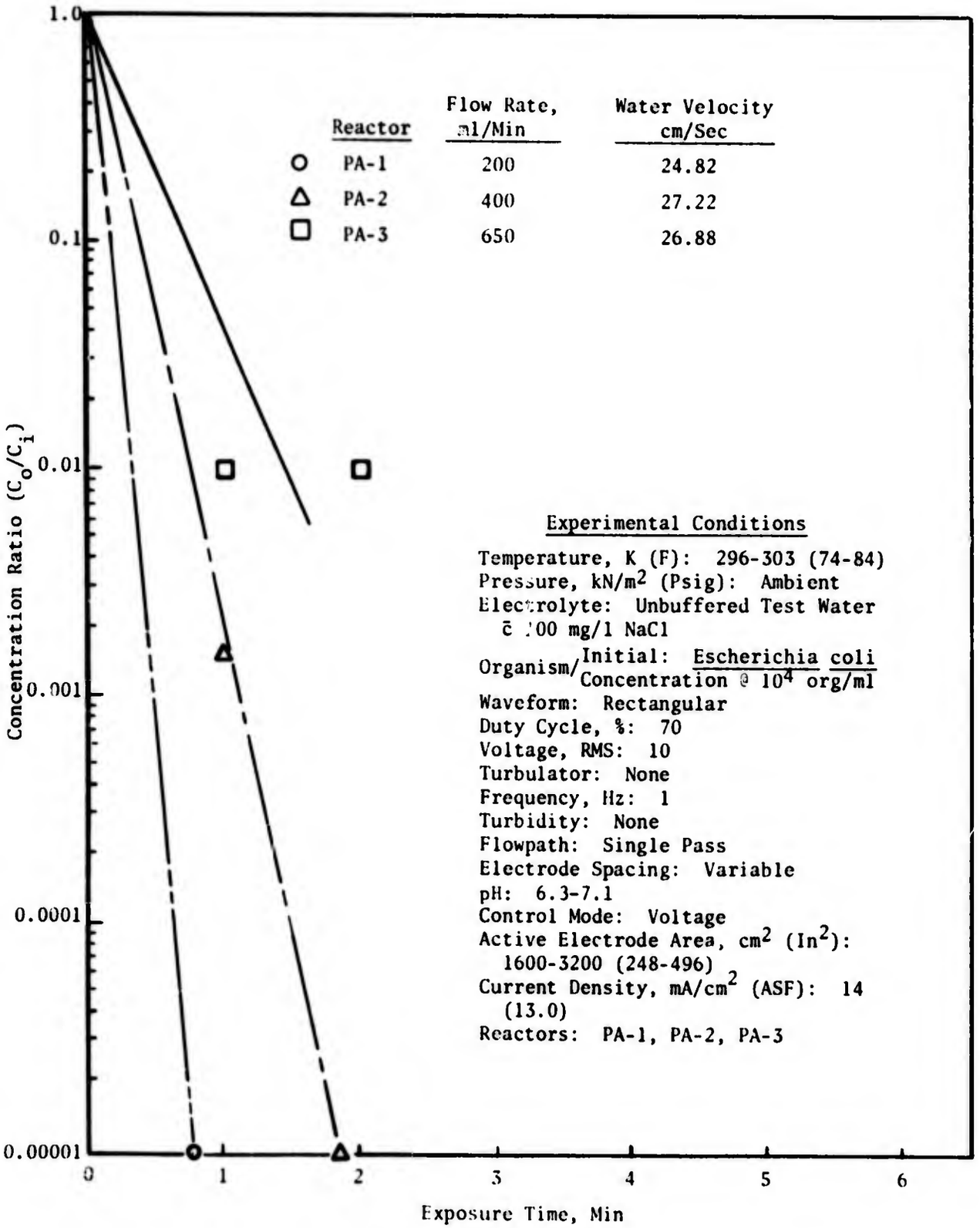


FIGURE 24 EFFECT OF ELECTRODE SPACING ON MICROORGANISM KILL

For test water flow conditions which do not change along the axis of flow, the mass transfer is a function of fluid velocity. However, due to entrance effects, a boundary layer forms on the surface of the electrodes at the entrance. The buildup of boundary layer was depicted in Figure 4. According to Equation 1, the entrance length of the three reactors, PA-I, PA-2 and PA-3, will be in the ratios of 1:4:9. In the boundary layer, mass transfer is slower and results in the lowest kill rate in the PA-3 reactor. The data presented in Figure 24, therefore, suggests that mass transfer is a key parameter in the Electrochemical Biocide process.

Process Water Flow Rate. The effects of test water flow rate are presented in Figure 25. The results with the Mark I-1 show that as the test water flow rate decreased, the microorganism kill increased for a given exposure time. A flow rate of 100 ml/min (1.6 gal/hr) gave the highest microorganism kill per unit exposure time. The experimental controls showed an increased microorganism background kill with increased test water flow rate.

The results are contrary to those shown above in Figure 24. These results may have been caused by the leaching of the test water stored in the titanium current collector back cavity. Higher leaching rates would be expected at increased test water flow rates due to the greater suction effect created and may be responsible for the different shapes of the flow rate curves. This leaching phenomenon may explain the survival ratio fluctuations that were observed in two experiments when the Escherichia coli concentration had been reduced to around 10^3 to 10^4 organisms/ml. Figure 26 illustrates this phenomenon. In fact, an increase in microorganism count was observed. Leaching of a ml of 10^6 organism/ml of original test water from the back cavity into the processed test water could explain this increase.

Another possibility for the decreasing kill rate at higher flow rates is that the organisms see higher complete electrical cycles.

Effects of Sodium Chloride. The review of prior effort results indicate that the Electrochemical Biocide process was not very effective without the presence of NaCl in the process stream.[48] It was, therefore, inferred that the presence of NaCl was necessary to enhance the microorganism kill and make the process effective and competitive with the more common disinfecting agents, namely chlorine, ozone, etc.

Under the current research program, however, the process has been shown to be effective without the presence of NaCl. Therefore, a chlorine-based biocidal specie probably is not responsible for microorganism destruction.

The differences in the prior efforts and current program results can be attributed to internal reactor gassing which is believed to mask the kinetics. It has been observed with the Mark I Reactor experiments that any slight amount of gassing affects the microorganism destruction process. It was also observed that gassing was dependent on the water conductivity and occurred at a much lower operating current when the test water did not contain NaCl. The lower kills reported in the prior efforts with the unbuffered test water were possibly due to the evolution and trapping of gas in the reactors. These experiments were conducted with and

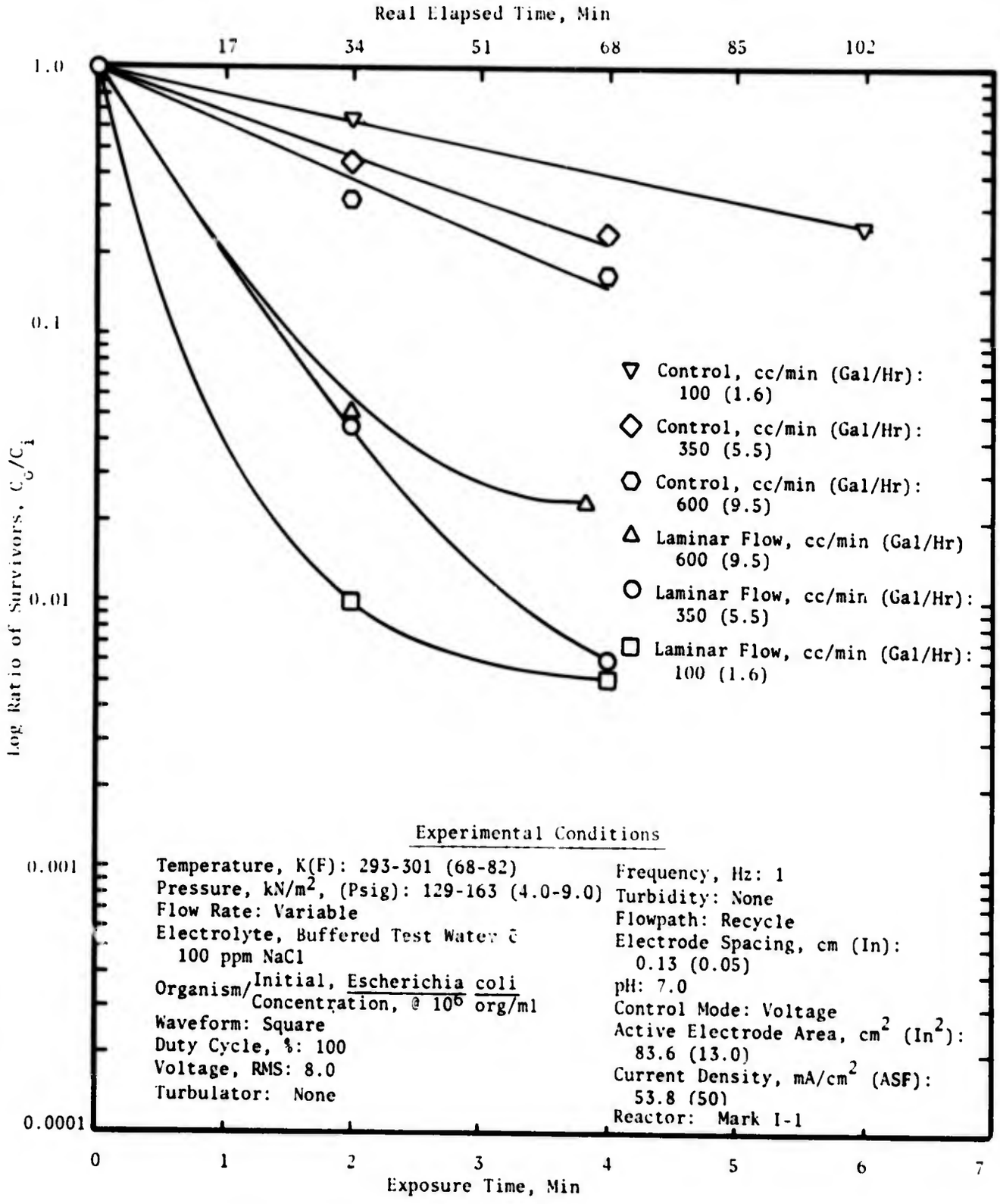


FIGURE 25 MICROORGANISM SURVIVAL VERSUS FLOW RATE

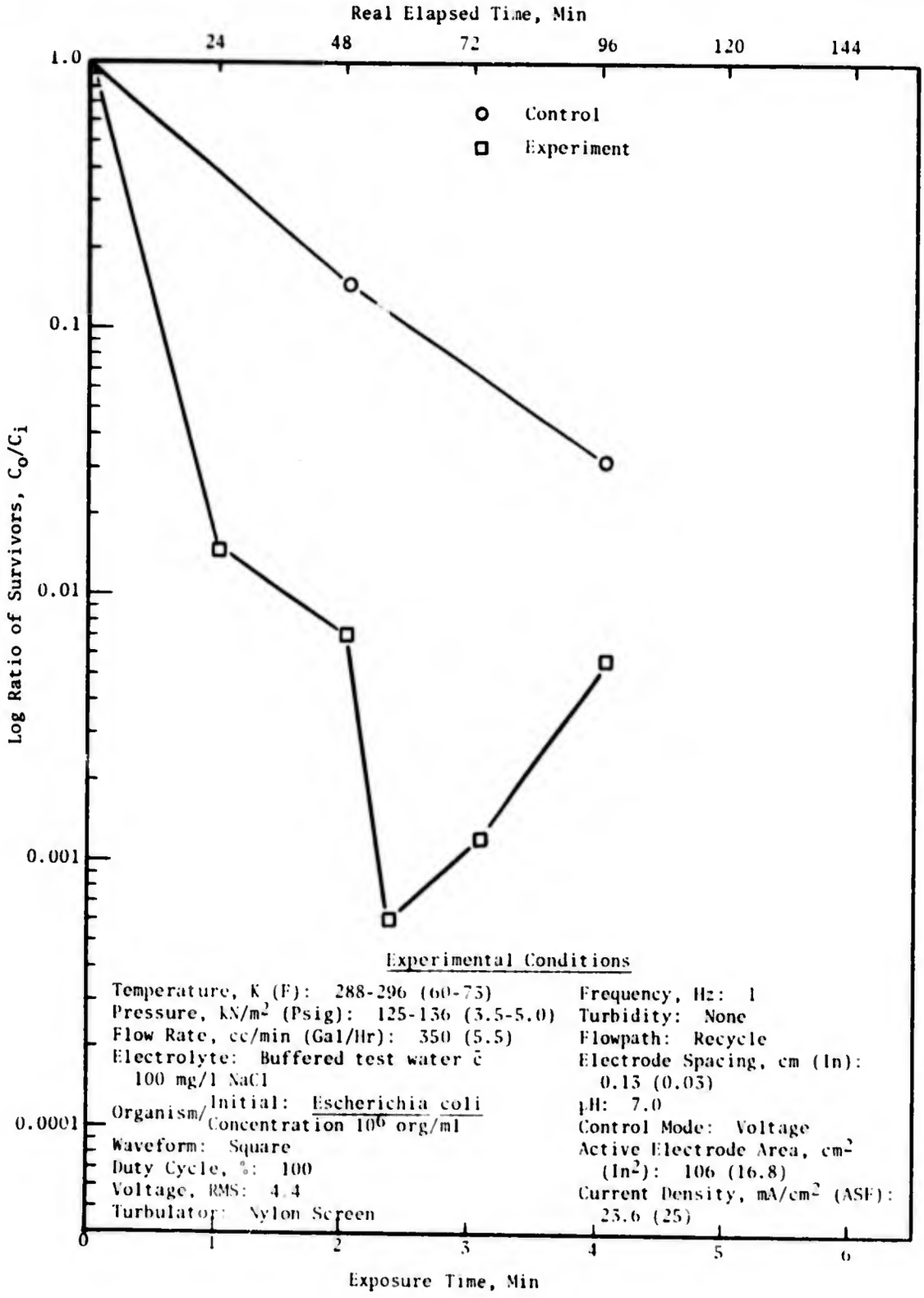


FIGURE 26 RANDOM FLUCTUATION OF ORGANISM COUNT

without NaCl at a constant current density. Gassing was not visible due to the opaque nature of the reactor housing. Experiments conducted with the transparent Mark I Reactor indicated that gassing did occur at similar process conditions.

The effects of varying NaCl concentration in the buffered test water with the modified Mark I-1 Reactor are shown in Figure 27. No appreciable difference was detected between the power experiments with 100 and 500 mg/l NaCl. No controls were run for these experiments. At 500 mg/l NaCl, the cell voltage required to produce a current density of 23.6 mA/cm^2 was 3.65V. This was very close to the reversible voltage (2.15V) required for Cl_2 generation. Hence, significantly higher Cl_2 generation was not expected at the 500 mg/l NaCl level.

Two additional experiments run with NaCl in the buffered and unbuffered unbuffered test waters are presented in Figures 28 and 29. Figure 28 represents an experiment run with the low conductivity unbuffered test water containing 100 mg/l NaCl. Figure 28 is an experiment conducted with the high conductivity buffered test water containing 500 mg/l NaCl.

In Figures 28 and 29, the slope of the lines between initial sample and the first assayed sample are of primary interest. The comparison of the data beyond these sample times is complicated by gassing at the electrodes in the two experiments. It is interesting to note that the slope of the low conductivity unbuffered test water was steeper than that of the high conductivity buffered test water. This is further supportive evidence that microorganism kill is not principally due to the generation of biocidal chlorine species.

In Figure 30, the survival data, minus controls are plotted for the Mark I-1 and Mark I-2 Reactors with and without 100 mg/l NaCl in the buffered and unbuffered test waters. These curves were synthesized from the results illustrated in Figures 27 and 28.

The results indicate that at the same current density, the higher conductivity buffered test water was less favorable for organism destruction or adsorption than the lower conductivity unbuffered test water run. This may be due to the (a) greater microorganism protective characteristics of the more numerous ionic species in the higher conductivity buffered test water, (b) nitrate present in the low conductivity test water responsible for generating bactericidal species, and (c) charge concentration through the organism in the low conductivity test water.

Spot tests for the presence of hydrogen peroxide, possibly generated during the power experiments, were negative. Spot tests were carried out with process water sampled at two- and six-minute exposure times.

Turbulence. Increased turbulence due to (a) decreased electrode spacing, (b) increased flow rate, and (c) introduction of a nylon screen turbulator results in a decreased laminar layer across which the mass transfer of the organism must occur to reach the active electrode surface. This results in a higher diffusion rate or driving force for mass transfer of the organisms to the electrode surface and, consequently, a higher organism kill rate.

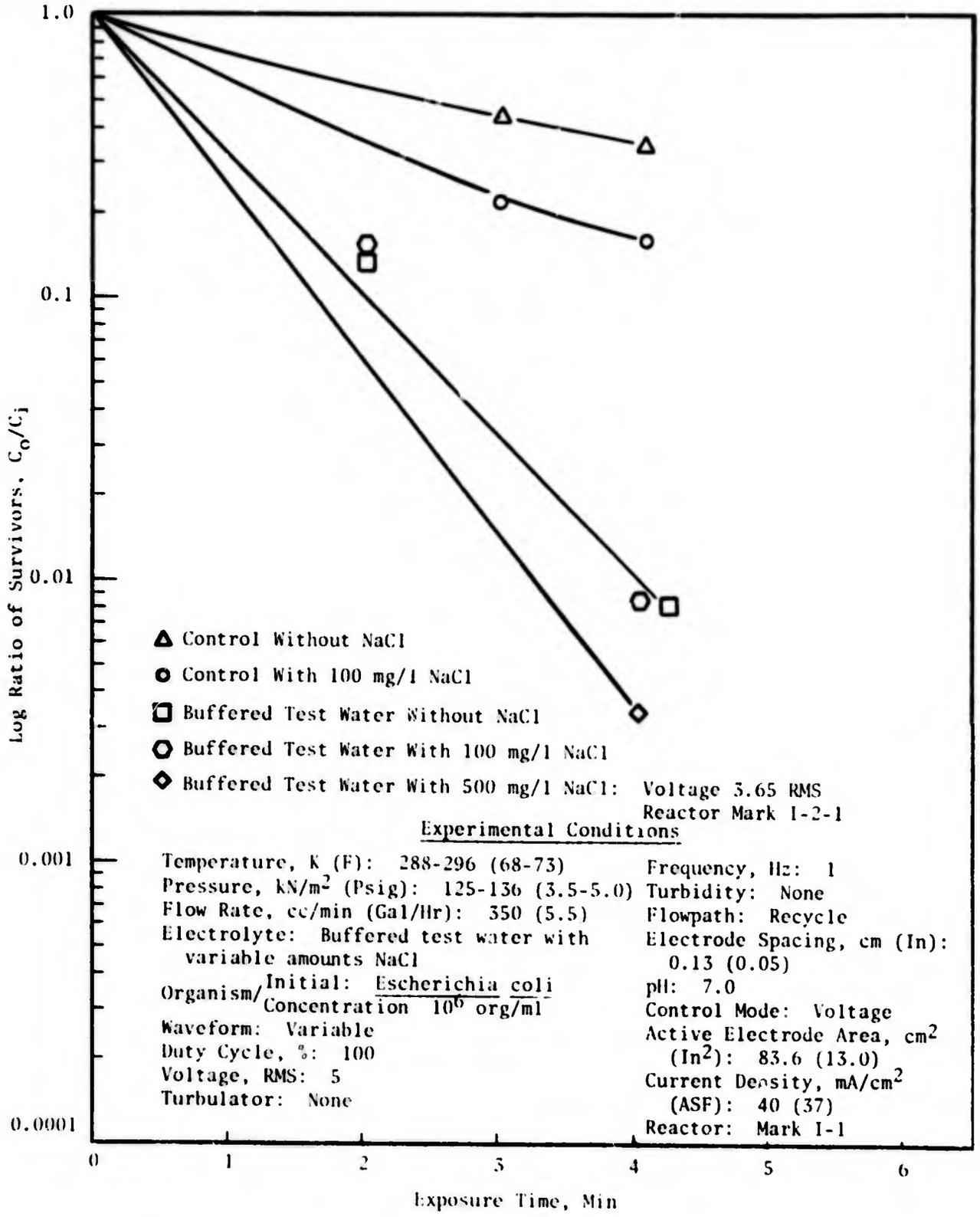


FIGURE 27 MICROORGANISM SURVIVAL VERSUS SODIUM CHLORIDE CONTENT

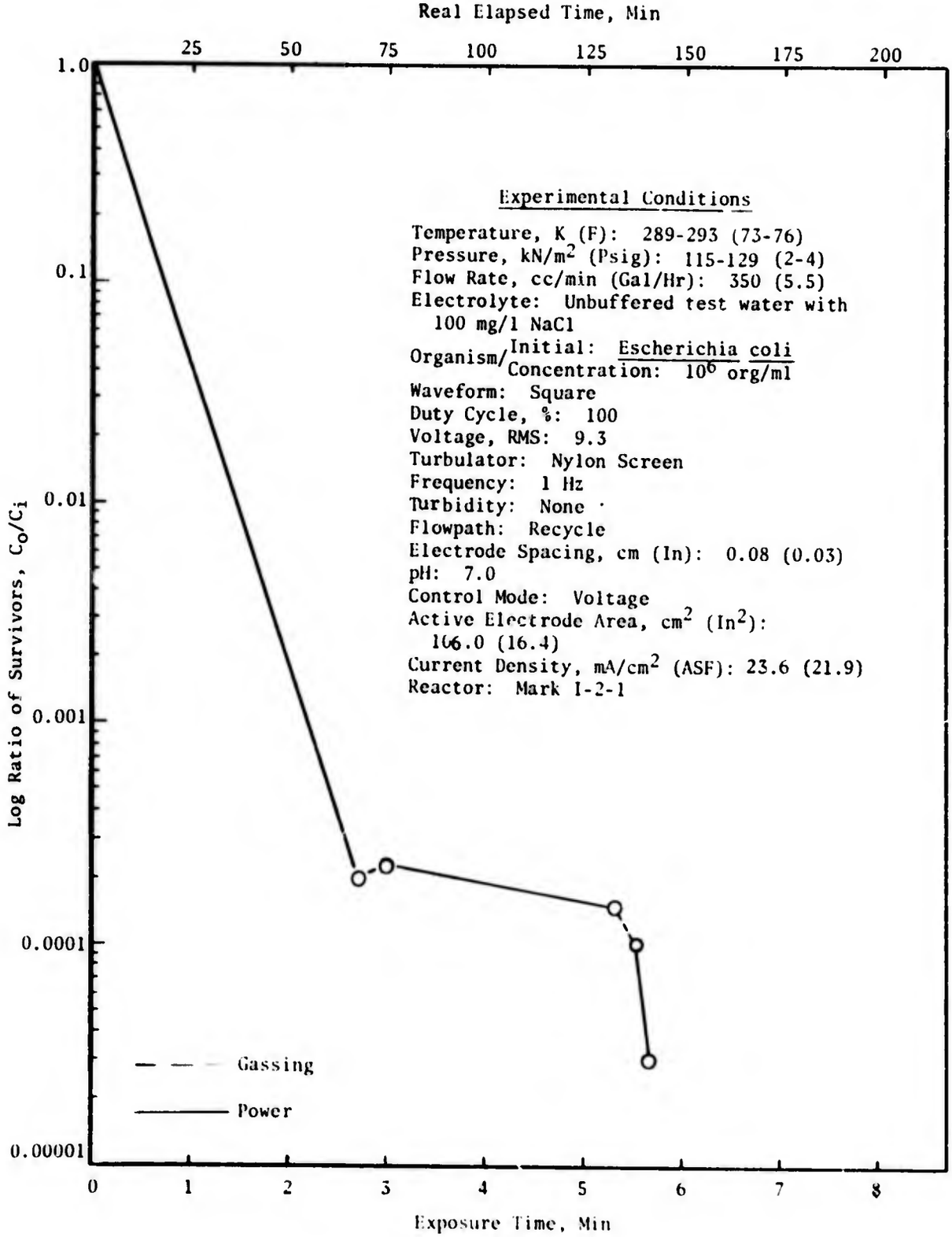


FIGURE 28 UNBUFFERED TEST WATER WITH 100 mg/l NaCl

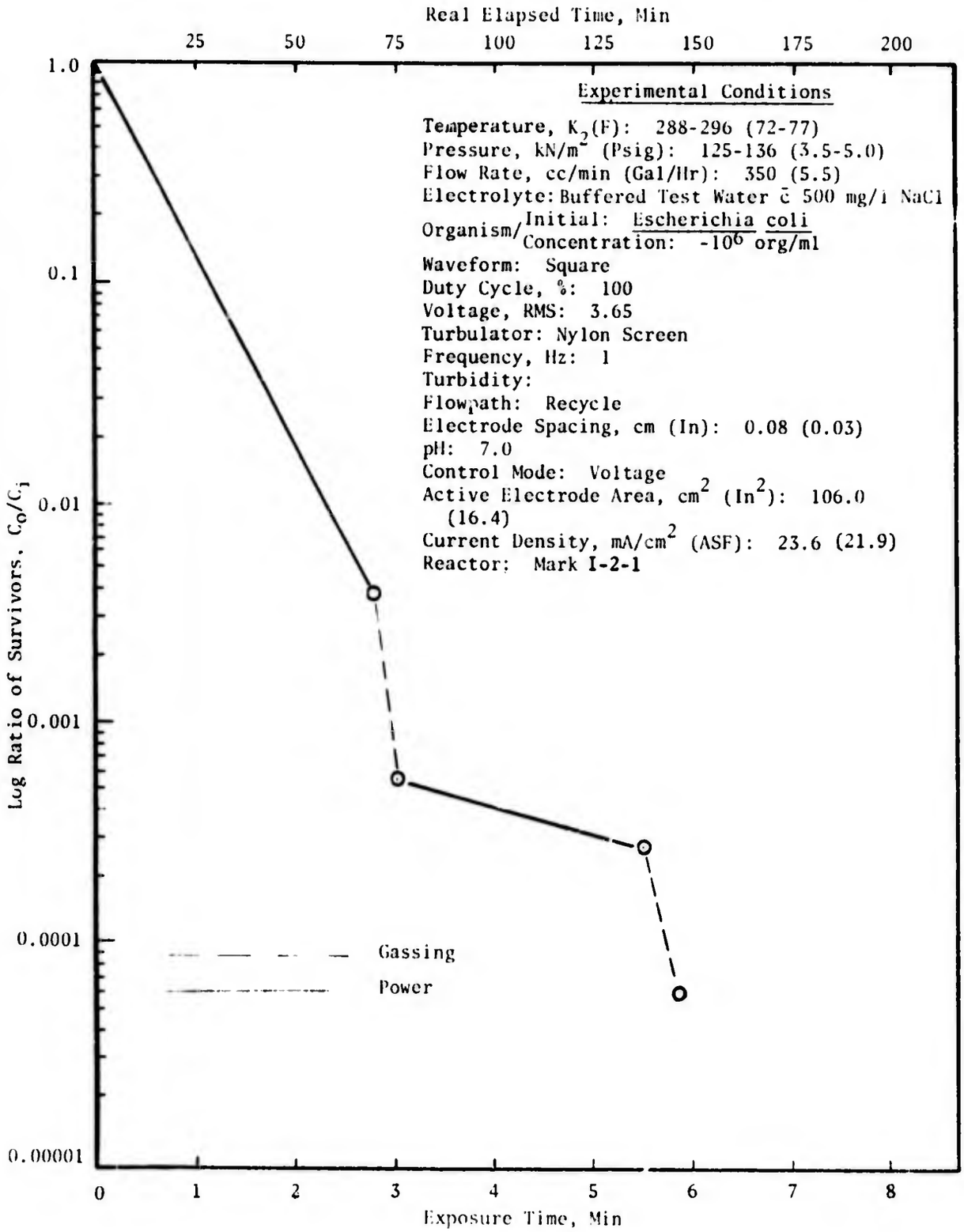


FIGURE 29 BUFFERED TEST WATER WITH 500 mg/1 NaCl

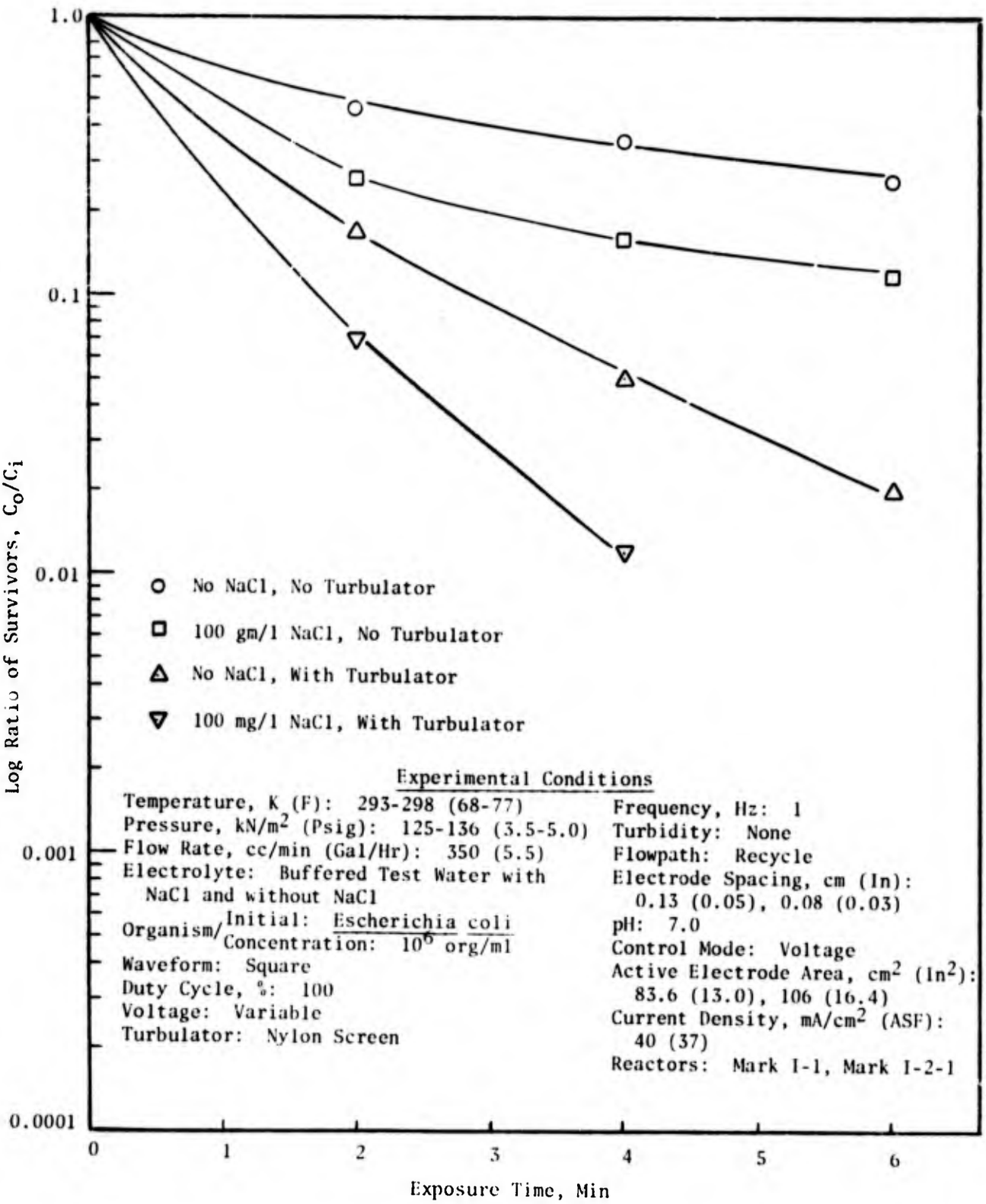


FIGURE 30 MARK-I SURVIVAL DATA MINUS CONTROLS

Figure 31 illustrates the effect of turbulence promotors on mass transfer in electrochemical reactors.[49] The introduction of more efficient turbulence promotors results in increased mass transfer of the undesirable specie to the electrode surface and, therefore, a more rapid decline of its concentration results. Figure 30 presented data on power experiments (corrected for control decrease in organism number) with and without turbulators. The no-turbulator experiments were run with the Mark I-1 Plug-Flow Reactor. The turbulator experiments were run in the Mark I-2-1 Plug-Flow Reactor. The Mark I-2-1 Reactor had a slightly smaller electrode spacing. The addition of a turbulator, coupled with closer spacing of electrodes, resulted in the most significant increase in kill, again supporting this mass transfer limitation concept.

Single-Pass Exposure Time. The testing program was not designed to determine whether microorganisms must be exposed to at least one complete electrical cycle during a single pass through the reactor. In future experimentation this question could be answered by exceeding the upper flow rate of the normal process feed flow range (100 to 700 ml/min).

Microorganisms Experimental Results. In a series of experiments conducted in a separate laboratory, little or no kill was reported when the Mark I-2-2 Reactor was used with the unbuffered test water.[48] An explanation for this phenomenon follows.

The unbuffered test water has a very low conductivity (120 μmho/cm) and, therefore, high voltages (12 to 19V) are needed to result in current densities of 10 to 20 mA/cm^2. At these high voltages gassing occurs rather vigorously. The gas bubbles have a tendency to get trapped in the turbulator screen, thereby increasing the reactor resistance and subsequently lowering the reactor current.

In experiments conducted in the separate laboratory, the reactor voltage was increased to compensate for this current drop. This led to increased gassing and a fall in current from the last set point. The above cycle was repeated until a stable current density between 10 to 20 mA/cm^2 was established. It is believed that the poor kill resulting in the above experiments was caused primarily by this excessive gassing and bubble formation. The rapid evolution of the bubbles at the electrode surface and their trapping in the turbulator screen would seriously limit mass-transfer of the organisms to the electrode surface.

References in literature illustrate the preferential migration of free-swimming bacteria to the gas/liquid interface in bubbles and show that it is a mechanism for releasing bacterial aerosols into the air as the bubbles break at the water surface.[50] Gas buildup in the electrochemical reactor appears to be a highly undesirable phenomenon since it hinders the transfer of microorganisms to the electrode surface and thereby results in poor microorganism kill.

The microorganism experiments were conducted in an open-loop recycle mode configuration. This eliminated the problems associated with gas bubble buildup in the reactor. The test water was held in an open reservoir and recycled through the reactor to obtain the necessary exposure time.

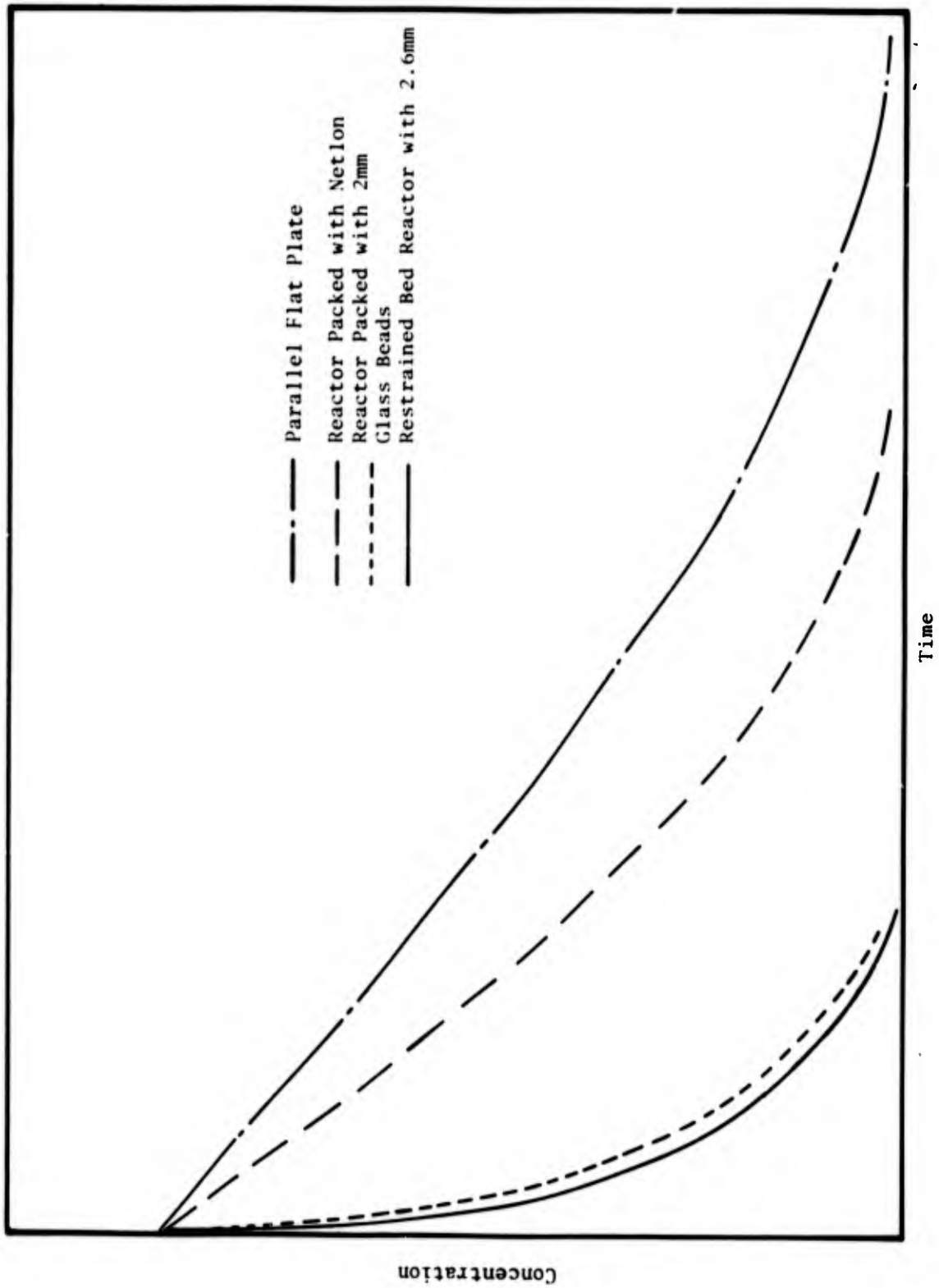


FIGURE 31 MASS TRANSPORT IN AN ELECTROCHEMICAL REACTOR

The open-loop operating mode resulted in four- to five-log order kills. The Mark I-2-2 Plug-Flow Reactor was used exclusively for these microorganism experiments. The current collector cavity in the modified reactor was sealed with Viton A flat gaskets and the manifolds sealed with RTV to prevent flow short circuiting of the test water in the reactor.

Bacteria and Yeast Experiments. The survival ratios of Escherichia coli based on initial concentration of the microorganism are plotted in Figure 32. The results of these experiments indicate a three-log cycle decrease in the above ratio for the power experiment when the control experiment decrease is subtracted.

In Figure 33, the survival ratio for Pseudomonas aeruginosa is plotted as a function of exposure time. Approximately a five-log cycle reduction in the survival ratio was obtained for a four-minute exposure period. A three-log cycle reduction in the survival ratio was recorded for the control. The rather high reduction in viable organisms in the control of this experiment may indicate that these organisms are more susceptible to the effects of the gear pump or passive adsorption on the carbon electrodes.

The results for Klebsiella pneumoniae assayed with two different media are presented in Figure 34. Both assays (on the same experiment) indicate a four-log cycle decrease below the control levels.

Principally, because of its much slower growth, Saccharomyces cerevisiae was tested at an initial concentration of 2×10^5 organisms/ml. No additional experiments were run at higher initial organism concentrations. The results of this experiment are plotted in Figure 35 and show a two-log cycle reduction in the power experiment after the kill shown in the control experiment is deducted.

Raw Settled Sewage Experiment. The total coliform survival ratios in raw settled sewage feed experiments are plotted in Figure 36. Over a four-log cycle reduction in the ratio occurs within a two-minute exposure time for an initial mixed coliform concentration of 5×10^6 organisms/ml. The Total Organic Carbon (TOC) content of the raw settled sewage was 27 mg/l. A slight increase in the TOC was noticed in the treated sewage. This increase could be due to the carbon from the carbon electrodes or leaching of organics adsorbed on wetted component surfaces. The TOC of the treated effluent in the no-power experiment was found to be 11 mg/l and the turbidity of the settled raw sewage decreased from 22.5 NTU to 2 NTU. It, therefore, appears that organics and possibly microorganisms have a tendency to be adsorbed on the passive electrode surfaces. Apparently during the power run these are not retained on the electrode surface. The specific power requirements for this raw settled sewage experiment were 21W-hr/gal/log organism reduction.

Virus Experiments. The results of testing Polio virus Type I are plotted in Figure 37. The reduction in the number of virions for the two trial runs represent approximately a two-log cycle reduction in the number of viral particles.

Coxsacki B survival ratios are presented in Figure 38. After four minutes of exposure time there was a two and one-half-log cycle reduction in number of virions compared to the shelf control.

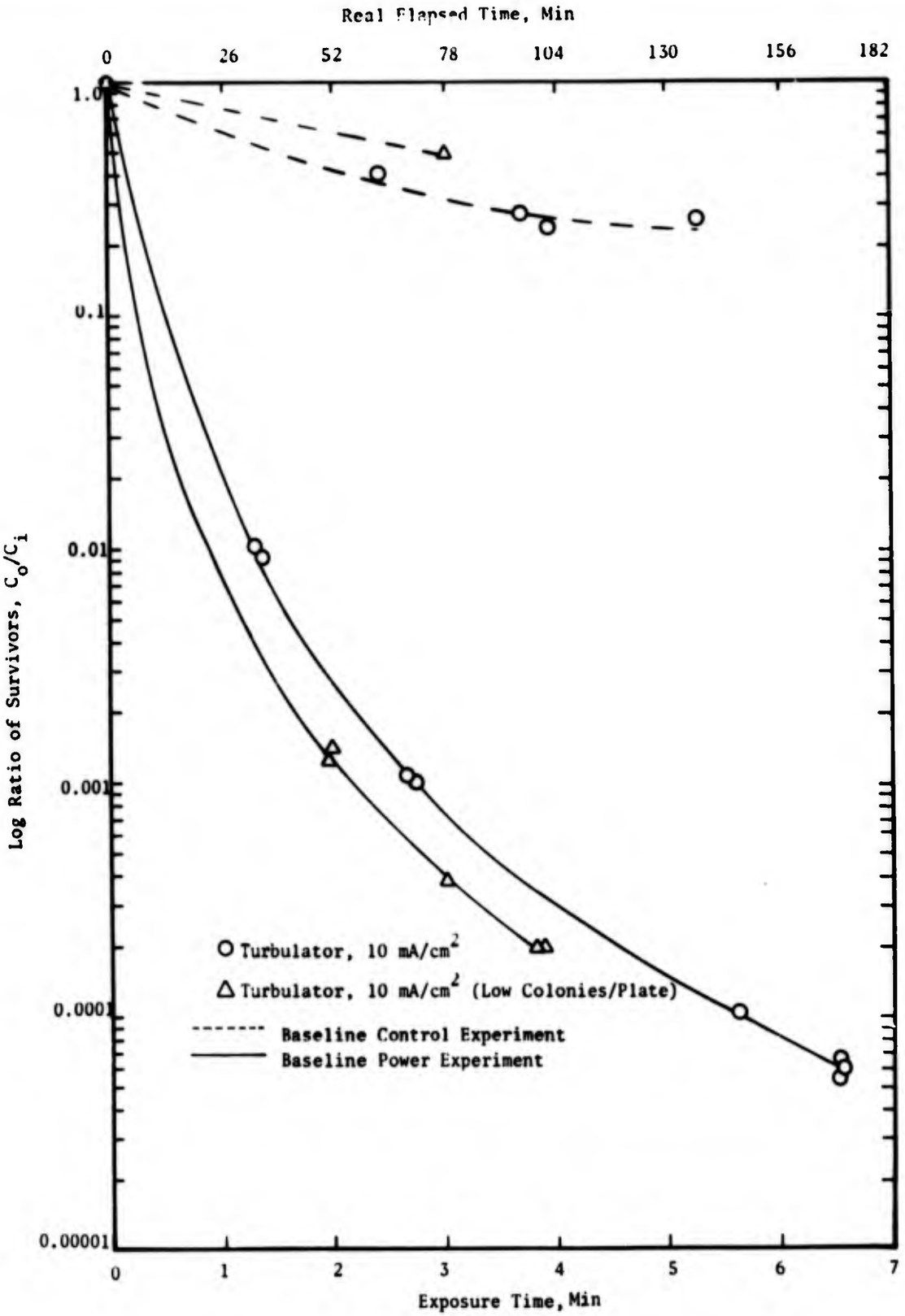


FIGURE 32 ESCHERICHIA COLI SURVIVAL RATIOS AT BASELINE CONDITIONS

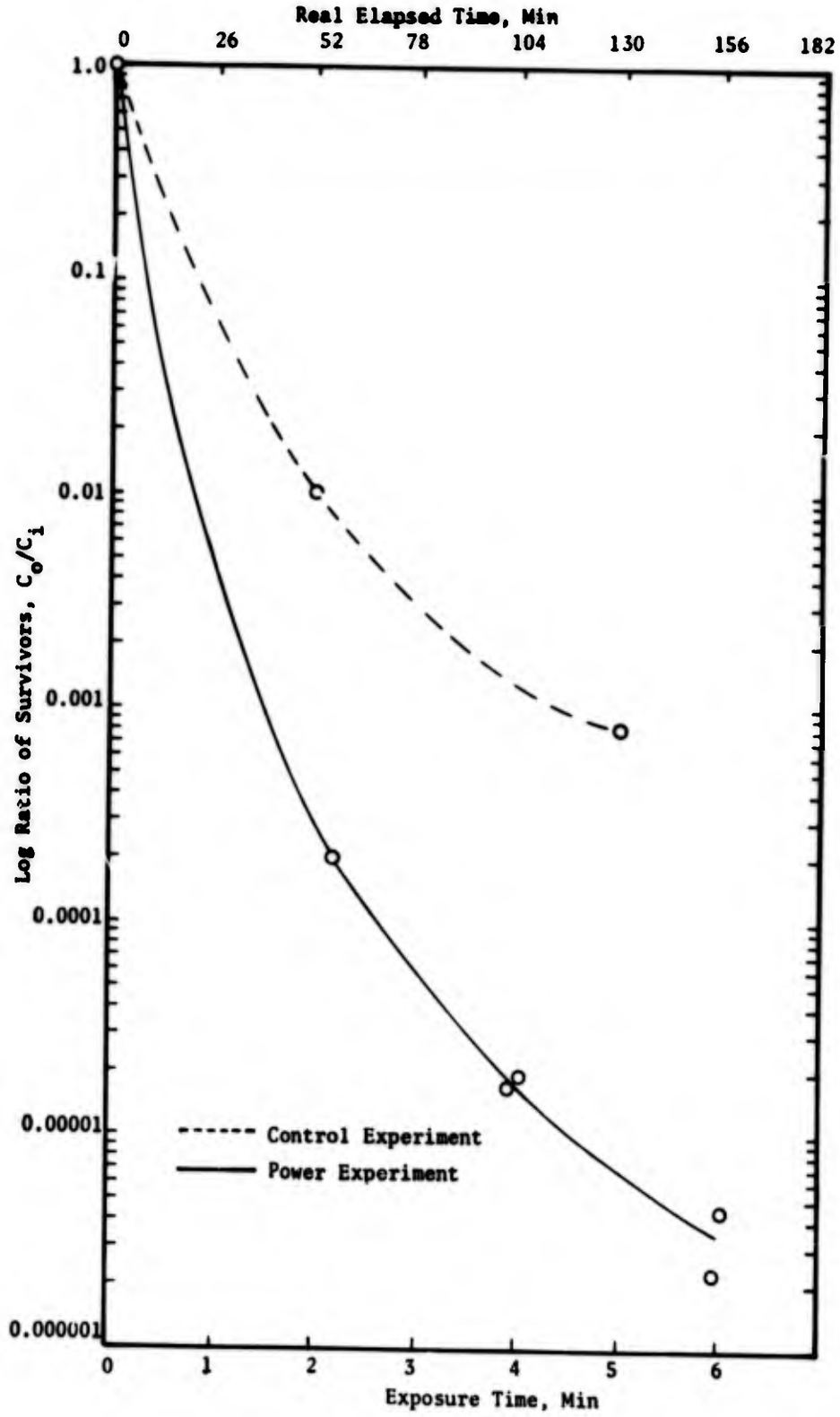


FIGURE 33 PSEUDOMONAS AERUGINOSA SURVIVAL RATIOS AT BASELINE CONDITIONS

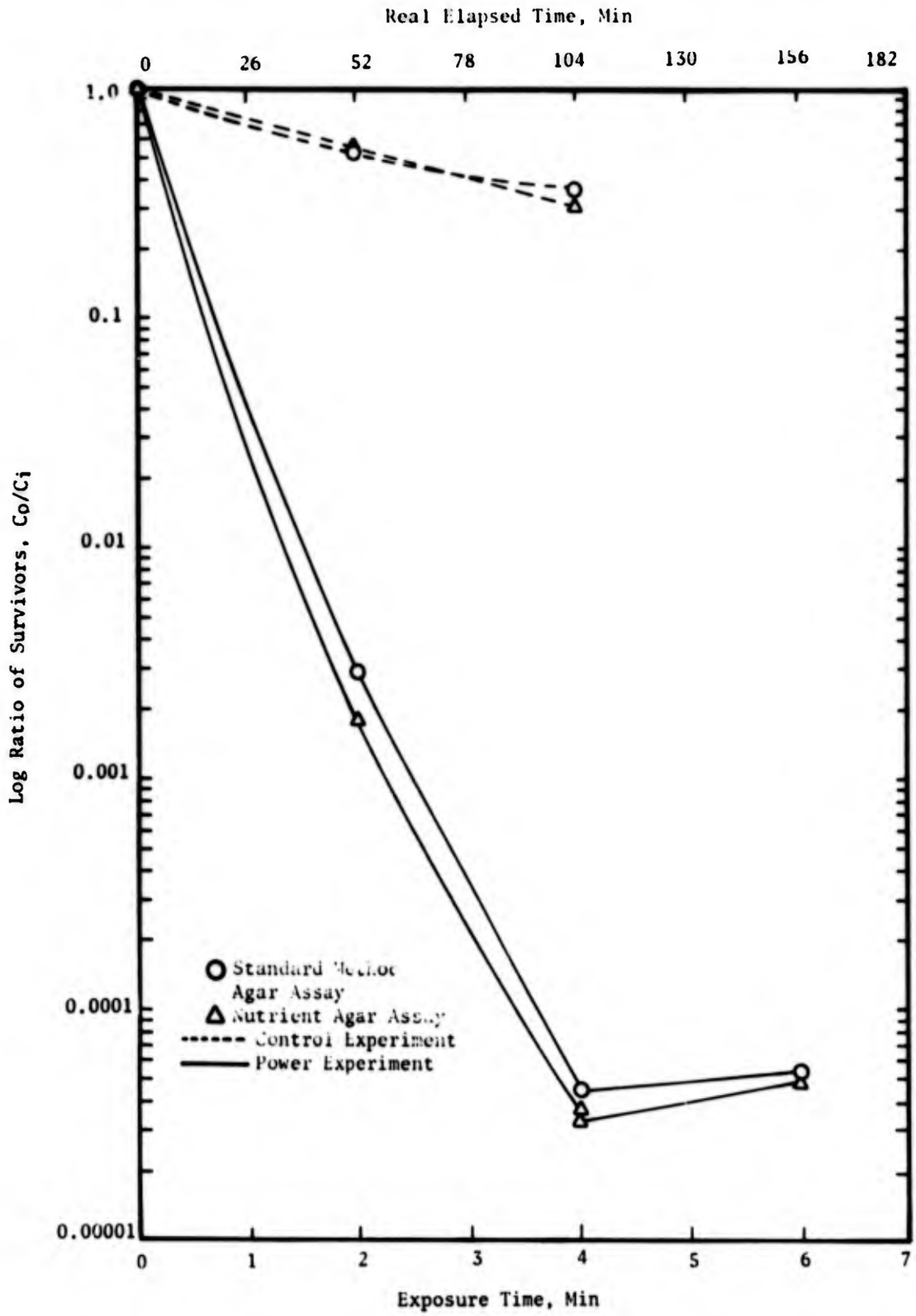


FIGURE 34 KLEBSIELLA PNEUMONIAE SURVIVAL RATIOS AT BASELINE CONDITIONS

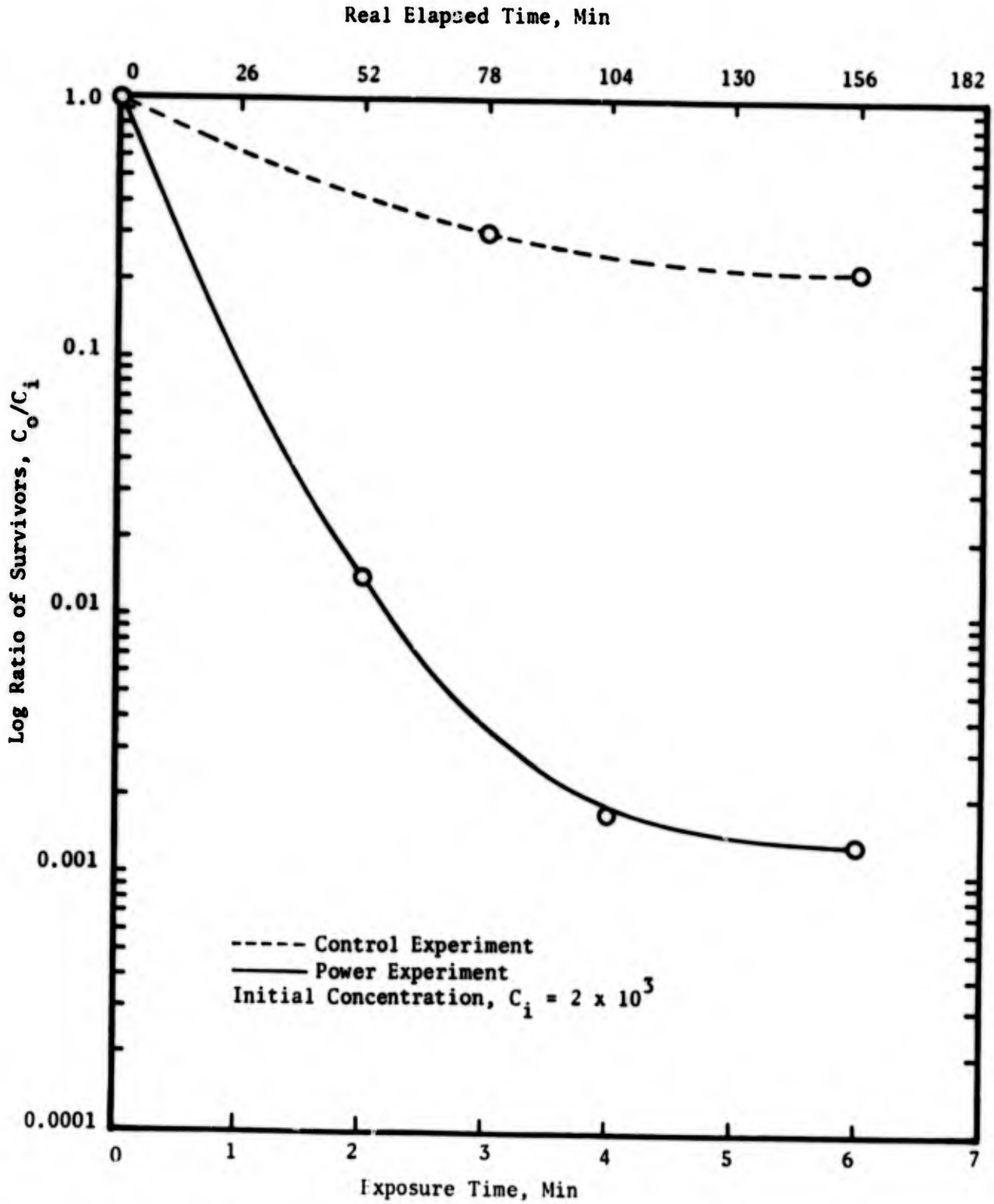


FIGURE 35 SACCHAROMYCES CEREVISIAE SURVIVAL RATIOS AT BASELINE CONDITIONS

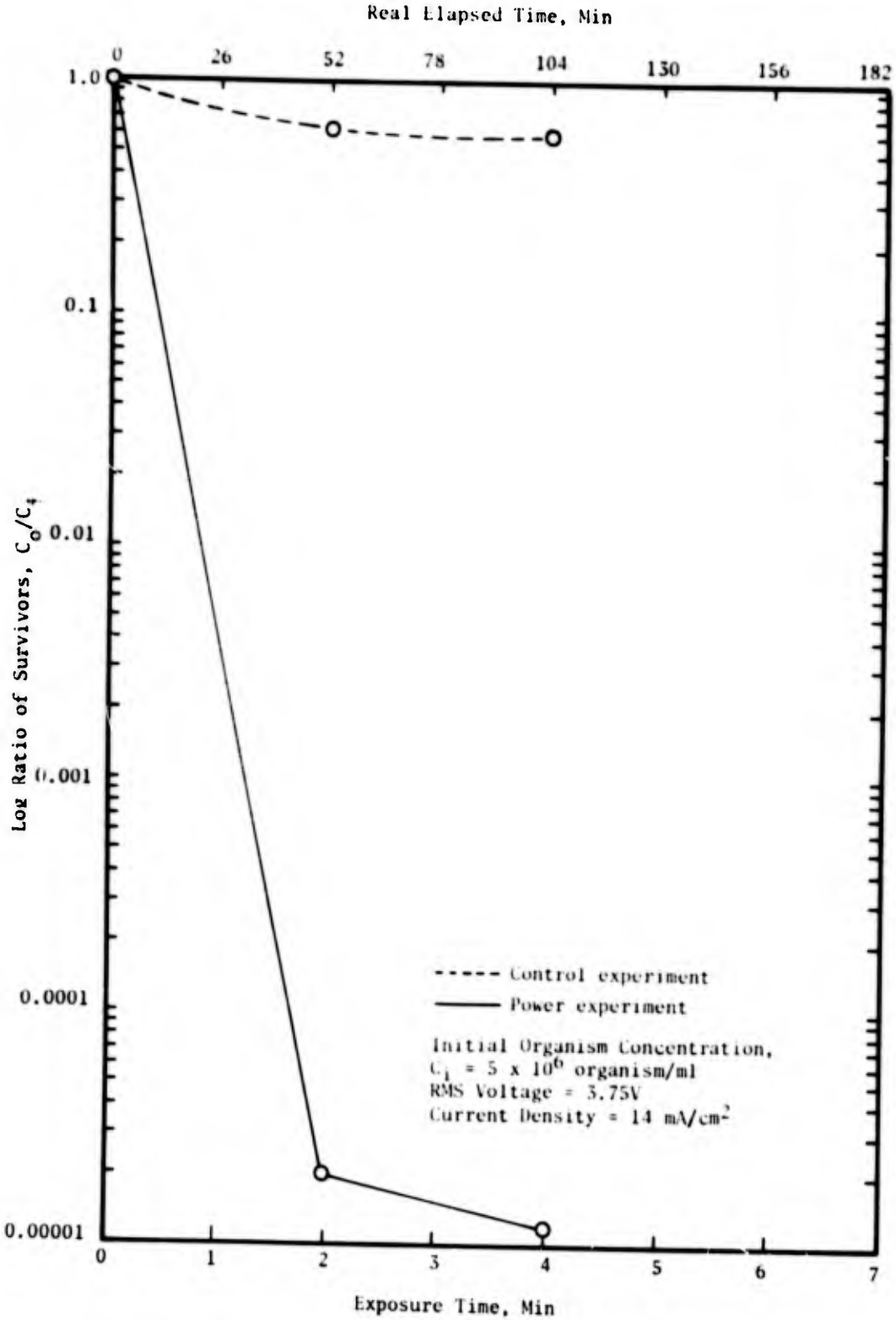


FIGURE 36 TOTAL ORGANISM SURVIVAL RATIOS IN RAW SETTLED SEWAGE AT BASELINE CONDITIONS

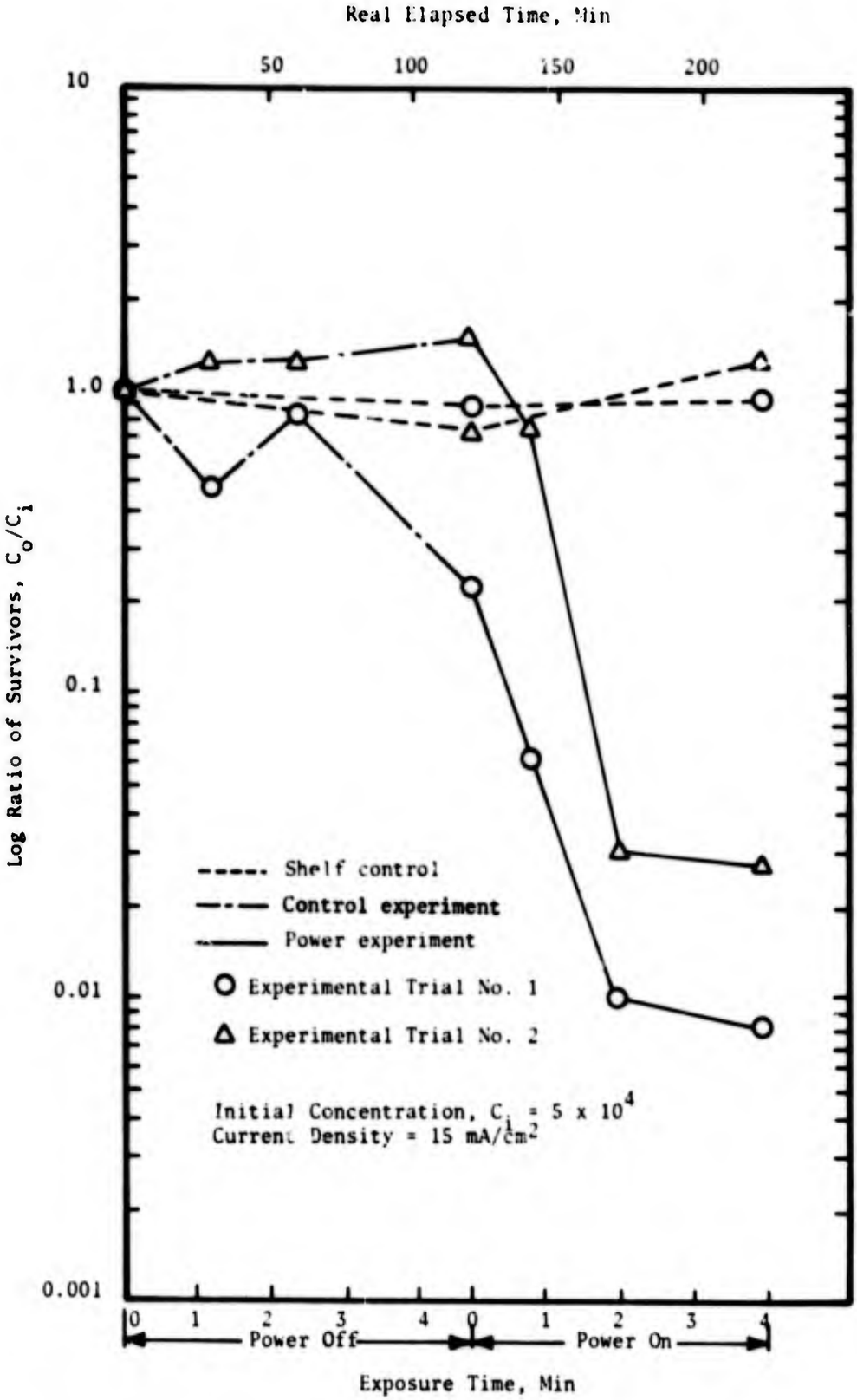


FIGURE 37 POLIO VIRUS TYPE I SURVIVAL RATIOS AT BASELINE CONDITIONS

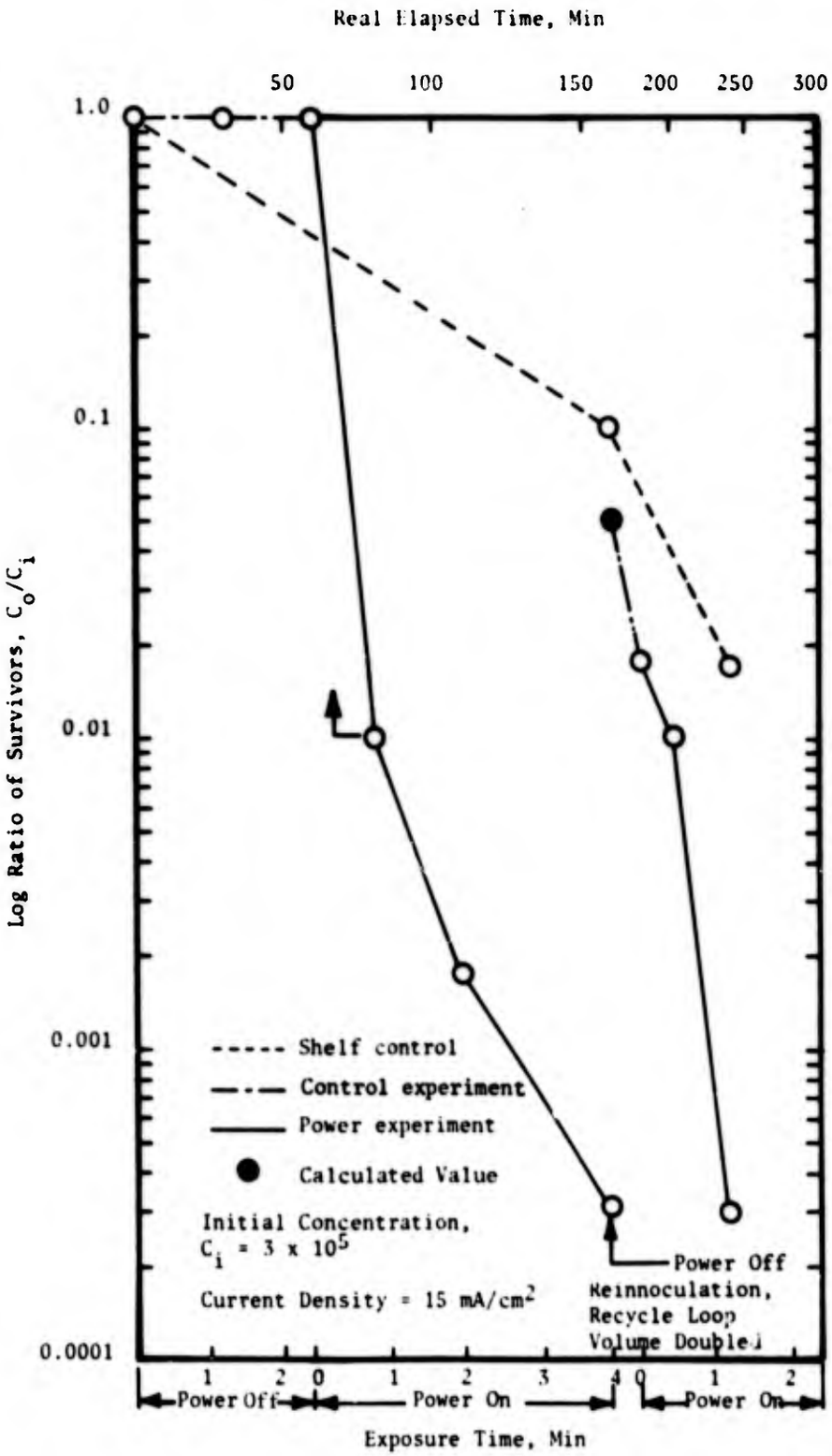


FIGURE 38 COXSACKI B SURVIVAL RATIOS AT BASELINE CONDITIONS

The Coxsacki B virus was more susceptible to inactivation by the Electrochemical Biocide process than Polio virus Type I. No structural difference can readily explain this since both Polio virus Type I and Coxsacki B are small RNA containing enteroviruses.

The Polio Type I and Coxsacki B virus experiments were conducted in a separate laboratory where no attempt was made to prevent electrode gassing.[48]

Post-Test Component Analysis

The Mark I Reactor was subjected to post-test component analysis at the completion of the program testing. The test hardware was disassembled and analyzed to obtain information pertaining to possible material degradation. There was no visual evidence of any material or component degradation. The carbon electrodes had a very slight bleached look. Also, there were some carbon fines lodged in the reactor housing. These had apparently been washed away from the carbon electrodes. Carbon electrode weight losses of four-tenths to eight-tenths of one percent were registered after 50 hours of intermittent system operation conducted over a period of four months. The carbon fines and slight loss in electrode weight may have been caused by vigorous gassing of the electrodes between experimental runs. The turbulator screen, titanium current collectors and expanded sheet, polysulfone electrode spacer, fittings, septums, O-rings, etc. showed no traces of degradation. The components selected for Mark I Reactors appear to be perfectly compatible with the process. No redesign or other corrective actions were suggested as a result of the post-test component analysis.

SYSTEMS EVALUATION OF THE ELECTROCHEMICAL BIOCIDE CONCEPT

The results of the effectiveness of the Electrochemical Biocide process against selected test organisms were illustrated in Figures 32 through 38. In general, the process has been shown to be effective against all of the microorganisms evaluated. An average reduction from 10^6 organisms/ml to between 58 and 4 organisms/ml was achieved in approximately a four-minute exposure time. The Polio Type I and Coxsacki B virus experiments were conducted in a separate laboratory where no attempt was made to prevent electrode gassing during system operation. Gassing has been shown to seriously limit mass transfer of the organisms to the electrode surface, thereby resulting in slower microorganism reduction rates. Gassing occurred above 10 mA/cm^2 (1 amp) with the sodium nitrate buffer used for Phase II baseline experimentation. In the raw settled sewage run, a near five-log order reduction in total coliform concentration was achieved in a two-minute exposure time. The raw settled sewage feed was recycled through the electrochemical reactor without any prefiltering.

Initially, the process feed is high in microorganism counts and the microorganism kill rate is limited by the rate of microorganism destruction on the active electrode surface. Mass transfer limitations predominate when the microorganism concentrations fall in the process feed. These phenomenon are explained with the aid of a simple model under the Microorganism Kill or Reduction Mechanism section. These limitations suggest that the optimum Electrochemical Biocide Reactor should have built-in parameters which increase the microorganism destruction rate at electrode surfaces at the feed entrance and parameters which increase the mass transfer of the microorganisms to the electrode surface at the product exit end.

From the kill results, for raw settled sewage and other specific microorganisms, it is evident that a conservative exposure time for a six- to eight-log order reduction in microorganisms would be six minutes.

Recommendations for a preliminary scale-up of the Electrochemical Biocide process for USAMRDC (4200 gal/20-hr day), NASA (20 gal/day), and a community (10^6 gal/day) water treatment system, based on the above microorganism kill rate estimate, are presented below. A comparison of the Electrochemical Biocide process operating costs with traditional sewage disinfection operating costs is also included. The subsection concludes with a comparison of the disinfection efficiency of the Electrochemical Biocide process with chlorine, bromine and iodine.

Process Scale-up Feasibility

The feasibility of the electrochemical biocide to destroy microorganisms was illustrated above. In this section, the application areas for the electrochemical biocide are discussed. A preliminary reactor design, size, volume and operational cost for these end applications are included in this discussion.

The evaluation was based on existing data with no advantage assumed in scale-up. Conservative values were selected to represent the worst condition scaled system. The actual optimized scaled system should be considerably better in overall feasibility and operation.

The applicability of the Electrochemical Biocide process to the Army MUST Hospital Water Processing USAMRDC (4200 gal/20-hr day), the NASA (20 gal/day) Space Station Prototype and a community (10^6 gal/day) water treatment system are typical examples of the general usage of this concept. The concept is also readily applicable to disinfection of non-domestic water such as those used for dairy and food processing, manufacturing of cosmetics and industrial applications such as alcoholic fermentations, etc., where disinfection or sterilization by addition of chemical agents to the water is not desirable. This is true of fish farming, poultry and fish washing, and in waters used to formulate cosmetics or produce alcoholic fermentations. In these applications, the Electrochemical Biocide process should be a highly competitive alternative.

The applications illustrate the wide spectrum over which the Electrochemical Biocide process can be efficiently employed for disinfection.

Army System (4200 Gal/20-Hr Day)

A 4200 gal/20-hr day electrochemical biocide system must treat water at 3.5 gpm To bring the processed water to disinfection levels, an exposure time of six minutes is assumed. Based on existing data, this should result in a six- to eight-log order reduction in microorganisms.

Due to reactor size and electrode limitation, it is necessary to recycle part of the effluent to achieve process water velocities of 15 cm/sec (0.5 ft/sec) with a 3.5 gpm system. Calculations for the engineering parameters were made by arbitrarily recycling three-fourths of the reactor effluent. A preliminary trade-off calculation showed that the engineering parameters were not significantly affected by this arbitrarily chosen recycle rate.

The 4200 gal/20-hr day reactor system characteristics are illustrated in Table 14. A bipolar electrode reactor design, similar to the one illustrated in Figure 39 was used as a basis for computing the characterization values.

These preliminary values point out some of the real world limitations such as the trade-off between available electrode sizes, electrode spacing and process water velocity. They also reflect the key limiting factors for the different scale-up sizes.

NASA System (20 Gal/Day)

The NASA six-man Space Station Prototype reclaimed water flow rates are shown Table 15. A minimum of 42 lb/day and a maximum of 172 lb/day of water must be treated to prevent biological growth. From existing electrochemical biocide data it is known that a two-minute exposure time is sufficient to result in two- to three-log order microorganism kill. In the closed Space Station Prototype reclaimed water system, a two- to three-log order kill should adequately prevent biological growth by back contamination.

From existing data, it is known that process water velocities of 15 cm/sec and higher are needed for reasonable microorganism kill rates. Also, a turbulence promotor (a nylon mesh screen, etc.) significantly increases the mass-transfer and, consequently, the kill rate. To treat 42 to 172 lb/day of reclaimed water, a four-parallel-flow compartment bipolar electrode module is suggested. Each module would then treat 43 lb/day of reclaimed water. A two-compartment-parallel bipolar electrode reactor design concept is illustrated in Figure 39. A serpentine process water flow channel is required to give a single pass residence time of 120 seconds. The dimensions, volume, power and operational cost for this reactor are summarized in Table 14.

Community System (10^6 Gal/Day)

Typical composition of domestic sewage is illustrated in Table 16.[51] Settled raw sewage is represented more typically by the values for weak sewage. Most sewage discharge spcifications require that the treated effluent must meet the following:

BOD^5:	15 mg/l
Suspended Solids:	10 mg/l
Coliform:	200/100 ml

From bench-scale tests it appears that, in the scaled system, a five- to six-minute exposure time should result in six- to eight-log order microorganism kill. This would result in the disinfection of the sewage without the addition of any chemical species which could form toxic by-products with the sewage contaminants.

Engineering parameters for an Electrochemical Biocide process for treating 10^6 gallons of raw settled sewage per day are listed in Table 14. A bipolar parallel electrode plate arrangement was assumed in calculating the values. One of the

TABLE 14 ELECTROCHEMICAL BIOCIDE PROCESS SCALE-UP

Capacity, Gal/Day	Electrode Size,[a] L x H, In	Flow Channel[b] H x W, In	Process Water Velocity, cm/sec	Bipolar Cells/ Module, Number	Module Size, L x H x W, Ft	Module in Parallel, Number	Module in Series, Number	Approximate Space Requirements, L x H x W, Ft	Specific Power[c] kW-hr/Gal	Operating Cost,[d] $/1000 Gal	Limiting Factors in Design and Other Comments
20	16 x 10	0.16 x 0.03	15	4	1.5 x 1 x 0.25	1	1	2.5 x 1.5 x 0.5	0.12	3.6	Single pass, high process water velocities dictate serpentine flow.
5040	52 x 4	4 x 0.03	15	8	5 x 0.5 x 0.5	1	10	6 x 2 x 2	0.10	3.1	Must increase process water velocities by recycling a major fraction of the effluent. Limited by available electrode lengths.
10^6	52 x 17	17 x 0.03	30	72	5 x 2 x 1.5	13	80	200 x 8 x 15	0.10	3.1	Limited by available electrode sizes and their structural strengths.

(a) Maximum size of currently available carbon electrodes, 52 x 17 in.
(b) Due to a screen turbulator, the equivalent width of the flow channel is 0.015 in.
(c) Based upon experimental data obtained under current contract. Linear extrapolation used for scale-up. Pumping power was calculated to be roughly 0.1 of cell power.
(d) Includes power cost at $.03/kW-hr. Labor and other operating costs are minimal.

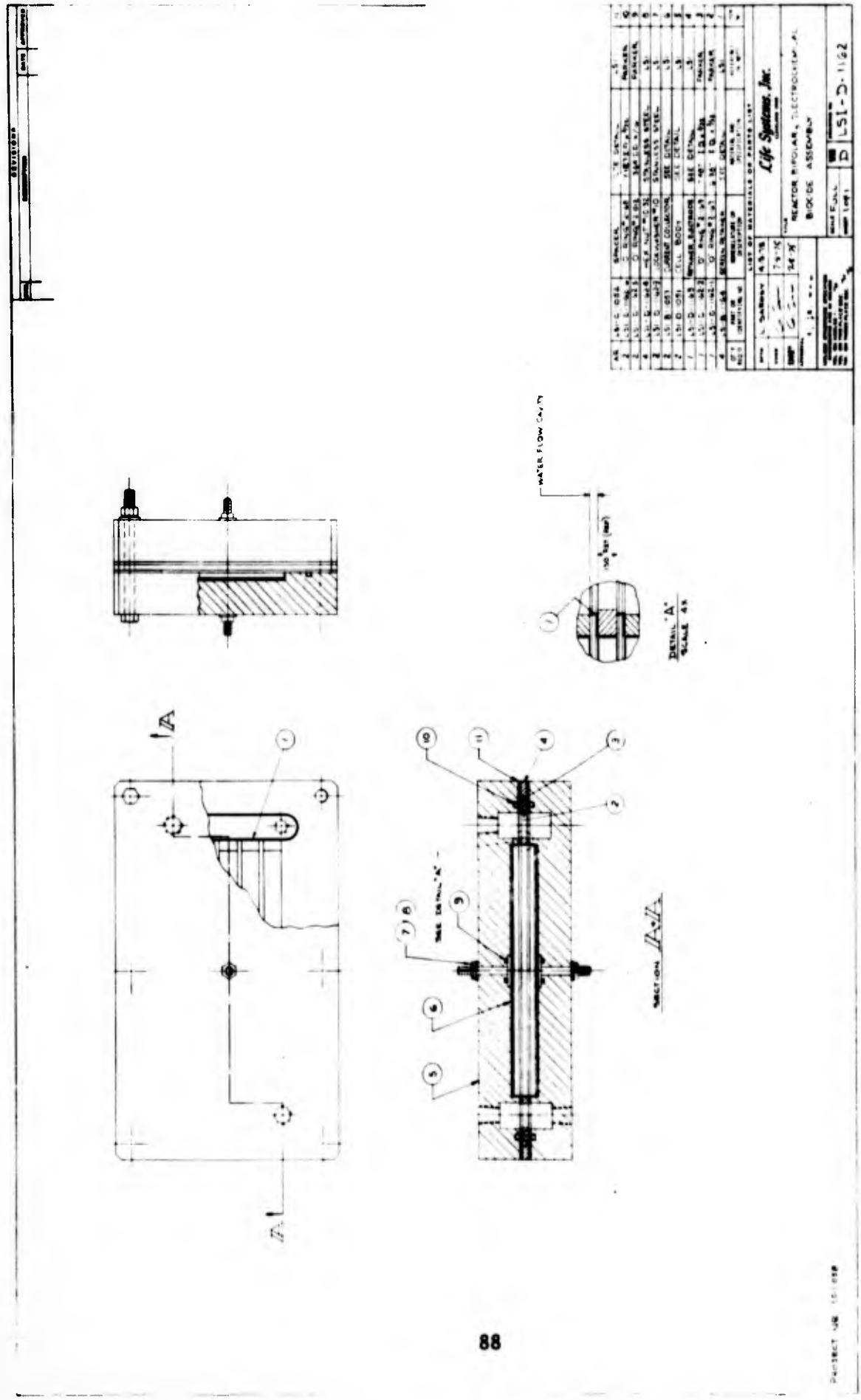


FIGURE 39 BIPOLAR PARALLEL FLOW ELECTROCHEMICAL BIOCIDE REACTOR ASSEMBLY DRAWING

TABLE 15 SPACE STATION PROTOTYPE RECLAIMED WATER FLOW RATES

Source of Water	Flow Rate, kg/Day (Lb/Day) Minimum	Normal	Maximum
Urine Recovery	9.3 (20.5)	15.6 (34.5)	33.6 (74.1)
Cabin Temperature and Humidity and Carbon Dioxide Reduction Subsystems	9.7 (21.4)	18.0 (39.7)	31.2 (68.8)
Total	19.0 (41.9)	33.6 (74.2)	64.8 (142.9)
Plus 10% Excess	20.9 (46.1)	37.0 (81.6)	71.3 (157.2)
Plus 20% Excess	22.8 (50.3)	40.4 (89.0)	77.7 (171.4)

TABLE 16 COMPOSITION OF DOMESTIC SEWAGE [51]

Constituent	Strong	Medium	Weak
Solids, total, mg/l	1000	500	200
Volatile	700	350	120
Fixed	300	150	80
Suspended, total, mg/l	500	300	100
Volatile	400	250	70
Fixed	100	50	30
Dissolved, total, mg/l	500	200	100
Volatile	300	100	50
Fixed	200	100	50
BOD (5-day, 20C), mg/l	300	200	100
Oxygen consumed, mg/l	150	75	30
Dissolved oxygen, mg/l	0	0	0
Nitrogen, total, mg/l	86	50	25
Organic	35	20	10
Free ammonia	50	30	15
Nitrites (NO_2)	0.10	0.05	0
Nitrates (NO_3)	0.40	0.20	0.10
Chlorides, mg/l	175	100	15
Alkalinity, mg/l	200	100	50
Fats, mg/l	40	20	0
Coliform, Org/ml	10^{9-12}	10^{7-9}	10^{5-7}

limitations of the parallel flow reactor is that to achieve effective mass transfer of the microorganisms to the electrode surface, high process fluid velocity and/or turbulence promotors are needed. Without high fluid velocities and/or turbulence promotors, low microorganism kills result.

One consequence of high fluid velocities is that long reactor paths are needed for two- to six-minute exposure times. Another is power loss due to high pressure drops.

To overcome these limitations, LSI has designed a proprietary flow-through reactor and proposed a second concept. A preliminary experiment indicated the flow-through reactor is much more efficient than the parallel flow reactors.

Preliminary tests conducted on a flow-through reactor have resulted in a three-log order kill (Escherichia coli) in a two-minute residence time. The power requirements were approximately one-fourth that of the parallel plate reactors with a turbulator. However, due to the lack of detailed experimental data characterizing the flow-through reactor, a scaleup for the 10^6 gal/day system based on the flow-through concept was not used.

Comparison with Traditional Sewage Disinfection

Traditional sewage treatment operating costs run between $0.30 to $0.60/1000 gallons depending on the type of facility, sewage characteristics and other factors. The Electrochemical Biocide process operating cost, based on existing data, was projected to be $3.00 to $[illegible].00/1000 gallons. These projections are based on a linear extrapolation of power requirements of the bench-scale Mark I-2 Reactor (including pumping power). Preliminary experiments conducted with the flow-through reactor reduced the cost figures to $1.00/1000 gallons. Under the current contract, the operating costs (major costs are energy costs) have been reduced from $19.00/1000 gallons for prior efforts to $1.00/1000 gallons (bipolar flow-through reactor). With increased mass transfer and reduced internal reactor resistance, projected operating costs place the electrochemical biocide near the operating cost of the traditional alternatives. A preliminary capital cost calculation places the electrochemical biocide on a comparable basis with current alternatives for sewage disinfection. As seen from Table 14, the space requirements are realistic. The above engineering and cost parameters should become more competitive with tradition secondary sewage treatment with continued development efforts on the parallel electrode and the flow-through Electrochemical Biocide Reactor designs.

Process Comparison with Other Biocides

Comparing the electrochemical biocide efficiency with other disinfecting processes is difficult. However, an indirect comparison can be made to put the process in perspective. Figure 40 is a plot of microorganism survival data for chlorine, bromine, iodine, and the electrochemical biocide.[52] The data shows that the chemical agents are more effective in destroying microorganisms at the current stage of development of the Electrochemical Biocide process. Increased efficiency must be achieved to make the electrochemical biocide directly competitive with chemical agents in large-scale systems where chemical residuals are not a concern. Where chemical residuals are a concern, the electrochemical biocide is superior.

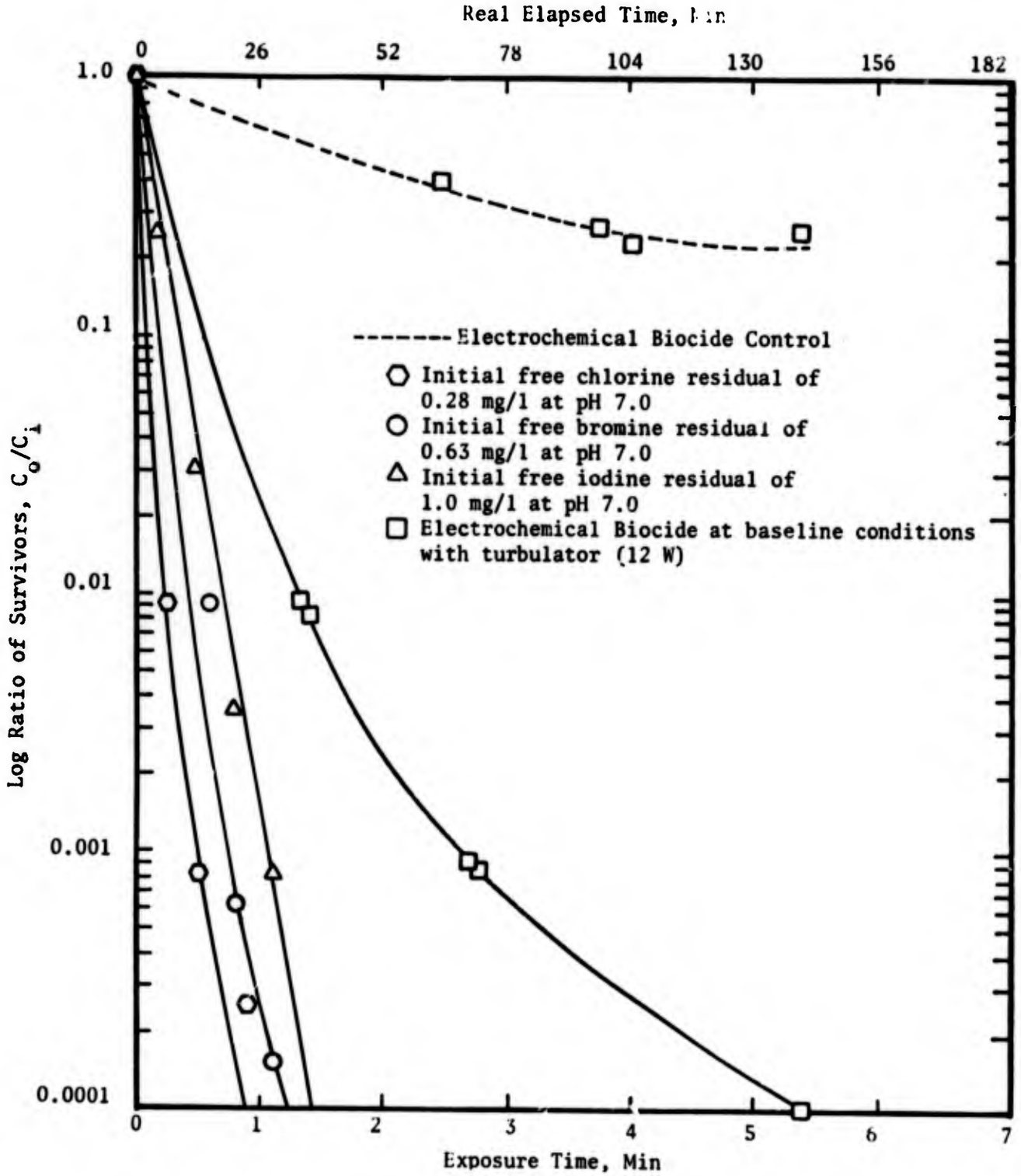


FIGURE 40 MICROORGANISM SURVIVAL RATIOS VERSUS DIFFERENT DISINFECTING AGENTS

SUPPORTING TECHNOLOGY STUDIES

The supporting technology studies include reviewing literature on prior electrolytic disinfections of water and waste water and proposing hypotheses for describing possible microorganism kill mechanisms.

Literature Review

The review of the state-of-the-art literature of electrolytic disinfection of water and waste water was summarized above. With two exceptions, all relevant literature references were related to processes using DC. The current electrochemical biocide research and development program used a square AC signal.

There was a conspicuous absence of any valuable reports on experimental studies of bacterial kill as an indicator of bactericidal effectiveness of the electrolytic disinfection process. In addition, no single study or data was found which explored the microorganism kill mechanism alternatives and the effects of process parameters on process effectiveness and efficiency.

Microorganism Kill or Reduction Mechanism

The current concept is that at least four microorganism kill or reduction mechanisms may be involved in the microorganisms' destruction process:

1. Reduction in number of viable microorganisms by adsorption onto the electrodes
2. Electrochemical oxidation of the microorganism components at the anode
3. Destruction of the microorganisms by production of a biocidal chemical species
4. Destruction by electric field effects

A discussion of each of the proposed microorganism kill mechanisms is included below. The discussion includes the steps involved in each of the kill mechanism processes and a model of the destruction process.

The phenomenon of protein and microorganism adsorption on electrodes with anodic potential has been documented in the literature.[29-34] The review of the literature and the TOC data recorded during the existing program suggests that electrode adsorption may be a necessary step in the microorganisms' destruction process, with the alternating current preventing electrode fouling by hydrogen gas production on the cathodic cycle. The steps involved in the process are believed to be:

1. Transport of the organisms to the anode
2. Adsorption of the organism on the anode
3. Destruction of the organism on the anode
4. Desorption of the destroyed organism

Results from an experimental run with raw settled sewage indicated that under control (no power) conditions, microorganism adsorption on the passive electrodes

is a possible mechanism for the microorganism reduction from the process fluid. Under control conditions, a reduction in TOC in the settled sewage product water was observed. No corresponding change in TOC was observed in the power run. This suggests that organics and/or organisms are adsorbed and held on the electrode surface under no-power conditions. Further, the desorption of the microorganism from the electrode surface is likely to be the limiting step in the microorganisms' destruction rate. Once the active electrode surface gets saturated with the organism, a leveling in the reduction rate should result. This was consistently observed in all control experiments.

Under the power run, no change in TOC was observed in the Electrochemical Biocide product water. The suspended colloidal matter in raw settled sewage does contain a significant amount of protein. Domestic settled sewage normally contains 15 to 35 mg/l of organic nitrogen chiefly as amino acids and proteins.[51] Based on the experimental results, it appears that proteins do not have a tendency to be irreversibly adsorped on the active electrode surface during power conditions. The desorption of microorganisms is, therefore, probably not a controlling step under the power conditions. The first three steps outlined above would dictate the kill rate.

A simple model for destruction of microorganisms by the adsorption and/or subsequent electrochemical oxidation mode is illustrated in Figure 41. The microorganisms must first diffuse from the main body of the fluid through the laminar liquid layer to the exterior surface of the carbon electrodes. Carbon electrodes have high surface areas to volume ratios due to their porosity. The interior of the electrode, therefore, contains more surface area than the exterior. Consequently, most of the kill would occur within the electrode pores. This would be especially true for the electrochemical biocide reactors based on a flow-through carbon electrode concept. The microorganisms must, in general, move into the electrodes through surface pores. This gives rise to pore diffusion resistance.

At some point in their wanderings, the microorganisms are associated with the surface of the electrode where they are destroyed to be released to the fluid phase within the pore. The killed microorganisms must now follow a reverse path to get back into the main process fluid stream.

The applicability of this model can best be understood by using it to explain the Escherichia coli kill illustrated in Figure 16. Initially, the high microorganism concentrations (10^6 organisms/ml) in the process feed result in a large diffusion of microorganisms to the electrode surface. This diffusion can simply be stated in terms of Flick's Law:

$$r_A = k\ (C_A - C_{Ae}) \qquad (5)$$

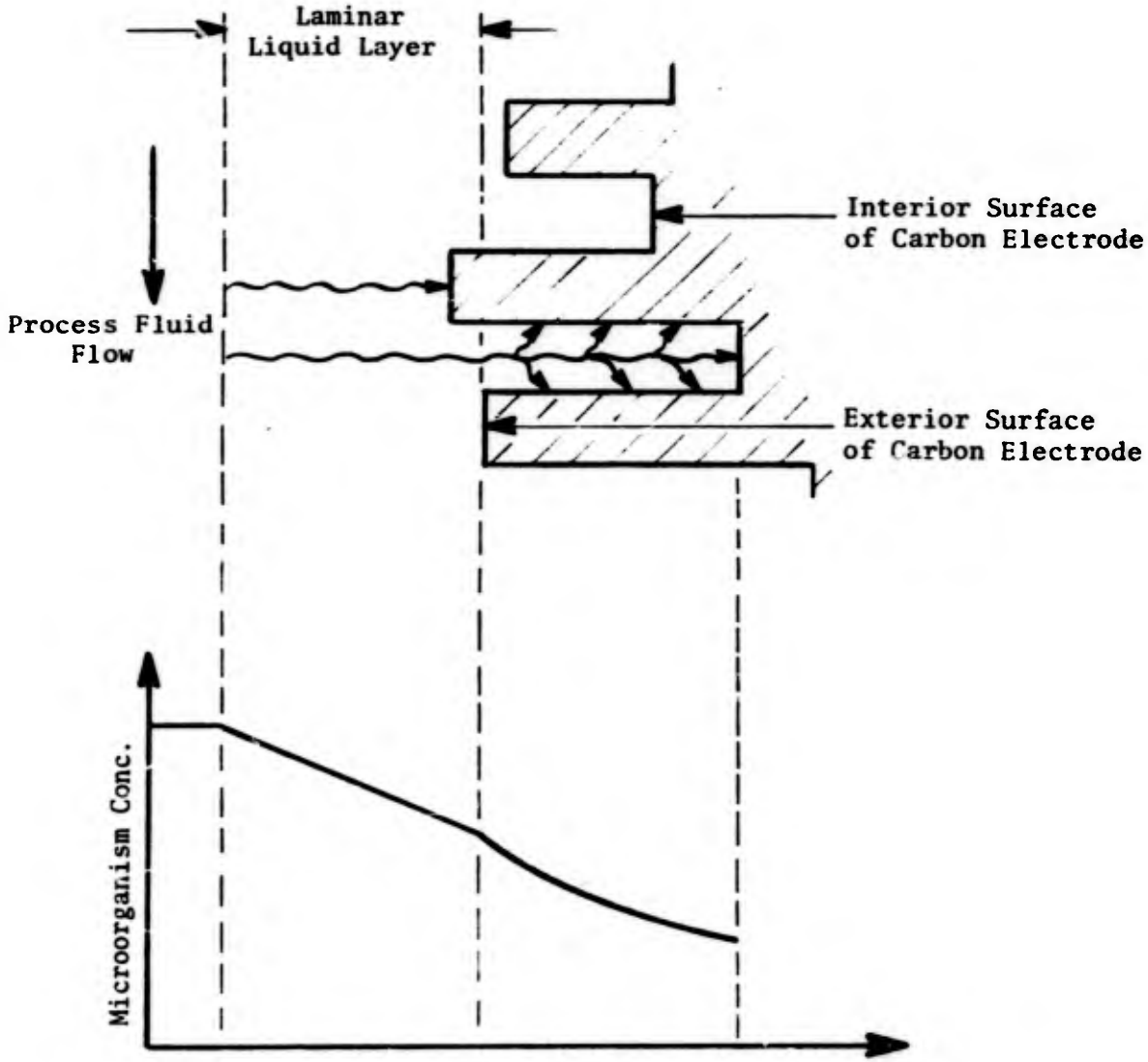
where

r_A = rate of diffusion of the microorganisms to the electrode surface

C_A = microorganism concentration in the process feed

C_{Ae} = microorganism concentration on the electrode surface

k = proportionality constant (diffusivity coefficient)



(a) Sketch of a carbon electrode surface

(b) Concentration of the microorganisms at the electrode surface

FIGURE 41 MODEL FOR DESTRUCTION OF MICROORGANISM BY ADSORPTION

The proportionality constant k is a function of the physical and chemical characteristics of the fluid microorganism pair. Table 17 lists the biochemical and physical characteristics of the various microorganisms studied under this program. Under these conditions, the microorganism kill rate is limited by the rate of microorganism destruction on the active electrode surface. The resident time of the microorganism on the electrode surface becomes the critical parameter.

However, when the concentration of the microorganisms in the main process fluid stream is small, very little diffusion of the microorganisms to the electrode surface occurs. Under these conditions, the mass transfer limitations predominate. The flattening of the microorganism survival ratio curve under the power condition at low concentrations illustrates the mass transfer limitation step.

The extent to which microorganisms are destroyed by the adsorption or electrochemical oxidation mechanisms should be governed to a large degree by the protein-coating of the organisms. Each organism would, therefore, exhibit different resistances to the Electrochemical Biocide process. Exact variations, typical of different organisms, have yet to be determined.

The third mechanism depends on a biocidal chemical species being produced by an electrochemical reaction at the electrode surfaces. The steps involved in this process would be:

1. Diffusion (or transport) of the reactants to the electrode
2. Production of a biocidal species by a reaction of the electrode
3. Diffusion (or transport) of the biocidal species into the bulk solution
4. Adsorption of the biocidal species onto the organism
5. Reaction of the biocidal species with the organism
6. Die-away of the biocidal species

Experiments conducted with two different test waters (buffered and unbuffered test water) with and without sodium chloride present showed no significant difference in the microorganism destruction rate at the same power level. These results indicate NaCl is not needed for effective operation in the destruction of microorganisms, and that no chemical species is being produced, which is unique to any one buffer solution. Also, hydrogen peroxide spot tests conducted on the reactor affluent gave negative results. These results tend to discredit the possibility that formation of biocidal chemical species are the predominant mechanism for the Electrochemical Biocide process. The destruction mechanism described for the adsorption and electrochemical oxidation phenomenon is also applicable to the production of chemical biocidal species and consequent destruction of microorganisms. There is greater probability that the organisms are destroyed at the electrode surface versus having the biocidal species conveyed from the electrode surface into the bulk solution. This is because the diffusion rate coefficients for the biocidal species (Cl^-, $HO^\cdot$, $O^\cdot$, ClO^-, HOCl) are very low.

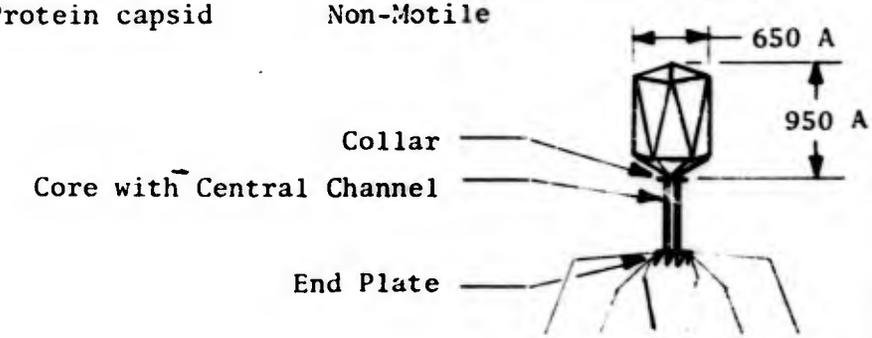
Adsorption is not in itself a destruction mechanism but it may play an important role in the electrochemical oxidation mechanism. Adsorption involves the contact and retention of the organism at the electrode surface. Retention might be achieved by a mechanical interlocking effect with the electrode surface (lock and key concept). The carbon electrode surface then could act as a catalyst,

TABLE 17 PHYSICAL AND BIOCHEMICAL CHARACTERISTICS OF TEST MICROORGANISMS

Bacteria

Organism	Approximate Size	Shape	Outer Layer Molecular Composition	Motility	Remarks
Escherichia coli	Width, μm: 0.4-0.7[b] Length, μm: 2.0-4.0	Bacillus or Rod-Shaped	Lipoprotein Lipopolysaccharide	Peritrichous Flagella	Gram Negative Bacterium
Klebsiella pneumoniae	Width, μm: 0.4-0.7 Length, μm: 2.0-4.0	Bacillus or Rod-Shaped	Lipoprotein Lipopolysaccharide (In virulent (smooth) form outer capsule-polysaccharides)	Non-Motile	Gram Negative Bacterium
Pseudomonas aeruginosa	Width, μm: 0.5 Length, μm: 1.5-3.0	Bacillus or	Lipoprotein	1-3 Polar Flagella	Gram Negative Bacterium
Fungi					
Saccharomyces cerevisiae	5 μm	Ovai or Elliptical	Polysaccharides chitin + (cellulose)	Non-Motile	Typical Yeast
Viruses					
Poliovirus	28 nm[c] (280 A)[d]	Icosahedral Symmetry	Protein capsid	Non-Motile	RNA Containing Animal Virus
Coxsackie	28 nm (280 A)	Icosahedral Symmetry	Protein capsid	Non-Motile	RNA Containing Animal Virus
T_4 (See Diagram)	Head, nm (A): 95 x 65 (950 x 650)	Helical Head	Protein capsid	Non-Motile	DNA Containing Bacteriophage
	Tail, nm (A): 17 x 115 (170 x 1150)	Icosahedral Tail	Protein capsid	Non-Motile	

(a) Sizes given, generally for stained bacteria
(b) μm = micrometer
(c) nm = nanometer
(d) A = Angstrom



enhancing the possibility of microorganism kill by electron transfer (oxidation). Kill, under power conditions, may be a result of the gas production at the electrodes, forcing the adsorbed organism to tear away from the surface. Under the no-power conditions, it is yet to be determined if the microorganisms are destroyed or just passively held.

The fraction of the microorganism kill not explained by the first three mechanisms are grouped under this fourth broad category called electrical field effect. Microorganism kill, under this electrical field effect, depends on the electromotive forces acting on the microorganisms. In experiments conducted under a microscope, under conditions which minimized generation of biocidal chemical species (Cl_2, ClO^-, HOCl, $O^\cdot$, etc.), large eucharotic microorganisms were visually observed to die midstream without contacting the electrodes. The microorganisms were observed to oscillate after apparent death. The oscillation appeared to be in phase with the electrical field. This microorganism kill is apparently caused by the changing electromotive forces resulting from the impressed AC.

CONCLUSIONS

The following conclusions are a direct result of the current research and development program:

1. The Electrochemical Biocide process has been shown to be effective against all the microorganisms tested, namely, three bacteria (Escherichia coli, Pseudomonas aeruginosa and Klebsiella pneumoniae), one yeast (Saccharomyces cerevisiae), two viruses (Polio I and Coxsacki B), and the flora of microorganisms found in domestic raw settled sewage. The results are summarized in Table 18.

2. The literature review conducted on prior processes for the electrolytic disinfection of water and waste water indicated that there was a conspicuous absence of any valuable reports on experimental studies of microorganism kill as an indicator of biocidal effectiveness of the electrolytic disinfection process.

3. The current microorganism kill mechanism concept is that four kill mechanisms may be involved in the microorganism destruction process:

   a. Reduction in number of viable microorganisms by adsorption onto the active electrode (adsorption may be a step in mechanism but not a kill mechanism)

   b. Destruction of the microorganisms by production of biocidal chemical species

   c. Destruction by electrical field effects

   d. Electrochemical oxidation of the microorganism components at the anode

TABLE 18 SUMMARY OF MICROORGANISM RESULTS

Initial Concentration (organisms/ml)	Organism	Final Concentration (organisms/ml) after 4-Min Exposure Time
7.6×10^6	Escherichia coli	480
2.0×10^6	Pseudomonas aeruginosa	35
1.1×10^6	Klebsiella pneumoniae	29
2.3×10^3	Saccharomyces cerevisiae	4
4.8×10^6	Raw Settled Sewage	56
	Virus	
5×10^4	Polio Virus Type I	880 (average of two experimental trials)
3×10^5	Coxsacki B	90

In summary, complete understanding of the microorganism kill mechanism does not exist. However, the Electrochemical Biocide process has been shown to be effective in the absence of NaCl in the test water.

4. The plug-flow reactor design is the optimum configuration for the Electrochemical Biocide process. Electrochemical biocide reactors based on stirrers have no potential for scale-up since the high resistivity of process water requires electrode separation of less than 4 to 8 cm (1.6 to 3.1 in). Further advantages of the plug-flow reactor are discussed in the section on the selection of the Electrochemical Biocide Reactor type.

5. In the AC operating mode, the Mark I Reactor behaves like an ohmic resistance device. This implies that the electrochemical polarization effects are either constant or zero and do not vary significantly with the impressed cyclic voltage and variable current density. This relationship does not apply above the current density where electrode gassing occurs.

6. The reduction in numbers of viable bacteria in control experiments can be attributed to dying of the microorganisms (osmotic shock, etc.), entrapment of organisms in mechanical dead ends of the test apparatus such as pressure gauges and some adsorption onto components of the test apparatus such as the carbon electrodes.

7. Reactors should not be designed with unsealed expanded titanium sheet current collector cavities. These cavities potentially serve as reservoirs for the high initial microorganism concentration test water. Leaching from these cavities during experiments may lead to experimental error.

8. The effects of voltage level, waveform and frequency on microorganism kill indicate that increased kill results from increased voltage up to 8V (with buffered test solution). At higher voltages, gassing at the electrode surface masks the reactor kinetics, resulting in poorer kills, and the process becomes more efficient as the electrical signal frequency approaches DC.

9. Pregassing of the electrodes before the start of the experiment resulted in a slight increase in microorganism kill.

10. Experiments conducted with the Mark I Reactor series indicate the effects of process water temperature, pH, turbidity, flow rate and NaCl content on microorganism kill indicate that (a) no appreciable difference in kill was observed at 283 to 286K (50 to 55.4F) and 293 to 296K (68 to 73.4), (b) no significant variation was noted for test water pH of 5 to 9, (c) the microorganism kill rate is significantly affected by turbidity, (d) a smaller electrode spacing results in better kill for a constant test water velocity, (e) no appreciable difference was detected with test water containing 100 and 500 mg/l NaCl, (f) evolution and trapping of gas between the reactor electrodes

hinders the mass transfer of the microorganism to the electrode surface resulting in poorer microorganism kill rates, and (g) increased mass transfer due to the addition of a turbulator to the reactor compartment results in a significant increase in microorganism kill.

The following indirect conclusions have resulted from the current research and development program:

1. A less than six-minute exposure time should be sufficient to result in six- to eight-log order reduction in microorganism concentration in the process feed.

2. The Electrochemical Biocide process can be successfully applied to a wide spectrum of end uses. Preliminary scaleup of the process for USAMRDC (4200 gal/20-hr day), NASA (20 gal/day), and a community (10^6 gal/day) water treatment applications was readily applicable to disinfection of non-domestic water such as those used for dairy and food processing, fish and poultry farming, manufacturing of cosmetics, and alcoholic fermentations. The process should prove to be highly competitive where disinfection or sterilization by addition of chemical agents to the water is not desirable.

3. A literature review comparison of the Electrochemical Biocide process with traditional disinfection agents (chlorine, ozone, bromine and iodine) shows that the chemical agents are probably more effective in destroying microorganisms at the current stage of the Electrochemical Biocide process development. Where chemical agents are undesirable, the Electrochemical Biocide process shows definite promise.

RECOMMENDATIONS

The following recommendations are a direct result of the program's conclusions:

1. The feasibility of the Electrochemical Biocide process has been demonstrated. Further design, development, fabrication and testing must be conducted to optimize the process to make it competitive with traditional disinfection processes.

2. To successfully meet the optimization goals, continued development is necessary for expanding the technology base, understanding the process effectiveness and increasing the process efficiency.

3. The flow-through electrode Electrochemical Biocide reactors appear to be more efficient than the parallel-plate reactors. Design, development, fabrication and testing of the flow-through reactor should be conducted to determine the process efficiency limits.

4. Any future research and development should include experiments designed to elucidate the microorganism kill mechanism(s). This will lead to better and more cost-effective process design(s).

5. Continuous process endurance testing should be conducted. This extended testing will determine if process fouling results in continuous operation.

6. An aquatic toxicity experiment should be conducted to evaluate the toxicity of effluent water from the Electrochemical Biocide reactor.

7. Process efficiency experiments should be conducted to increase the number of microorganisms destroyed per unit energy. Process efficiency will be increased by increased mass transfer within the reactor (flow rate and flow compartment geometry), reducing internal resistance and reducing the RMS power (duty cycle) delivered to the reactor.

8. Multiple parameter experiments should be conducted to establish the true optimum levels of critical system parameters together with mutual and interaction effects, and define the variation in process efficiency and effectiveness in the neighborhood of the optimum. A statistical protocol, based upon two-level fractional factorial design and central composite rotable design, should minimize the number of experiments.

9. The Electrochemical Biocide process should become competitive with traditional secondary sewage treatment with continued development efforts on the current and newer flow-through reactor designs. These efforts should be directed toward increased mass transfer within the reactor(s) and reduction in the power required for effective process operation.

REFERENCES

1. McDermott, J. H., "Virus Problems and Their Relationship to Water Supplies," Journal of American Water Works Association, Vol. 66, No. 12, pp. 693-698, December, 1974.

2. Katzenelson, E. B., Kletter, B. and Shuval, H. I., "Inactivation Kinetics of Viruses and Bacteria in Water by Use of Ozone," Journal of American Water Works Association, Vol. 66, No. 12, pp. 725-729, December, 1974.

3. Bellar, T. A., Lichtenburg, J. J., and Kroner, R. C., "The Occurrence of Organohalides in Chlorinated Drinking Waters," Journal of American Water Works Association, Vol. 66, No. 12, pp. 703-706, December, 1974.

4. White, G. C., "Disinfection: Present and Future," Journal of American Water Works Association, Vol. 66, No. 12, pp. 689-690, December, 1974.

5. Miller, H. C., and Knipe, W., "Electrochemical Treatment of Municipal Waste Water," U. S. Public Health Publication 999-WP-19, 1965.

6. Kuhn, A. T., "Electrochemistry of Cleaner Environments," Ed. John O'M. Bockris, Plenum Press, New York, 1972.

7. Mantell, C. L., "Electro-Organic Chemical Processing," Noyes Development Corp., Park Ridge, New Jersey, 1968.

8. Wei, N. S., and Heinke, G. W., "Sewage Electrolysis," Water and Pollution Control, Vol. 112, No. 5, pp. 31-32, 1974.

9. Hiler, E. A., and Lyle, W. M., "Electrophoretic Clarification of Water," Texas A & M University, Water Resources Institute Technical Report 31, NTIS PB19456, 1970.

10. Hallum, J. V., "Treatment of Microorganisms," U. S. Patent 3,058,894, October 16, 1962.

11. Inoue, K., "Method and Apparatus for Purification of Water Containing Organic Contaminants," U. S. Patent 3,518,174, June 30, 1970.

12. Treharne, R. W., "Method for Controlling Algae Pollution," U. S. Patent 3,752,747, August 14, 1973.

13. Velas, J. L., and Puig, L. C., "Equipment for Purification and Sterilization of Swimming Pool Waters," U. S. Patent 3,192,142, June 29, 1965.

14. Velas, J. L., and Puig, L. C., "Equipment for Purification and Sterilization of Swimming Pool Waters," U. S. Patent 3,192,146, June 29, 1965.

15. Wikey, A., "Water Treatment Apparatus," U. S. Patent 3,769,196, March 11, 1971.

16. Meyers, R. R., "Selective Destruction of Bacteria," U. S. Patent 3,753,886, August 21, 1973.

17. Neidl, Georg, "Method of and Apparatus for Purification of Sewage and Sludge," English Patent 882,709, November 15, 1961.

18. Stoner, G. E., "Electrochemical Inactivation of Pathogens," U. S. Patent 3,725,226, April 3, 1973.

19. Hershey, A. B., and Chase, M., "Independent Functions of Viral Protein and Nucleic Acid in Growth of Bacteriophage," Journal General Physiology, Vol. 36, pp. 39-56, 1952.

20. Lovtsevich, E. L., and Sergunina, L. A., "Disinfection of Drinking Water Containing Enteroviruses with Electrolyte Products of Common Salt," Hygiene and Sanitation, Vol. 33, No. 9, pp. 334-341, 1968.

21. Kunina, L. A., "Some Experience in the Electrolytic Disinfection of Drinking Water," Hygiene and Sanitation, Vol. 32, No. 10, pp. 115-118, 1967.

22. Kunina, L. A., "Decontamination of Drinking Water by Electrolysis," Hygiene and Sanitation, Vol. 29, No. 12, pp. 27-30, 1964.

23. Hallum, J. V., and Youngner, J. S., "The Effect of Oxidative Controlled Potential Electrolysis on Viruses," Virology, Vol. 12, pp. 283-308, 1960.

24. Paul, S. K., Chari, K. V., and Bhattacharyya, B., "Electrolytic Control of Algae," Journal of American Water Works Association, Vol. 67, No. 3, pp. 140-141, March, 1975.

25. Neidl, Georg, "Method of and Apparatus for Treating Sewage Containing Biologically Decomposable Organic Matter," U. S. Patent 3,336,220, August 15, 1967.

26. Sabins, R. C., "Electrolytic Treatment of Aqueous Solutions," U. S. Patent 3,600,286, August 17, 1971.

27. Davis, J. G., "Progress in Industrial Microbiology," Ed. D. J. D. Hockenhull, J. and A. Churchill LTD., London, 1968.

28. Culp, R. L., and Culp, G. L., "Advanced Waste Water Treatment," Van Nostrand Reinhold Co., 1971.

29. Gileadi, E., Ed. "Electrosorption," Plenum Press, New York, 1967.

30. Gileadi, E., Rubin, B. T. and Bockris, J. O'M, "Electrosorption of Ethylene on Platinum as a Function of Potential, Concentration and Temperature," The Journal of Physical Chemistry, Vol. 69, No. 10, pp. 3335-3345, 1965.

31. Heiland, W., Gileadi, E., and Bockris, J. O'M., "Kinetic and Thermodynamic Aspects of the Electrosorption of Benzene on Platinum Electrodes," The Journal of Physical Chemistry, Vol. 70, No. 4, pp. 1207-1216, 1966.

32. Stoner, G. E. and Srinivasan, S., "Adsorption of Blood Proteins on Metals Using Capacitance Techniques," The Journal of Physical Chemistry, Vol. 74, No. 5, pp. 1088-1094, 1970.

33. Mattson, J. S. and Smith, C. S., "Enhanced Protein Adsorption at the Solid-Solution Interface: Dependence on Surface Charge," Science, Vol. 181, pp. 1055-1057, 1973.

34. Duic, L., Srinivasan, S., and Sawyer, P. N., "Electrochemical Behavior of Blood Coagulation Factors," Journal Electrochemistry Society, Vol. 120, No. 3, pp. 348-353, 1973.

35. Ramasamy, N., Ranganathan, M., Duic, L., Srinivasan, S., and Sawyer, P. N., "Electrochemical Behavior of Blood Coagulation Factors," Journal Electrochemistry Society, Vol. 120, No. 3, pp. 354-361, 1973.

36. Levenspiel, O., "Chemical Reaction Engineering," John Wiley and Sons, Inc., New York, New York, 1973.

37. Perry, J. H., Ed., "Chemical Engineers' Handbook," Fourth Edition, McGraw-Hill Book Company, New York, New York, 1963.

38. Fried, I., "The Chemistry of Electrode Processes," Academic Press, London, 1973.

39. Hoare, J. P., "The Oxygen Electrode on Noble Metals Advances in Electrochemistry and Electrochemical Engineering," P. Delahay, Ed., Vol. 6, Wiley Interscience, New York, 1967.

40. Burbank, J., Simon, A. C., and Willihngang, E., "Advances in Electrochemistry and Electrochemical Engineering," The Lead-Acid Cell, Vol. 8, C. W. Tobias, Ed., Wiley-Interscience, New York, 1971.

41. Fontana, M. G., and Staehle, R. W., Ed., "Advances in Corrosion Science and Technology," Vol. 3, Plenum Press, New York, 1972.

42. Langhaar, H. L., "Steady Flow in the Transition Length of a Straight Tube," American Society of Mechanical Engineers Proceedings, Vol. 64, pp. A55-A58, 1942.

43. "Standard Methods for the Examination of Water and Waste Water," 13th Edition, published jointly by the American Public Health Association, the American Water Works Association and the Water Pollution Control Federation, 1971.

44. Houck, I. K., and Wynveen, R. A., "An Automated Water Iodinating Subsystem for Manned Spaceflight," Paper No. 74-ENAs-54, American Society of Mechanical Engineers, Seattle, Washington, July 29-August 1, 1974.

45. Dahling, D. R., Berg, G., and Berman, D., "BGM, A Continuous Cell Line More Sensitive Than Primary Rhesus and African Green Kidney Cells for the Recovery of Viruses from Water," Health Lab. Science, Vol. 11, No. 4, pp. 275-282, 1974.

46. White, G. C., "Handbook of Chlorination," Van Nostrand, Reinhold Company, New York, 1972.

47. Fair, G. M., Morris, J. C., and Chang, S. L., "The Dynamics of Water Chlorination," Journal New England Water Works Association, Vol. 61, pp. 285, 1947.

48. Private Communications, See, G. G., Life Systems, Inc. and Parker, C. E., Department of Civil Engineering, University of Virginia, August 1974-July 1975.

49. Houghton, R. W., and Kuhn, A. T., "Mass Transport Problems and Some Design Concepts of Electrochemical Reactors," Journal of Applied Electrochemistry, Vol. 4, No. 3, pp. 173-191, 1974.

50. Private Communications, Kacholia, K. K., Life Systems, Inc. and Kirk, B. S., Airco, Inc., New Jersey, July, 1975.

51. Babbitt, H. E., and Bauman, E. R., "Sewerage and Sewage Treatment," John Wiley and Sons, New York, 1958.

52. Kuzminski, L. N., and Feng, T. H., "Comparative Death Kinetics of Indicator Microorganisms Upon Halogen Disinfection," presented before the Division of Environmental Chemistry, American Chemical Society, Chicago, Ill., August, 1973.