

**CAPACITIVE DEIONIZATION TECHNOLOGY™:
DEVELOPMENT AND EVALUATION OF
AN INDUSTRIAL PROTOTYPE SYSTEM**

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SYNOPSIS

The Lawrence Livermore National Laboratory (LLNL), in Berkley, California, developed a laboratory scale non-membrane electrosorption process known as Capacitive Deionization Technology™ (CDT™) for the continuous removal of ionic impurities in water. A saline solution flows through an unrestricted capacitor type module consisting of numerous pairs of high-surface area (carbon-aerogel) electrodes. The electrode material (carbon aerogel) contains a high specific surface area (400 – 1 100 m²/g), and a very low electrical resistivity (< 40 mΩ.cm). Anions and cations in solution are electrosorbed by the electric field upon polarization of each electrode pair by a direct current (1,4 Volt DC) power source.

Testing conducted on a laboratory scale unit at LLNL has proved that CDT™ has the potential to be an alternative desalination technology (Farmer⁵ *et al.*, 1995). The primary objective of this research was to continue, where the laboratory scale research ended. Thus taking CDT™ from a laboratory scale technology to an industrial scale process, by developing and evaluating an industrial CDT™ prototype system.

First, a process was developed to manufacture a cost effective industrial sized CDT™ module. During this process various manufacturing techniques were evaluated to produce an optimum prototype. As part of the developmental process the prototype was tested and water treatment efficiency results were first compared to results obtained on the laboratory scale module and secondly to established desalination technologies like reverse osmosis, electrodialysis, and distillation.

Due to the wide variety of potential saline feed water sources, research for this dissertation focused on brackish water applications (which includes wastewater reuse applications). After establishing a cost effective small-scale model of a potential industrial manufacturing process, the prototype was tested with regard to water treatment efficiency. Test results on brackish type waters (1 000 mg/l), indicated that the industrial CDT™ prototype had an energy requirement of 0,594 kWh/1000 liters. Research results compared well to the laboratory scale energy consumptions of 0,1 kWh/1000 liters (Farmer⁵ *et al*, 1995) and to the best available existing brackish water membrane based desalination systems with energy requirements of 1,3 to 2,03 kWh/1 000 liters (AWWA, 1999). The thermodynamic minimum energy required (due to osmotic pressure) to desalinate a 0,1% or 1 000 mg/l sodium chloride solution, is 0,0234 kWh/1 000 liters.

Development and evaluation results indicated that CDT™ industrial modules could be manufactured cost effectively on a large scale and that such units have the potential to be very competitive with existing technologies with regards to overall operational and maintenance costs. Therefore Capacitive Deionization Technology™ can be viewed as a potential alternative to membrane technologies in the future. Regardless of the benefits to the potable water industry, CDT™ have the potential to incur a dramatic step reduction in the operational costs of desalination plants, which will make desalination a more viable alternative technology for large-scale agricultural and industrial uses.

KEY WORDS: brackish water, carbon aerogel, desalination, electrochemical, Capacitive Deionization Technology™.

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NOMENCLATURE / TERMINOLOGY AND UNITS

Standard Symbols

Unless stated otherwise the symbols used in this manuscript have the following meanings and if no dimension appears in brackets it means that the symbol is dimensionless.

A	Unit Area (m^2)
C	Capacitance (F)
d	Distance (m)
E	Energy (J)
E_0	Standard Redox Potential
F	Faraday's constant (= 96 487 C/mol)
gpd	gallon per day
I	Applied Electric Current (A)
i	Current density (mA/cm^2 or A/m^2)
lpd	liter per day
m	mass (kg)
mgd	million gallons per day
mg/l	milligrams per liter
n	Number of electrodes
P	Power (W)
Q	Electric Charge (C)
R	Electric resistance (Ω)
T	Temperature ($^{\circ}\text{C}$)
V	Volume (<i>l</i>)
V	Applied electrical potential (V)

Standard Abbreviations

AA	Atomic Adsorption Spectroscopy
BET	Brunauer-Emmett-Teller
CDT™	Capacitive Deionization Technology™
CBMA	Coal Bed Methane
ED/EDR	Electrodialysis/Electrodialysis Reversal
LLNL	Lawrence Livermore National Laboratory
RO	Reverse Osmosis
TDS	Total Dissolved Solids

Unit Conversions

1 acre-foot = 43 560,17 ft³ = 1 233,49 m³ = 1 233 486,65 liters

1 US gal = 3,785 liters

Numeric Conventions

As this dissertation is submitted to a South African and metric orientated University the following numeric conversions were followed.

- Thousands are separated by a space and not by a comma as per US practice.
Example 1 000 and not written as 1,000.
- A comma indicates fractions and not a point as per US practice.
Example: 5,5 is equal to 5.5 (US numeric system)

CHAPTER 1

INTRODUCTION

“We have made some exceptional scientific advances in the last decade and some of them – they are not as spectacular as the man-in-space, but are important..... If we could ever competitively, at a cheap rate, get fresh water from seawater, that would be in the long-range interests of humanity and would dwarf any other scientific accomplishment”.

John F. Kennedy: April 12, 1961

1.1 BACKGROUND

Capacitive Deionization Technology™ (CDT™) is a low-pressure non-membrane desalination process, with the potential to be a “power tool” in the desalination toolbox of the future (Farmer⁵ *et al.*, 1995). However at the time when this research was started in 1998, the technology was only at the laboratory scale level. The research objective was to move from laboratory scale to industrial scale by developing and evaluating the first industrial CDT™ prototype.

The motivation for this research came from the continuous global need to improve on existing desalination technologies to facilitate a major step-change in the overall cost of desalinated water to make it viable not only for potable use, but also for industrial and agricultural uses as well (USA-Bureau of Reclamation, 2004). It is important to view the research conducted for this dissertation, against the existing world water crises, which is briefly summarized in the rest of this section.

The Problem, Solution and Tools

The existing global water crises is covered in detail by various authors (Simon, 1994/1998; Gleick, 1993/ 2000; Postel, 1992; Montaigne, 2002), where they discuss several aspects of the growing need for water over the next century.

Solutions require both national and international measures be taken, including resolution of water disputes and increased funding for desalination research and alternative technologies. One of the key tools to resolve future international water crises is the continued research into methods that will provide low-cost desalination. Thereby creating greater economic and political stability in many regions of the world, where scarcity of water could lead to warfare in the same way that oil has lead to wars in the past (Simon, 1998).

“The consequences of the increasing global water scarcity will largely be felt in the arid and semi-arid areas, in rapidly growing coastal regions and in the megacities of the developing world. Water scientists predict that many of these cities already are, or will be, unable to provide safe, clean water and adequate sanitation facilities for their citizens — two fundamental requirements for human well being and dignity.” (United Nations, 1999)

Already in 1992, more than 7 500 desalination plants operated worldwide, turning 4,8 billion cubic meters of salt water into fresh water annually. Nevertheless, this accounts for only one percent of the world's water use. The reason for desalination's small contribution to the water supply is its cost (Postel, 1992). Most existing technologies like reverse osmosis and distillation require a great deal of energy. Even nuclear power has proven too expensive for large-scale desalination.

Existing advances in membrane technology is gradually reducing the required cost to produce potable water for human consumption. However, membrane technologies are not yet economically viable for the mass desalination of industrial and agricultural markets. These markets utilize $\pm 85\%$ of all water used by humanity (Simon, 1998). Existing energy consumption levels, as for membrane processes, would need to be dropped drastically before desalination becomes a source for industrial and agricultural water supply (USA-Bureau of Reclamation, 2004).

Most of the existing industrial scale desalination facilities get their energy from the combustion of fossil fuels, and thus in effect exchange potable water for CO₂, which causes global warming and eventually contributes to the demise of fresh water (Simon, 1998). As a result, Global warming increases the need even more for additional desalination. Therefore, it is imperative to find more energy efficient methods to desalinate water. Electrochemical desalination tools like Capacitive Deionization Technology™, as the first new desalination technology in over 50 years (Farmer⁵ *et al.*, 1995), have the potential to be such an energy efficient desalination method.

1.2 OBJECTIVES OF RESEARCH

CDT™ has been identified as a potential mass desalination alternative in laboratory conditions by Lawrence Livermore National Laboratories (Berkeley, USA). The overall objective for this research was to convert a laboratory scale CDT™ system into an industrial system to be used in the “real world”. Previous laboratory scale test work has been conducted successfully (Farmer^{1,2,3,4,5,6,7} *et al.*), but in order for the technology to be evaluated a potential competitor for existing technologies, a more industrialized prototype test unit was needed.

The research objective was to develop and evaluate an “industrially re-producible” CDT™ module by using the initial laboratory scale test work as a starting point. “Industrially re-producible” in this contents meaning a small-scale model of a future industrial manufacturing process.

Once a successful industrial prototype is created, an evaluation phase would be used to determine if the industrial CDT™ prototype could compete as a unit alternative to desalination processes in the future. The following criteria were identified to serve in the comparison of a “real world” CDT™ prototype unit to other desalination processes:

- i) Feed and product water quality requirements

- ii) Energy consumption per volume water treated
- iii) Pre-and-post treatment requirements
- iv) Overall water recovery rate
- v) Automatic Control or Operation/Maintenance Requirements
- vi) Fouling and scaling tendencies

By comparing these six operational parameters to existing desalination technologies like reverse osmosis and electrodialysis, it is possible to establish the potential of CDT™ as a future alternative desalination method.

1.3 SCOPE OF RESEARCH

Due to the relatively young (less than 10 years) nature of this technology, most of the research had to be conducted in the USA, more specifically Tucson, Arizona and San Diego, California (both areas are considered water poor, with ample brackish water). It must further be noted that although various international patents currently exist for the electrochemical desalination of brackish and seawater, the research conducted for this dissertation focused on Capacitive Deionization Technology™ specifically.

It was further decided to limit the scope for the research, to brackish water applications. The main reasons for this scope selection was that 70% of the worlds available ground water is brackish (Simon, 1998) and the need for desalination of brackish water sources is increasing more rapidly than the need for seawater desalination (International Desalination Association, 1997).

Also, initial laboratory test work at LLNL has indicated a major energy benefit for specifically brackish water applications (Farmer⁵ *et al*, 1995). It must be noted that CDT™ could also be a future cost effective desalination tool for seawater applications (Farmer⁷ *et al*, 1995), however seawater applications did not form part of this dissertation's scope.

Capacitive Deionization Technology™ has an extremely wide potential application field, it was therefore decided to limit the scope of this research to brackish desalination applications, namely the removal of ions or dissolved solids from brackish water sources like ground waters, secondary municipal effluent, industrial effluent, river and dam waters.

Other potential future applications of CDT™ include:

- i) Boiler feedwater treatment
- ii) Ultrapure water production
- iii) Hydrogen fuel cell water treatment
- iv) Selective removal of resources dissolved in water streams like precious metal extraction and recovery. For example, dissolved gold recovery from water-based streams.
- v) Seawater desalination.

The research scope for this dissertation can be summarized as follow:

Develop (Design & Manufacture) an industrial scale CDT™ prototype, based upon LLNL laboratory scale test work and evaluate it as a viable industrialized desalination technology by focusing on brackish water applications.

1.4 METHODOLOGY

The following research methodology was used:

- i) **Background and Literature Review:** Conduct a thorough literature review of CDT™ research already conducted. The literature review included an intensive review of existing desalination technologies to determine realistic evaluation criteria for the CDT™ industrial prototype.

ii) **Development Phase:** Design and manufacture an industrial prototype unit.
This phase served as the main research objective.

iii) **Evaluation Phase:**

- Establish experimental operating procedures - Collect and manage data.
- Compare desalination efficiency and energy requirements of the “real world” CDT™ prototype unit to previously conducted laboratory scale CDT™ experiments.
Compare desalination efficiency and energy consumption and overall cost (capital and operations/maintenance) to existing technologies.
- Economics Evaluation.: Estimate CDT™ treatment costs and compare to existing technologies to determine if the technology has the potential to be competitive in the future.

iv) **Conclusion and Recommendations:** If results from a “real world” CDT™ unit compares well to existing technologies, then it would have the potential to be an alternative desalination technology, once manufacturing and industrialization of the full-scale units are complete.

The above-mentioned methodology, which was followed to prepare this dissertation, can be illustrated graphically as per **Figure 1.1**.

1.5 FLOW DIAGRAM OF DISSERTATION PREPARATION.

Figure 1-1 illustrates the dissertation planning and preparation process.

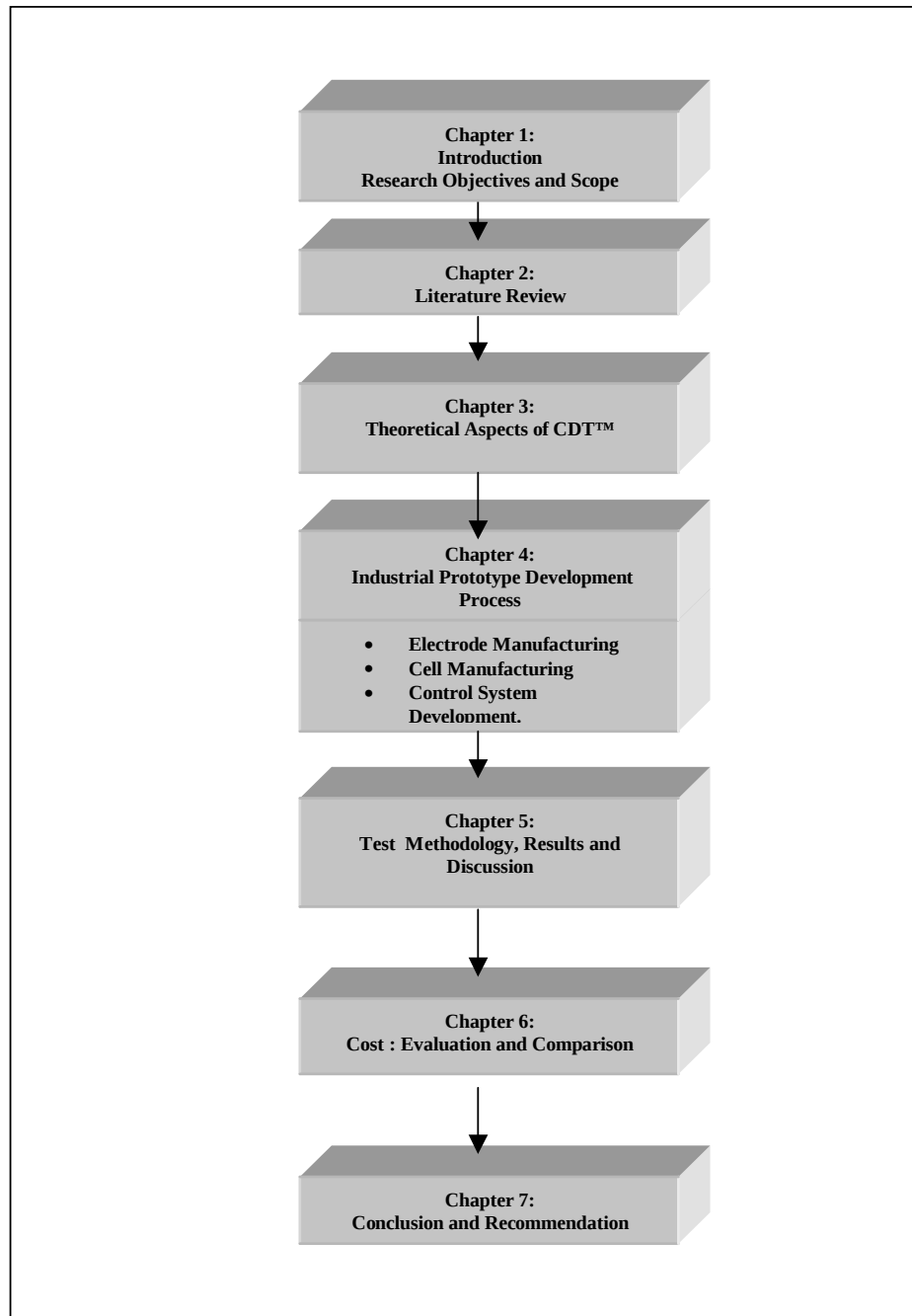


FIGURE 1-1: Flow Diagram of Dissertation Preparation

CHAPTER 2

LITERATURE REVIEW

Existing information, with regard to the various desalination technologies, and more specifically CDT™, was reviewed to assist with the design/manufacturing of an industrial prototype test unit, and with planning the required evaluation (test work) methods. To effectively evaluate CDT™ as an alternative desalination technology, a thorough understanding of the latest benefits and disadvantages of existing technologies was required.

2.1 EXISTING TECHNOLOGIES

There are several existing desalination technologies in use, with each source water presenting its own unique design and operational challenges. Desalination technologies are primarily used to reduce the total dissolved solids content of a source water. Typical applications are potable water, boiler feed water, and ultra pure water production. Existing competing desalination technologies in use on a global scale can be categorized into thermal and membrane processes.

Other processes such as freezing, gel filtration, and two-film gas membranes process are in research and did not form part of this dissertation's literature survey.

Table 2.1 summarizes the main technologies in each category with a description of the basic operating principle. Ion exchange technologies are also listed as they form part of the overview of existing technologies used to remove ions. However, a typical ion exchange technology does exactly what its name implies, it exchanges one undesirable ion for a more acceptable ion on the solid surface of a resin. Therefore, depending on the type of resin used, the overall TDS content of the source water is not really reduced. However, residential water softeners (regenerated with sodium chloride) are in wide use today, and CDT™ is a potential alternative to traditional ion exchange softeners.

Table 2.1: Existing Desalination Technologies and Operating Principles

Technology	Typical Application	Operating Principle
Thermal Processes		
Multistage Flash Evaporation (MFE)	Sea water desalination	Thermal evaporation. Less scale formation problems as compared to submerged tube distillation.
Multiple effect Distillation with Mechanical Vapor Recompression (MED-MVR)	Sea water desalination	Thermal evaporation with mechanical vapor recompression to improve energy efficiency.
Multiple Effect Distillation with Thermal Vapor Recompression (MED-TVR)	Sea water desalination	Thermal evaporation with thermal vapor recompression. More energy efficient than typical direct distillation, but less energy efficient than MVR.
Membrane Processes		
Reverse Osmosis	Sea water and brackish water desalination.	Pressure driven and diffusion controlled membrane process. Removes particles down to 0,0001 µm.
Nanofiltration	Industrial process/waste water and potable water treatment	Pressure driven and diffusion controlled membrane process. Removes particles down to 0,001 µm to 0,01 µm.
Ultrafiltration	Industrial process/waste water and potable water treatment	Pressure driven membrane process, but does not remove ions. Removal of dissolved substances are based on a sieving mechanism, down to 0,01µm. to 0,1 µm.
Microfiltration	Industrial process/waste water and potable water treatment	Pressure driven membrane process, but does not remove ions. Removal of substances are based on a sieving mechanism. 0,1 µm. to 1,0 µm.
Electrodialysis/Electrodialysis Reversal	Primarily brackish water desalination	Charge driven membrane process that removes ions, but not turbidity or micro-organisms.
Ion Exchange Processes		
Anion/Cation Exchange	Boiler feed water and water softening.	Anion and Cation ions in a source water is exchanged for more desirable, less troublesome ions.
Electro deionization (EDI)	Ultra pure water production.	Charge driven ion exchange process.

Data Source: Frammer⁵ *et al*, 1995

One of the main operating cost components for the desalination of sea-and-brackish water is the amount of energy required to produce a fixed volume of product water. This is also the reason why energy consumption formed primary criteria for evaluating CDT™ as a potential alternative desalination technology. **Table 2.2** lists the average energy requirement for some of the main desalination technologies. As the two main source waters are sea water and brackish water, the associated energy requirements are listed as such.

Table 2.2 : Energy Requirement Per Desalination Technology

Desalination Technology	Energy Requirement
Mechanical Vapor Compression (MVR)	6,6 kWh/m ³ (~ 25 Wh/gal) – Sea Water
Multiple Effect Distillation with Mechanical Vapor Compression (MED-MVR)	7,9 – 10,8 kWh/m ³ (30-41 Wh/gal) – Sea Water
Multiple Effect Distillation with Thermal Vapor Compression (MED-TVR)	56,8 – 83,2 kWh/m ³ (215-315 Wh/gal) Sea Water
Multi Stage Flash Evaporation (MFE)	~ 84,5 kWh/m ³ (~320 Wh/gal) – Sea Water
Reverse Osmosis (RO) (Depending on energy recovery)	6,6 – 9,3 kWh/m ³ (25-35 Wh/gal)– Sea Water 2,3 kWh/m ³ (8,5 Wh/gal)- Brackish Water
Electrodialysis	2,03 kWh/m ³ (7,7 Wh/gal) – Brackish Water
CDT (Includes Energy Recovery)	~ 4.2 – 8.5 kWh/m ³ (16-32 Wh/gal) – Sea Water 0,05-0,1 kWh/m ³ (0,2 – 0,4 Wh/gal) – Brackish Water

Brackish Water TDS : 800 – 3 200 mg/l

Sea Water TDS : 35 000 mg/l

Data Source: CDT - Lawrence Livermore National Laboratory, USA
Other Desalination Technologies - AWWA

Initial laboratory test work (Farmer⁵ *et al*, 1995) indicated that the potential energy advantages of CDT™ to that of thermal processes are dramatic and very competitive with regards to membrane process.

The energy requirements stated in **Table 2.2**, are typical and more accurate energy consumptions are available per technology for specific TDS removal requirements (Farmer⁶ *et al*, 1997). In 1993 typical desalination costs could be summarized as follows: reverse osmosis costing US \$97 to US \$322 per acre foot, while distillation costs ranged from US \$530 to US \$880, freezing US \$299 to US \$513, and electrodialysis US \$224 to US \$435 per acre foot (Gleick, 1993). More detailed RO costs are presented in section 2.2.

Figure 2.1 illustrates the installed desalination capacity in 1998 on a global basis, as listed by the International Desalination Association.

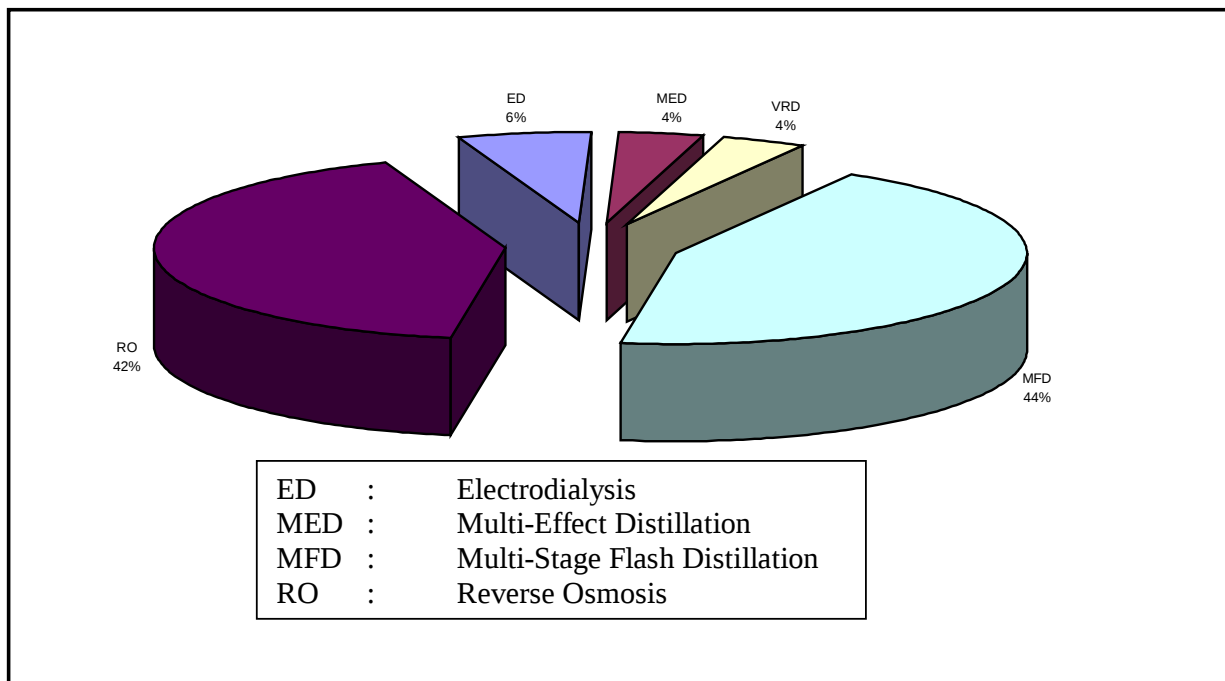


FIGURE 2.1: Installed Global Desalination System (1998)

Source: International Desalination Association

2.2 MEMBRANE PROCESSES

2.2.1 OVERVIEW

As illustrated above, with regards to energy requirements, membrane processes will ultimately be the main competitor to alternative desalination technologies, for example CDT™. It was therefore important to review and understand the existing status of membrane processes, specifically reverse osmosis. A literature study followed to ensure that the most recent data is used in the comparing/evaluation of CDT™ as an alternative technology to membrane process.

Reverse osmosis, nanofiltration, and electrodialysis/electrodialysis reversal are the membrane processes with comparable applications to CDT™. For the desalination of sea water via membranes, RO is the existing technology of choice. High pressures (5 515 to 8 273 kPa or 800 to 1 200 psi) are typically required for sea water desalination. Brackish water desalination via RO requires less pressure, typically 1 723 – 2 758 kPa (250 – 400 psi) (AWWA M46, 1999).

Membrane processes are capable of desalting, softening, removing THM precursors, pathogens, suspended particulate material, and specific organic compounds. A potential alternative technology must also be able to deliver at least the same level of treatment, either directly or by secondary integrated technologies.

Most source waters used to feed membrane processes must undergo some form of pretreatment. Acid and/or antiscalant addition are required to prevent precipitation of salts during membrane filtration, followed by 5 to 15 µm cartridge filtration. Additional pretreatment might be required if the source water contains excessive fouling materials. After membrane filtration, typical potable water post treatment includes processes like aeration-degasification, disinfection, and corrosion control. Specific care must be taken in feed waters containing high Ferrous (Fe^{2+}) concentrations, as not to introduce oxygen and thus precipitate the iron as Ferric (Fe^{3+}) compounds.

A thorough understanding of source water characteristics is vital to the successful design and operation of a membrane plant. Brine concentrate produced during the operation of a membrane plant, depending on the plants location, might require significant treatment before disposal. In the USA, the concentrate is regulated as a industrial waste, and a permit from the USEPA (United States Environmental Protection Agency) is required for disposal. Existing membrane brackish water desalination facilities in the USA vary in size from 50,5 liters/second (800 gpm) to 613,3 liters/second(14 mgd). With the average size at 22 liters/second (0,5 mgd).

Membrane processes are typically used in the following applications:

- Desalting (TDS removal)
- Disinfection By-Product Precursor Removal
- Hardness, Color and Turbidity Removal
- Inorganic Chemical Removal
- Nitrate Removal
- Fluoride Removal
- Synthetic Organic Chemical Removal
- Pathogen Removal

2.2.2 COST

Capital Costs

For reasons mentioned in Chapter 1, the scope of this dissertation was limited to brackish water applications. In Chapter 6, CDT™ is evaluated by comparing construction and operations and maintenance costs to that of reverse osmosis. For specifically brackish type feed water construction costs can vary considerably depending on site-specific factors. Site-specific factors that have an influence on a membrane plant construction costs include:

- Plant size and capacity
- Blending of source water with permeate.

-
- Source water quality (TDS and other constituents removal required)
 - Concentrate disposal
 - Intake type for source water.
 - Pre-and post treatment requirements
 - Indirect costs

Typical construction costs for a brackish water (Feed TDS 2 000 mg/l) membrane treatment plant, with a capacity of 3,785 Ml/d (1 mgd) is estimated at US \$0,82/lpd (US \$3,14/gpd) (AWWA M46, 1999: 94). For the following estimate, the source water is from a natural gas well field and concentrate disposal is to a surface body of water. Site specific factors are very important and can have a huge influence on the final construction costs. For the above mentioned example (1 mgd brackish water treatment plant) the construction cost can be as low as US \$2 million, or as high as US \$7 depending on site specific requirements. The construction cost can further be broken down as follows:

- Membranes and Skid: 26%
- Storage and Pump: 25%
- Feed: 14%
- Building: 10%
- Cleaning: 2%
- Instrumentation and Control: 5%
- High-Pressure Pumping: 7%
- Electrics: 4%
- Pretreatment and Post treatment: 8%

The unit costs for process equipment decreases as the overall plant capacity increases due to economy of scale factors. The unit process equipment capital costs for a 20 mgd plant is roughly two thirds that of a 1 mgd plant (US \$1,49/gpd for a 1 mgd plant vs. US \$1,00/gpd for a 20 mgd plant) (AWWA M46, 1999).

Operations and Maintenance Costs

From a survey conducted in the USA for 22 brackish water treatment plants (AWWA M46, 1999: 5), the average operations and maintenance cost was US \$0,33 per 1000 liters (US \$1,28 per 1000 gallons) of permeate produced.

The operations and maintenance costs can be broken down as follows:

- Management: 22 % (3.2 persons per 1 mgd capacity)
- Power: 33 %
- Chemicals: 16 %
- Maintenance: 7 %
- Other: 22 % (including membrane replacement)

For a brackish water source (< 2 000 mg/l TDS), ED/EDR and low-pressure reverse osmosis have very competing power consumption rates at around 1,3 kWh/1000 liters (4,9 kWh/1000 gallons).

2.3 CAPACITIVE DEIONIZATION TECHNOLOGY™

Non-membrane electrochemical technologies like Capacitive Deionization Technology™ (CDT™) have the potential to desalinate, remediate nuclear waste streams, and recover resources all via the same basic principal. The principle and mechanism used in CDT™ is not a recent discovery, however researchers were challenged by identifying an optimum material for electrode manufacturing (Farmer⁶, *et al*, 1997). Recent advances in material sciences lead to the development of materials like carbon aerogels and carbon nanotubes. CDT™ has been developed as a non-polluting, energy-efficient and cost-effective alternative to ion exchange, reverse osmosis, electrodialysis, and evaporation.

Extensive laboratory scale research regarding CDT™ has been completed at LLNL prior to establishing the research objectives for this dissertation, which were to design, manufacture, and test an industrial prototype module based upon the laboratory test work already completed (Farmer¹, 2000; Farmer², *et al*, 1995; Farmer³, *et al*, 1996; Farmer⁴, *et al*, 1995; Farmer⁶, *et al*, 1997; Farmer⁷, *et al*, 1995; Farmer⁸, *et al*, 1996). Chapter 3 will describe CDT™ in more detail, and summarizes some of the earlier research work conducted at LLNL. CDT™ has a number of potential advantages over current membrane and distillation processes:

- i) Less energy is needed for the desalination process because high-pressure pumps are not required, particularly for the desalination of brackish water where the actual work is only performed on the unwanted species and not on the total volume of water, as is the case with membrane and distillation processes.
- ii) Due to the low amounts of energy required (potentially 30% to 60% less than existing technologies), it is possible to make use of existing solar/wind power technology to power remote desalination units. It can also be used as a sustainable development water treatment tool in communities where no electrical power is accessible and the water quality available is of a non-potable nature.
- iii) The carbon aerogel electrodes can withstand much higher temperatures than membranes, and thus can be more efficient for applications such as boiler condensate polishing, and fuel cell water deionizing systems.
- iv) The fact that the liquid flows in a non-restricted path ensures that no aggressive secondary effluents are generated due the extensive cleaning operations as required by today's reverse osmosis type processes.
- v) Volumes of brine that need to be disposed of are less than that for membrane processes due to the re-use of brine in the regeneration phase. As brine disposal is a problem, especially at inland applications, a smaller brine volume to manage is a big advantage.
- vi) High-pressure equipment is not required, and the use of durable electrodes further decreases the operations and maintenance cost of CDT applications.

vii) As the modules act as capacitors, the actual energy recovery possible could be far more efficient than the methods used in current membrane processes.

However, it is important to realize that CDT™ currently also has some disadvantages :

- As the technology is relatively new compared to membrane processes, no long-term operational data is available for industrial size systems.
- As long term operational data is not available yet, it is difficult to predict the electrode lifetime and/or the effect of electrode fouling due to biological and/or chemical means.

CHAPTER 3

THEORETICAL ASPECTS OF CDT™

3.1 BASIC ELECTROCHEMICAL CELL

In order to fully explain capacitive deionization, it is necessary to review some basic electrochemical principles. The basic electrochemical cell consists of a pair of electrodes, connected externally and immersed in an electrically conducting liquid or paste. The liquid is usually referred to as the electrolyte. **Figure 3.1** illustrates the basic electrochemical cell.

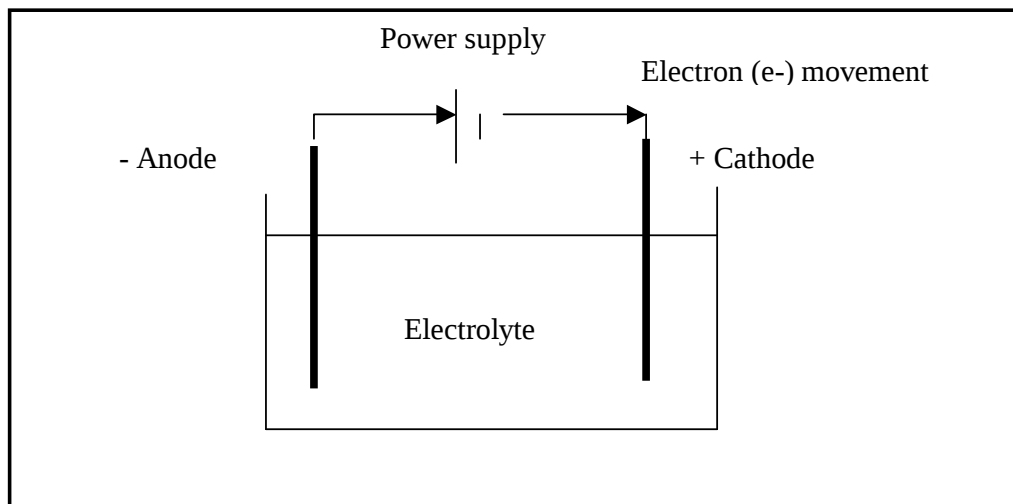


FIGURE 3.1: Basic Electrochemical Cell

The anode and cathode can be made out of any material, not necessarily only metals. In the case of capacitive deionization, the material is an inert carbon based solid (aerogel or other nanostructure). When two dissimilar metals with different electrochemical potentials are used as the anode and cathode, a current will flow in the external connection, without the need for a power supply (battery or voltaic cell). In a case where the anode is made from mild steel a typical anode reaction will be as follows:



The above-mentioned reaction is a typical corrosion reaction, taking place on the surface of steel in contact with an electrolyte. To balance the overall reaction, a cathodic half reaction is needed in both the cases of an electrochemical or voltaic cell. Typical reactions that take place at the cathode are as follows:

- Hydrogen Liberation: $2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2$ (2)
- Acid Solutions - Oxygen Reduction: $\text{O}_2 + 4\text{H}^+ + 4\text{e} \rightarrow 2\text{H}_2\text{O}$ (3)
- Basic/Neutral Solution Oxygen Reduction: $\text{O}_2 + 4\text{H}_2\text{O} + 4\text{e} \rightarrow 4\text{OH}^-$...(4)
- Metal Ion Reduction: $\text{Metal}^{+3} + \text{e} \rightarrow \text{Metal}^{+2}$ (5)
- Metal Plating: $\text{Metal}^+ + \text{e} \rightarrow \text{Metal}$ (6)

The first three reactions are the most common, and the last two reactions only occur in certain conditions, typically when high concentrations of chromium, copper and/or zinc are present in the solution. Usually only wastewater from plating plants contains such high concentrations.

The above mentioned basic electrochemical principles are applicable to all electrochemical type water treatment technologies, including CDT™. Water treatment technologies either use the electrode in the solid state (e.g. Electrodialysis, electrodeionization and CDT™), or in the colloidal state (e.g. coagulation and flocculation) to achieve a specific water treatment goal. The goal is usually to remove an unwanted ion and/or particle from solution, thus purifying the electrolyte (water).

Electrode Surface Chemistry

When an object is electrically charged in an electrolyte (voltaic or electrolytic cell), an environment is created around the object, which has unique physical features. Such an object can be a solid-state electrode or a colloidal particle. There are interactions between the dissolved ions and the charged surface, the ions and the bulk liquid, and between the bulk liquid and the solid surface.

Water is a polar molecule, and is thus also electrochemically involved. The electrodes in capacitive deionization and other electrodes generally follow the electric double layer theory. This theory states that if an electrode is negatively charged and immersed in an electrolyte, then positively charged ions and solvent molecules (water in the case of this research) are adsorbed onto the surface, thus forming a layer of positive charge on the surface.

A second negative layer is formed by negative ions attracted to the positive charge, thus the double layer. The second layer contains less charge (negative) as compared to the total charge (positive) of the first layer. This is due to the effect of distance and shielding by solvent (water) molecules. Water molecules also undergo Brownian movement between the layers (Heald & Smith, 1974). **Figure 3.2** illustrates a simplified version of the Stern Double-Layer Theory.

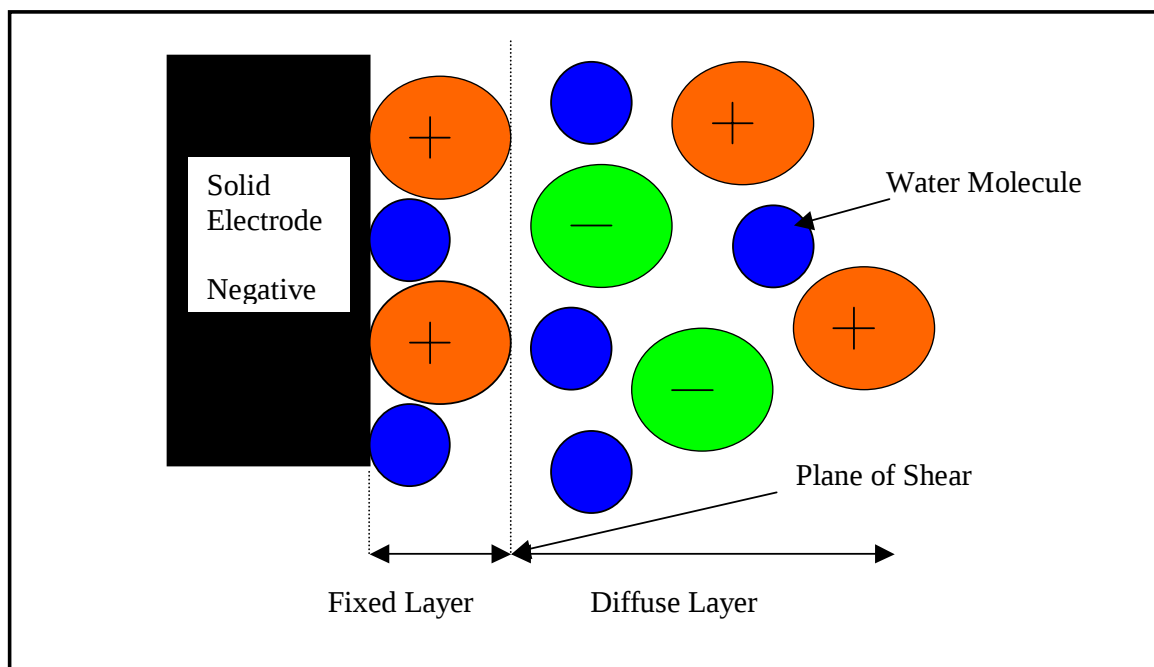


FIGURE 3.2: Stern Electric Double Layer Theory

Capacitance

Two parallel plates immersed in an electrolyte form a parallel plate capacitor. Electrical energy is stored in the capacitor when charged by an applied potential. The capacitance can be calculated by (Halliday & Resnick, 1988: 627):

$$C = Q/V \quad (3.1)$$

$$C = \frac{\kappa \cdot \epsilon_0 \cdot A}{d} \quad (3.2)$$

κ = Dielectric constant for a specific medium

= 80.4 for water at 20 °C and 78.5 for water at 25 °C

ϵ_0 = $8.85 \times 10^{-12} \text{ C}^2/\text{N.m}^2$

A = Area of electrode plates

d = Distance between the plates

Capacitors can be connected in parallel or series, and the equivalent capacitance can then be calculated by:

$$\frac{1}{C_{eq}} = \sum_n C_n \quad \text{Capacitors in Parallel} \quad (3.3)$$

$$\frac{1}{C_{eq}} = \sum_n \frac{1}{C_n} \quad \text{Capacitors in Series} \quad (3.4)$$

3.2 CAPACITIVE DEIONIZATION

CDT™ utilizes all of the above-mentioned basic electrochemical principles to remove dissolved ions from an electrolyte (water) stream. **Figure 3.3** illustrates the basic operating principle applicable to CDT™.

An electrolyte stream flows between two electrodes. The electrodes typically have a potential difference of 1,2 – 1,5 volts (Direct Current). The various cations (positive charge) and anions (negative charge) in solution are attracted to opposite charged electrodes. The ions are adsorbed on the electrode surface and held in electric double layers (Stern Double Layer Theory). The normal operational cycle continues until the electrode surfaces are saturated with adsorbed ions.

During the regeneration cycle, the two electrodes are shorted, or to recover stored energy the capacitor can be discharged under controlled conditions. The ions are released into a rinse stream, which can have a much higher TDS level, as compared to the feed stream. CDT™ does not require high-pressure pumps, which contributes to the overall low energy requirements.

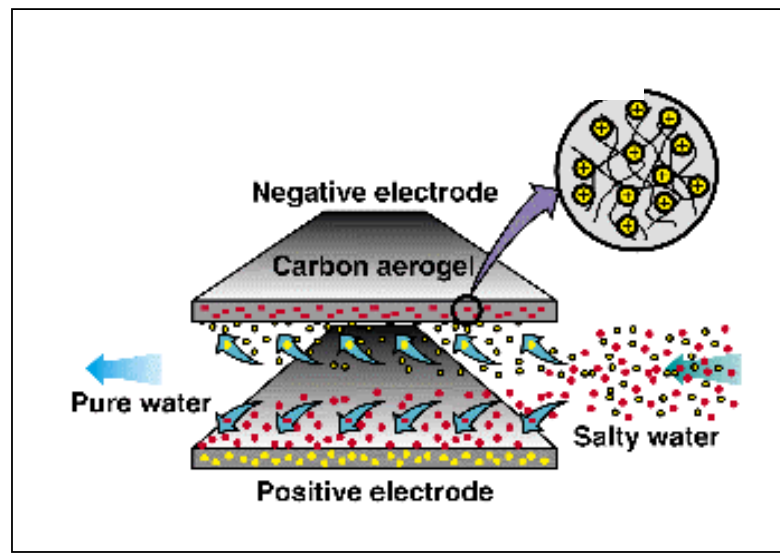


FIGURE 3.3: Illustration of Capacitive Deionization Process

Energy Requirement

The minimum theoretical work required by an isothermal process to separate seawater (35 000 mg/l) and brackish water (1 000 mg/l) into saturated brine and a 10 mg/l potable water stream can be calculated. The estimated minimum work required for desalination of seawater (35 000 mg/l TDS) and brackish water (1 000 mg/l TDS) are ~ 1,06 Wh/liter (4 Wh/gal) and 0,005 Wh/liter (0,02 Wh/gal) respectively (King, J.D, 1980 : 662).

The energy required by CDT™ is approximately $\left(\frac{Q \cdot V}{2}\right) \cdot (1 - e^{(-t/\tau)})$, where Q is the stored electrical charge, V is the voltage between adjacent electrodes, t is the charging time, and τ is the time constant of the CDT™ module.

The time constant is determined by the internal resistance and capacitance of the CDT™ cell (Farmer⁵,1995). Earlier laboratory work by Dr. Farmer and his team at LLNL determined that CDT™ could effectively desalinate brackish water (1 000 mg/l) by using only 0,095 kWh/m³ (0,36 Wh/gal). This laboratory CDT™ unit energy requirement served as a benchmark for the industrial prototype unit.

3.3 CARBON AEROGEL ELECTRODES

Carbon Aerogel is an ideal electrode material because of its low electrical resistivity ($< 40 \text{ m}\Omega \text{ cm}$), high specific surface area ($400 - 1\,100 \text{ m}^2/\text{g}$), and controllable pore size distribution ($< 50 \text{ nm}$). Aerogels are unique materials. They are known for their extremely low density, but because both their pores and particles are smaller than the wavelength of light, they have other important properties. Aerogels can be transparent, giving rise to the nickname "frozen smoke".

Discovered in the 1930s, they were initially thought to have no practical use. However, new and improved processing techniques, and newly developed varieties are beginning to prove their commercial potential.

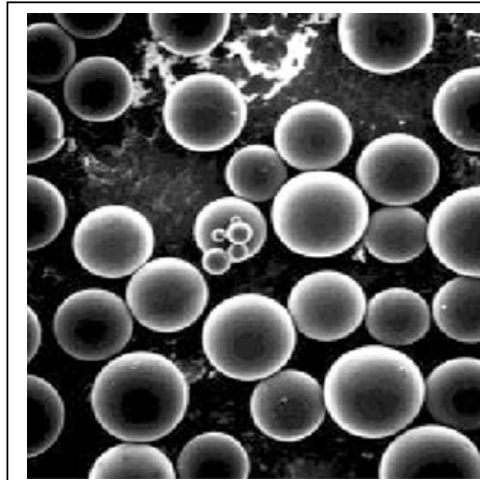
Aerogels can be made using several different compounds including silica, other metal oxides, resorcinol-formaldehyde (RF) and melamine-formaldehyde (MF). The RF and MF aerogels are pyrolyzed to form carbon aerogels. Each of these various aerogels was created for specific properties:

- Silica Aerogels - nonflammable, nontoxic, lightweight, transparent, and thermally stable to about 650°C, almost 30 times lighter than earlier aerogels, and possessing unique thermal and dielectric properties.
- Organic Aerogels (Carbon Aerogels) - created for their thermal capabilities, stiffer and stronger than silica aerogels. Carbon allows aerogels to become electrically conductive.
- Other Metal Oxide Aerogels

LLNL has been active in the development of carbon, silica and metal oxide aerogels. LLNL has developed patented methods for tailoring aerogel properties. These materials:

- Contain exceptionally large internal surface areas - 400 to 1 000 m²/g - about the size of one to two basketball courts
- Provide exceptional mechanical integrity, supporting over 1 500 times their own weight
- Provide exceptional optical clarity
- Are exceptionally poor conductors of heat and sound
- Can be manufactured with a low density so that it is nearly as light as air

Carbon aerogel can be produced as monoliths, composites, thin films, powders and microspheres. **Figure 3.4** illustrates a spherical carbon aerogel structure, magnified 300 times.



Scanning electron micrograph of carbon microspheres (300x). Although the aerogel structure within the microspheres cannot be delineated, it is clear that the particles are spherical with smooth surfaces.

FIGURE 3.4: Micrograph of Aerogel Microspheres

Monolithic aerogels are ideal for applications such as transparent window insulation, but the expensive processing equipment needed to produce these large aerogels has limited their commercial appeal.

Aerogel microspheres offer an attractive alternative to monolithic aerogels because they can be produced in a semi-continuous process. Silica microspheres have been produced commercially, and their thermal performance is known. Air-filled, thermal conductivities for monolithic aerogels are 12 m.W/m·K; for silica microspheres, they are 20 m.W/m·K.

Currently CDT™ utilizes a resorcinol-formaldehyde (RF) aerogel. Resorcinol-formaldehyde (RF) and melamine-formaldehyde (MF) microspheres should have even better thermal properties because their solid conductivity is lower than that of silica. RF microspheres can also be pyrolyzed in an inert atmosphere to produce carbon aerogel micro-spheres with properties different from those of conventional carbon blacks. Gas adsorption measurements reveal the microspheres to have cell-pore sizes greater than 100 nm and surface areas from 400 to 1 100 m²/g - similar to those of their monolithic counterparts. The solid matrix within the aerogel microspheres is composed of interconnected colloidal like particles or fibers with characteristic diameters of 10 nm. **Figure 3.5** shows a magnified version of the carbon fibers.

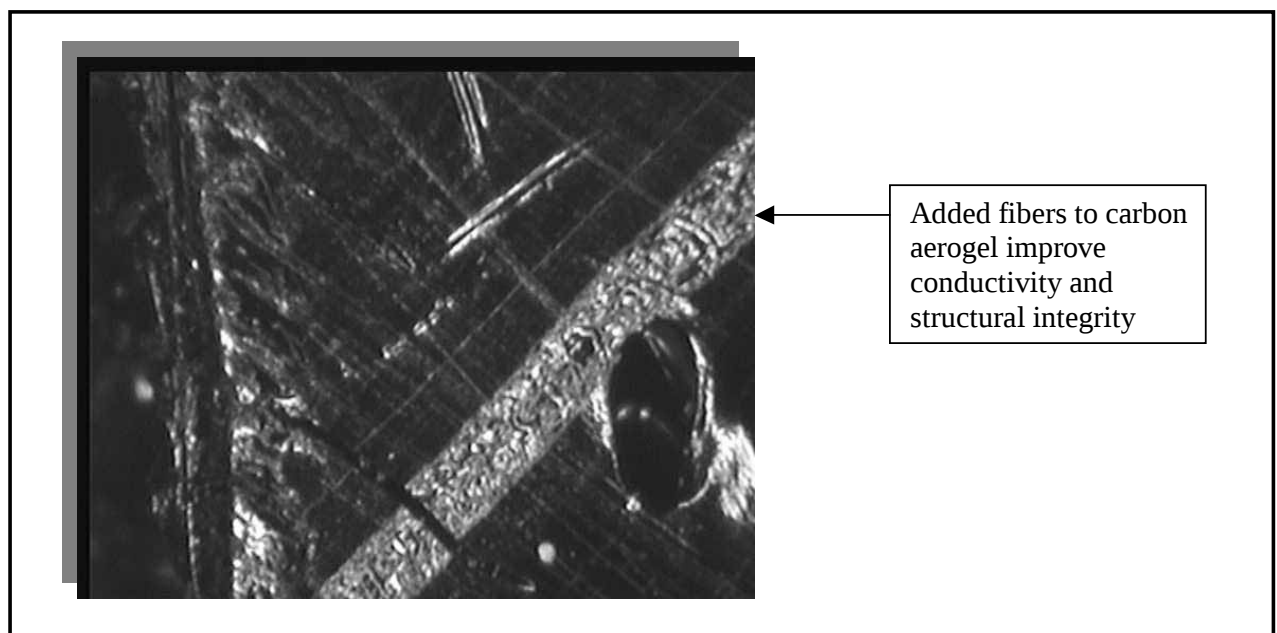


FIGURE 3.5: Magnified Aerogel Fibers

3.3.1 ELECTRICAL PROPERTIES

Dielectric Properties

Highly porous materials with unique nanostructures, aerogels exhibit unusual dielectric properties that are more like those of a gas than of a solid.

Their low dielectric constants, low loss tangents, and controllable thermal expansion properties will soon make aerogels the material of choice for thin films in high-speed, integrated digital and microwave circuitry.

- Dielectric constants of 1,008 to 1,990 (3–40 GHz)
- Loss tangents of 10^{-4} to 10^{-2} (3–40 GHz)
- Volume resistivities of 10^{13} to 10^{15} Ohm·cm
- Dielectric strengths of 120 to 140 kV/cm.

3.3.2 PHYSICAL PROPERTIES

Aerogels are the best thermal insulators available today. Two organic aerogels developed at LLNL have equivalent R-values of 12 when air-filled (equivalent to the insulating capacity of 152 mm (6 in.) of fiberglass batting) and greater than 38 when evacuated (equivalent to 483 mm (19 in.) of fiberglass). **Figure 3.6** shows the thermal conductivity of various types of aerogels and their associated relative densities.

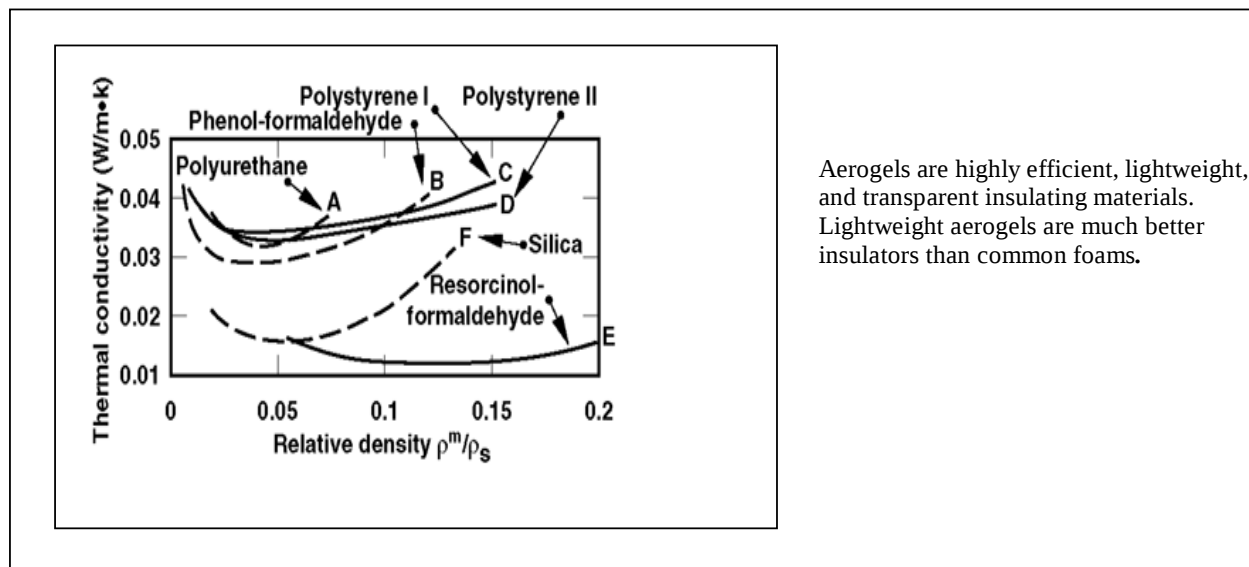


FIGURE 3.6: Thermal Conductivity of Aerogels

Measurable, low thermal conductivities:

- Silica aerogels at 300 °K and 1 atm have measured conductivities as low as 0,020 W/m·K (an R per inch value of about 7).
- Organic aerogels, like the existing RF aerogels in CDT™ have thermal conductivities of 0,012 W/m·K (an R per inch value of 12).
- Carbon particle-loaded (opacified) silica aerogels have thermal conductivities of 0,013 W/m·K (an R per inch value of 11).

Organic aerogel materials have lower intrinsic thermal conductivity than silica, and up to a factor of four higher infrared extinction coefficients than unmodified silica aerogel. Adding carbon particles to the silica aerogel decreases the dependence of the thermal conductivity on temperature. The dependence of thermal conductivity on density shows that conductivity is minimum at an optimal density, typically about 0,15 g/cm³.

The unique microstructure of aerogels - nanometer-sized cells, pores, and particles - means low thermal conduction and superior insulation. Thermal conduction through the solid portion of the aerogel is limited by the small connections between the particles making up the conduction path. Gaseous conduction is limited because the cells/pores are only the size of the mean-free path for molecular collisions - molecules collide with the solid network as frequently as they collide with each other. Radiative conduction is low because aerogels have small mass fractions and large surface areas, although conductivity increases with temperature. This feature makes CDT™ an ideal candidate for water treatment at high temperatures, like fuel cells or condensate treatment.

CHAPTER 4

INDUSTRIAL PROTOTYPE DEVELOPMENT PROCESS

4.1 BASIS OF DESIGN

As stated in Chapter 1, the main objective of this research was to take CDT™ from laboratory scale to a “real world” industrially reproducible prototype scenario. The research conducted for this dissertation regarding the design, manufacturing, and testing of an industrial prototype, would serve as a foundation to future commercialization efforts and industrial pilot scale testing projects. In order not to reinvent the wheel, the main components of the technology as identified by the original laboratory research conducted at Lawrence Livermore National Laboratories were used as a starting point in the development an industrial prototype.

Physical size and weight constraints limited the maximum practical size of a full-scale industrial CDT™ cell. To assist with future design/construction of industrial plants, and to ensure that a single treatment module is of a practical size, the design team decided that the basis for the design of an industrial unit is to be 1 000 ft² (92,9 m²) of aerogel/electrode surface area. Earlier laboratory test work indicated that on average, such an electrode surface area should be able to reduce the TDS of a feed stream by 1 000 mg/l at a flow rate of 1 000 gallons per day (3 785,4 liters per day). This basis of design would also make future scale-up formulations, more linear.

The above mentioned electrode surface area of 1 000 ft² (92,9 m²), should be viewed as a maximum and it is possible, that as the technology is developed further, the water production capacity per module would increase, due to material and module design improvements. For the development process, it was decided to make the industrial prototypes as a fraction of the above-mentioned maximum. Such a step would allow the development team to design, manufacture and evaluate various alternatives to optimize the prototype to be evaluated. The prototype was around 1/40th (per total aerogel surface area) the planned size of a full-scale industrial unit, with a total electrode surface area of $\pm 24,7$ ft² (2,29 m²).

LLNL laboratory experiments were conducted by utilizing extremely thin carbon aerogel films in expensive titanium housings. **Figure 4.1** illustrates the first laboratory scale capacitive deionization module developed by Lawrence Livermore National Laboratory.

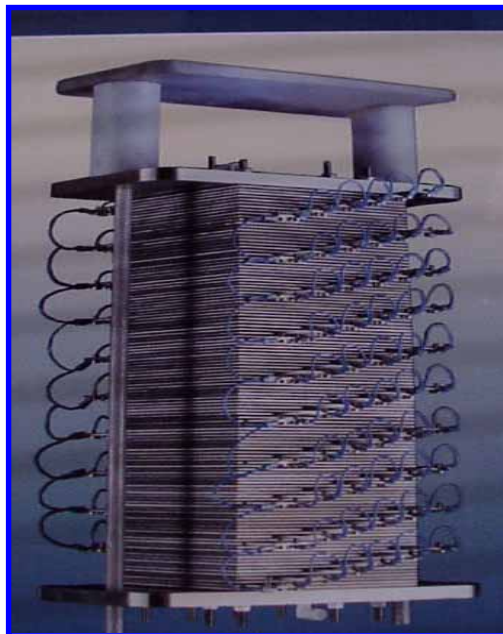


FIGURE 4.1: Laboratory Scale Capacitive Deionization Module : LLNL

Although these initial experiments were very successful ((Farmer¹, 2000; Farmer², *et al*, 1995; Farmer³, *et al*, 1996; Farmer⁴, *et al*, 1995; Farmer⁶, *et al*, 1997; Farmer⁷, *et al*, 1995; Farmer⁸, *et al*, 1996), the technology still needed to be taken to the next level to prove cost effective industrial scale manufacturing and operation in a “real world” environment.

4.2 THE DEVELOPMENT PROCESS

The development (designing, engineering and manufacturing) process can be broken-down into three phases. The three phases are discussed in paragraphs 4.2.1, 4.2.2 and 4.2.3, and can be summarized as follow:

Phase 1: Electrode Manufacturing Process Development

During this phase, the aerogel electrode pilot manufacturing process was established. The researcher functioned as a resident chemical engineer during this phase, to assist with the design and construction of the resorcinol/formaldehyde aerogel manufacturing process. Due to the hazardous nature of the manufacturing process, the researcher was also the lead environmental engineer, responsible for air quality monitoring and treatment to comply with the United States Environmental Protection Agency (USEPA) requirements.

Phase 2: Cell/Module Manufacturing Process Development

During this phase the aerogel electrodes manufactured in phase 1, needed to be stacked and housed in a single module. A module thus needed to consist of a series of electrode pairs, with each pair making-up the anode and cathode of a capacitor.

During this phase, the researcher worked with an electro-mechanical engineer in producing the housing module design specifications and drawings.

Specifications and drawings were submitted to a machining contractor for final manufacturing. Once manufactured, the researcher assisted in final assembly and quality control operations.

Phase 3: Control System Development

Once an industrial prototype alternative is successfully manufactured, it was needed to “plug” it into a control system to evaluate it’s water treatment efficiency. A control system was developed to switch between the two main cycles, which is operation and regeneration. During this phase the researcher collected and interpreted water treatment efficiency data for an instrumentation and control specialist, who was responsible for the electronic circuit design of the control system. Water samples were taken during operational and regeneration cycles, analysis was conducted and the data was used to optimize instrumentation and control specifications.

The end result of completing the above mentioned three phases, for various alternatives, was an operating industrial prototype system, ready for more intensive water treatment testing and the basis of design for future full size industrial units. The three development phases are discussed in more detail during the following three paragraphs, 4.2.1, 4.2.3 and 4.2.4. It should be noted that the following description of the manufacturing process is a summary, a lot more information was developed during this research period, but could not be published due to the propriety nature of the technology.

4.2.1 ELECTRODE MANUFACTURING PROCESS – PHASE 1

The aerogel originally used in laboratory experiments were paper thin and within titanium frames (See **Figure 4.1**). The laboratory scale method of construction was not cost effective for an industrial type unit. Therefore an electrode pilot manufacturing process was developed that represented a typical full scale manufacturing process. The raw materials for the manufacturing of carbon aerogel electrodes used in this research project are formaldehyde, resorcinol, and carbon fiber veil. A pilot electrode manufacturing process was constructed in Tucson, Arizona and can be described as per the following three stages:

Stage 1: Polymerization

During this stage, carbon fiber veil is trimmed in sections and set in a polypropylene mold. Next a formaldehyde/resorcinol resin was prepared via a batch mixing operation in 5-gallon (18.93 liter) batches. The carbon veil was placed in a polypropylene molds. The veil was soaked with the resin and the molds containing the resin/carbon veil sheets were staked in a drying oven.

The polymerization process was completed in a temperature controlled (85°C) oven over a period of 48 hours. The cured sheets were removed from the molds and solvent washed to eliminate any impurities and retained water. The solvent extracted sheets were then air-dried in ambient temperature.

Stage 2: Pyrolization

The air-dried polymerized sheets where then stacked in a furnace and connected to nitrogen gas to ensure a non-oxidizing environment.

The furnace temperature was controlled at 1 000°C for 72 hours. After pyrolyzation, the sheets were retort cooled in ambient temperature.

Stage 3: Cell Assembly

The carbon aerogel sheets were now ready to be stacked and included as electrodes in a specially machined polypropylene housing. A series of stacked electrodes in the polypropylene housing are known as a cell.

Electrode Production Quality Control

As in any manufacturing process, a quality control system had to be developed. After the manufacturing of the aerogel electrodes, a quality control test was conducted to ensure that the electrodes to be used in the prototype unit conformed to certain minimum standards.

Due to the fact that each pair of electrodes acts as a capacitor, the total energy stored and discharged from a electrode pair is measurable. The total potential capacitance of a series of electrodes or a cell can be calculated using equations 3.1 or 3.2 in Section 3. The energy storage capacity of an electrode is directly proportional to its ion storage capacity. A small quality control test unit was constructed whereby each batch of carbon aerogel produced could be quality controlled. One random sheet per batch were chosen and two 25 mm x 25 mm pieces were cut from the sheet. The two pieces of electrode were submerged in a 10 000 mg/l NaCl solution, at a fixed distance from each other. Energy to (capacitor charge cycle) and from (capacitor discharge cycle) the test capacitor could be determined by measuring the current (I) to the capacitor and potential difference (V) across the capacitor at fixed time intervals.

For the regeneration cycle, the capacitor was discharged through a resistor, and the associated energy calculated by means of the resistor size as well as the measured discharged current. The equations used to determine the energy for the charge and discharge cycles were as follows:

$$E = V \times I = I^2 \times R \quad (4.1)$$

Equation 4.1 was then used to generate quality control graphs, as illustrated in **Figure 4.2** for each batch of electrodes. **Figure 4.3** illustrates the laboratory set-up used to generate quality assurance data during electrode production.

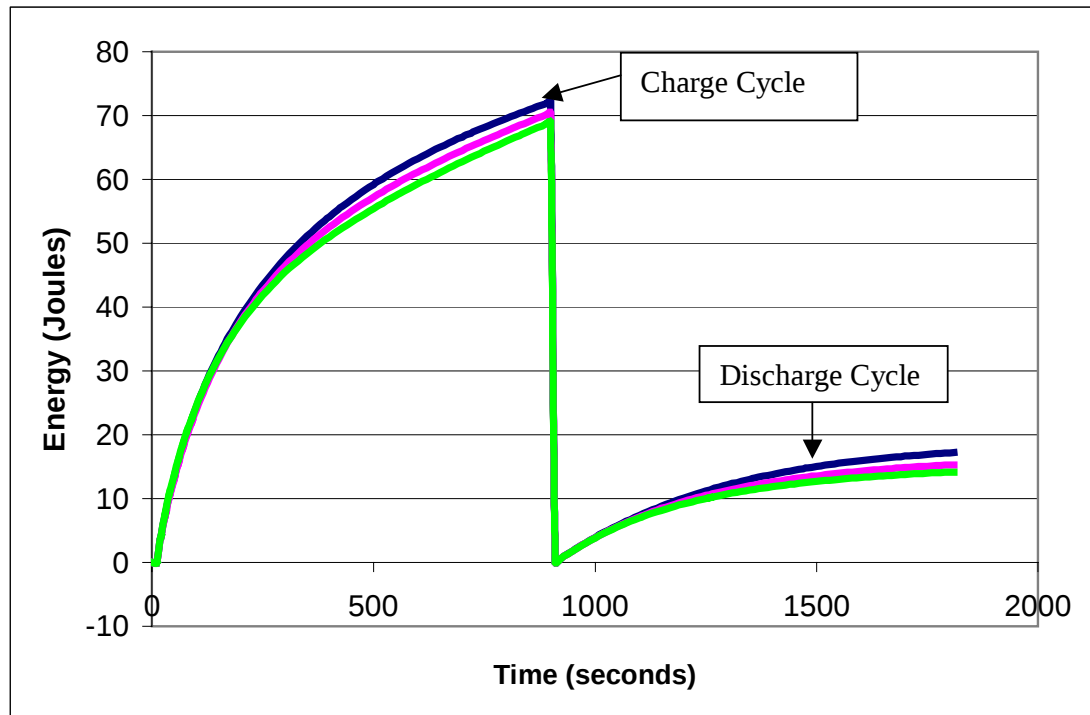


FIGURE 4.2: Electrode Quality Assurance Test: Charge & Discharge Cycles

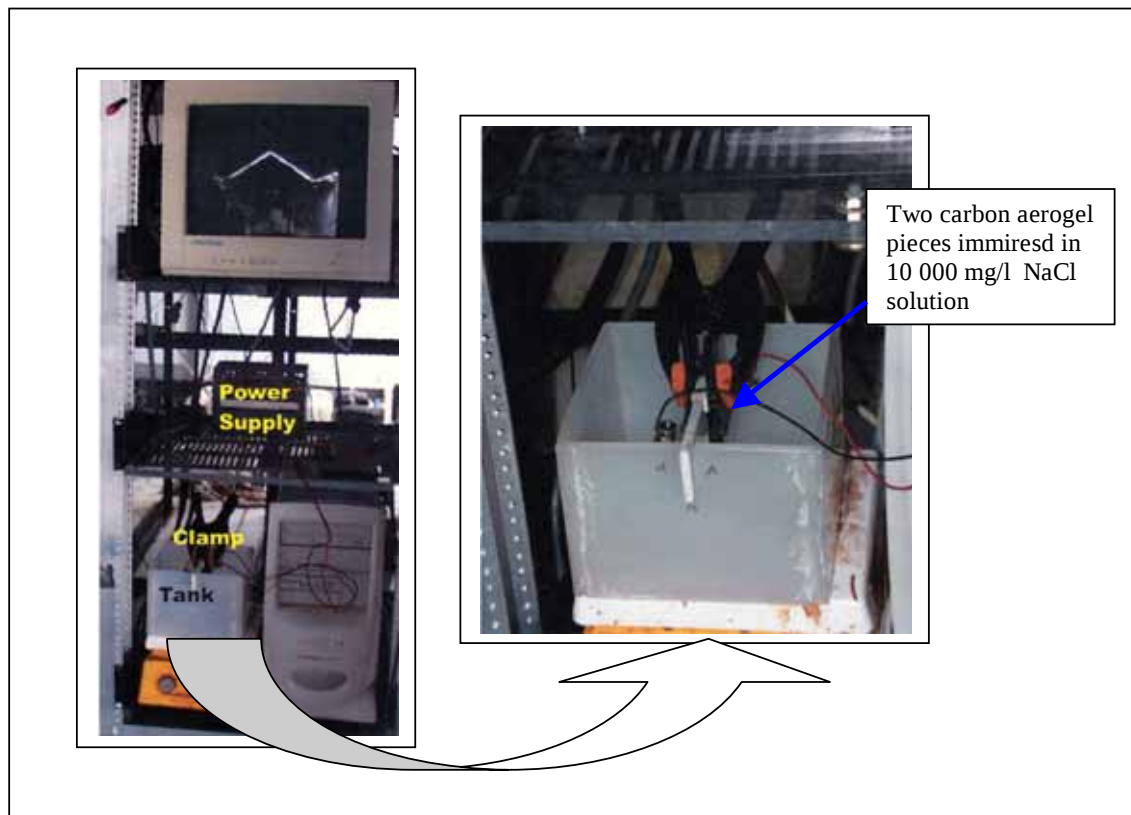


FIGURE 4.3: Electrode Quality Assurance Test Set-Up.

Appendix A contains typical quality control log sheets and data sets collected. The aerogel density was also checked as a quality assurance procedure. The average density was $0,78 \text{ g/cm}^3$. The aerogel sheets were then cut/trimmed into the following dimensions:

Length: 301,24 mm (11,86 inches)

Width: 158,75 mm (6,25 inches)

Thickness: 0,8128 mm (0,032 inches)

Various numbers of electrodes were tested and the optimum prototype unit, named MK-8A contained 24 sheets of electrodes (12 Cathodes + 12 Anodes).

This means that the total electrode area inside the unit, accessible to ions, was $2,29 \text{ m}^2$ ($24,7 \text{ ft}^2$) or nearly 2.5 % ($1/40^{\text{th}}$) of a future full scale industrial unit ($92,9 \text{ m}^2$ or 1000 ft^2). The aerogel produced during this research had the following typical physical and electrical characteristics:

Avg. BET Surface Area	: $600 \text{ m}^2/\text{g}$
Bulk Resistivity	: 20 m ohm cm
Specific Capacitance	: $> 2 \text{ Farad}/\text{cm}^2$

4.2.2 CELL MANUFACTURING PROCESS – PHASE 2

The basic building block the industrial module/cell is a single electron pair. A pair of aerogel electrodes forms a basic capacitor. An industrial module will need to consist of multiple electrode pairs/capacitors inside a durable housing.

As no high pressures are required, the module design pressure could be low. It was decided to use $41,3 \text{ kPa}$ (6 psi) as the module design pressure.

It is necessary to control the potential difference over each cell at relatively the same voltage. Therefore, a monopolar electrode arrangement, connected in parallel, was chosen for the electrode pair wiring arrangement inside the module. **Figure 4.4** illustrates a typical monopolar cell-wiring diagram, as used for the CDT™ prototype.

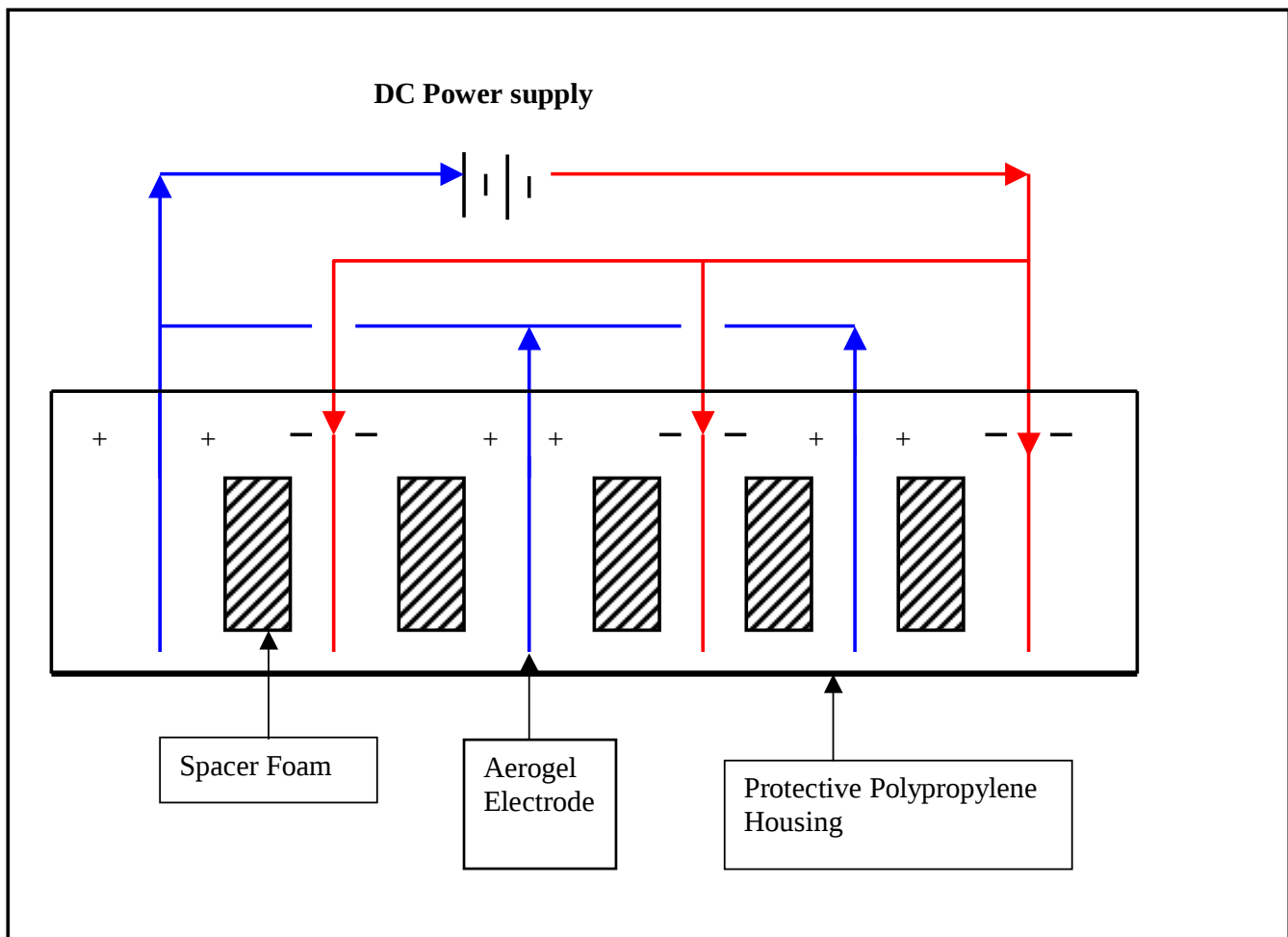


FIGURE 4.4: Typical Monopolar Cell Wiring Arrangement

The distance between each electrode is $\pm 0,8$ mm (0,032 inches). Using non-conductive spacer foam between each electrode pair prevented short circuiting effects. The path that the water stream follows is between each electrode pair, through the spacer foam matrix (out of the page).

The cell arrangement as shown in **Figure 4.4** has several advantages:

- The potential difference over the entire module and between adjacent electrodes can easily be controlled at the required low values of 1,2 to 1,5 Volts. This low voltage arrangement makes it safer for operational personnel.
- Uniform conditions exist between all electrode pairs, thus ensuring a more uniform ion adsorption environment.
- Should fouling occur between one electrode pair, it won't influence the operation of the other pairs.
- All electrodes (except two at the end) are flanked by electrodes of the opposite charge, thus reducing losses due to electrical stray currents.

Monopolar electrodes in parallel do have some disadvantages as well.

- In industrial applications, large currents will be needed. This means very thick conductors from the power source to the cells.
- Generation of large electrical currents at low voltages is not ideal.
- A short between one electrode pair is detrimental to the efficiency of the entire module.

Various other cell arrangements exist, but did not form part of this dissertations scope.

In summary stacking 24 carbon aerogel electrodes and their associated electrical bus connections inside a polypropylene housing was the method used to manufacture the prototype unit. Maintaining to a simple manufacturing process was an objective.

Figure 4.5 illustrates the assembly of the preferred prototype (MK-8A).



Stacked aerogel electrodes, with stainless steel nickel-plated bus connectors. Eventually graphite bus connectors proved to be more effective, as they could not corrode.

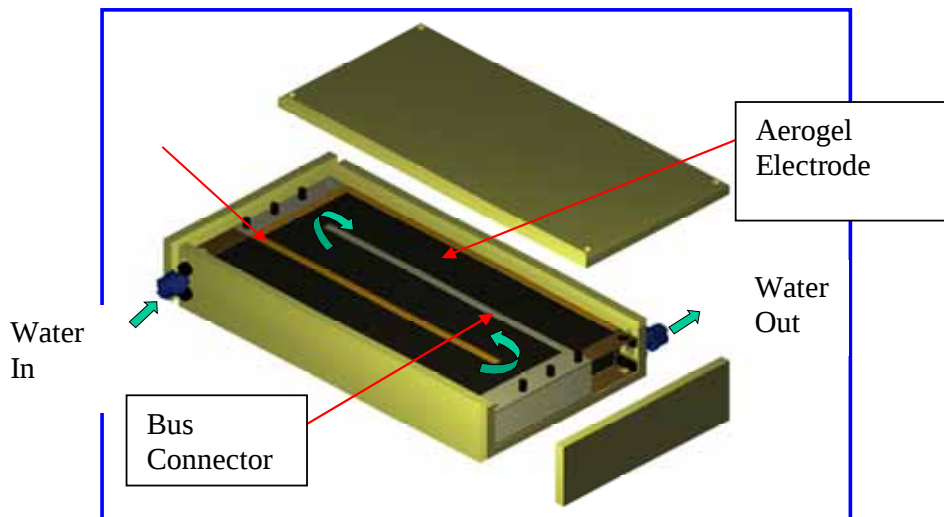


FIGURE 4.5: Industrial Prototype (MK-8A): Module Assembly

The first prototypes had stainless steel bus connections. Bus connections are the electrical connections to the electrode, dictating to the electrode to function as a cathode or anode. The high electrical currents and high salinity of the electrolytes created a very corrosive environment, even for stainless steel. **Figure 4.6** illustrates the stainless steel corrosion problems encountered. The final prototype module bus connections were machined from graphite and proved to be more effective than their stainless steel predecessors. Chapter 5 illustrates in more detail the benefits that were seen by using graphite instead of stainless steel as bus connector manufacturing material.

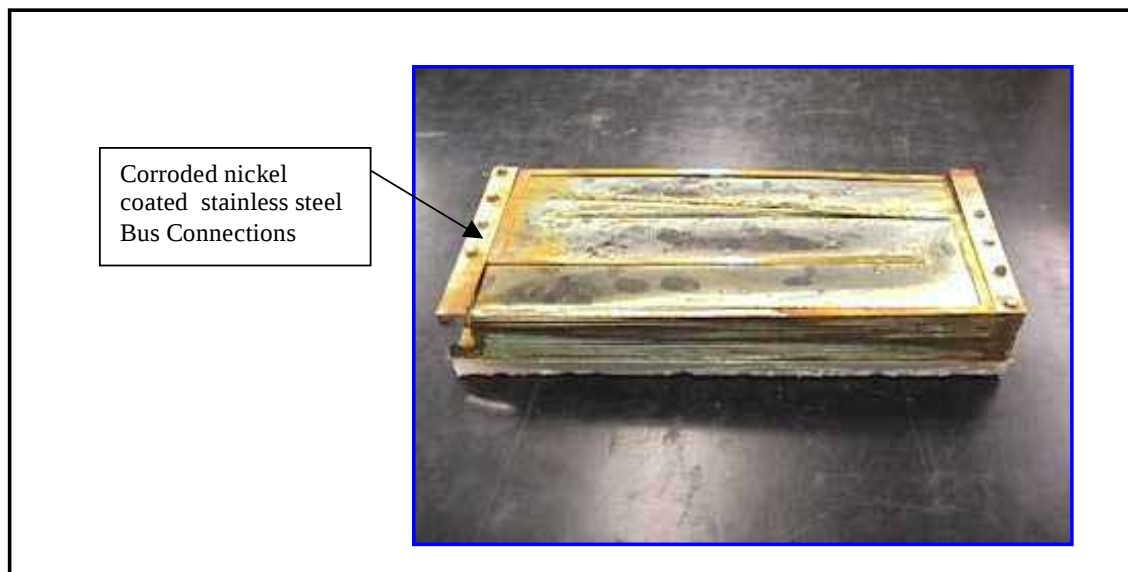


FIGURE 4.6: Stainless Steel Bus Connections : Corrosion Problem

Appendix B contains more detailed technical bulletins regarding the cell developmental process, with the final material of choice being graphite bus connectors in the MK-8A prototype module.

4.2.3 CONTROL SYSTEM DEVELOPMENT – PHASE 3

After the successful manufacturing of a prototype unit, it was necessary to develop a control system to operate the prototype during the evaluation phase. The control system had to have basically two flow paths, a once through scenario and a recycle scenario. **Figure 4.7** illustrates the overall control system set-up used for the prototype water treatment evaluation test runs.

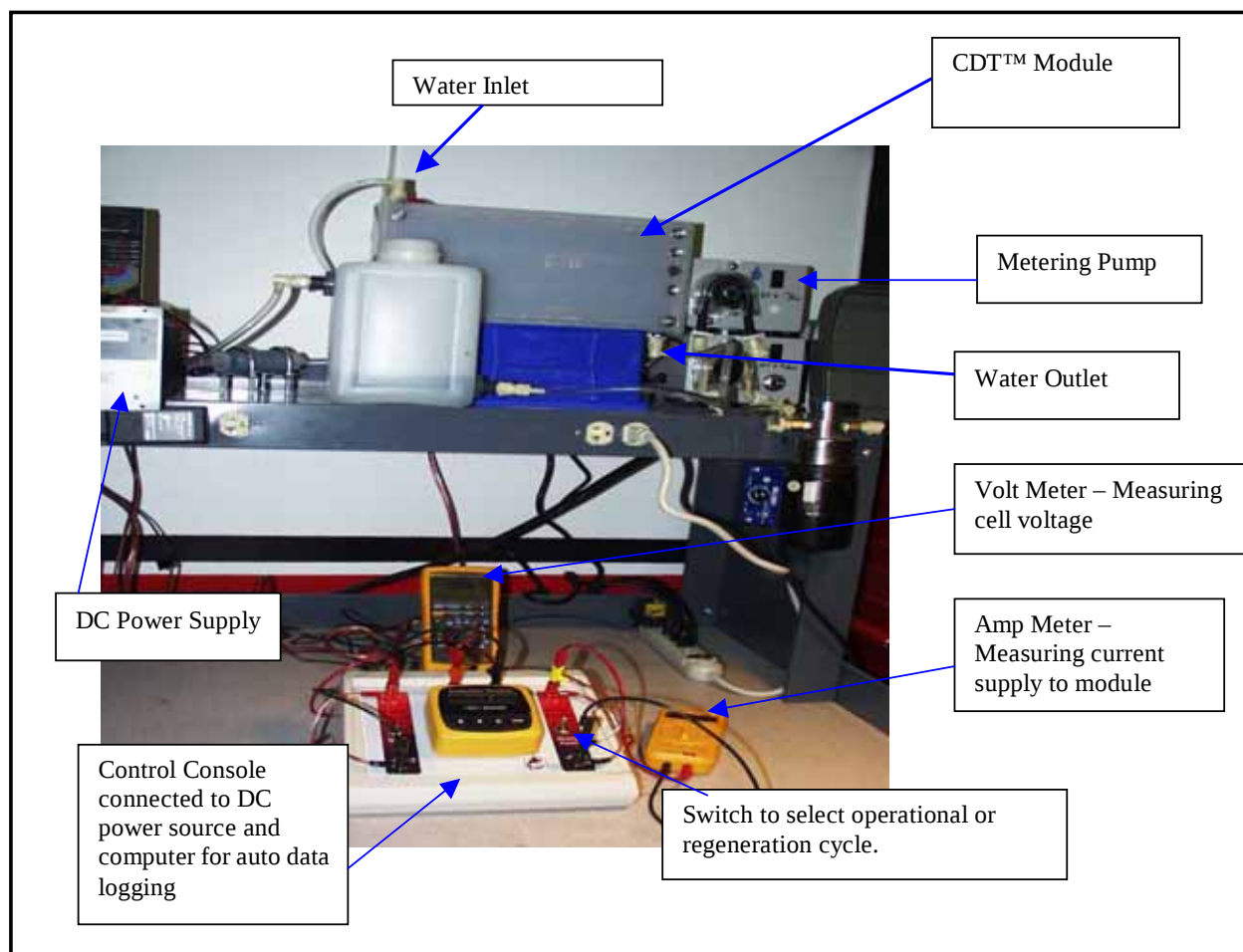


FIGURE 4.7: Prototype Control System Set-Up

A DC power supply was connected to the control console, and from the control console the DC power supply was connected to the cathode and anode connections of the prototype. The basis of all test runs was to monitor conductivity change of a metered feed stream, and the associated voltage and current requirements as a function of time.

Voltage and current as a function of time were automatically recorded on a computer.

Appendix A contains an example of typical voltage and current data as a function of time. Once data has been recorded, a mass and energy balance was performed to determine the following main evaluation criteria:

- The quantity of ions adsorbed and at what rate (water production rate)?
- The quantity of energy required to adsorb the ions?

The control console, shown in **Figure 4.7** made it easy to switch from an operational cycle to a rinse cycle. Cutting the DC power to the brick and shorting the cathode and anode terminals, while a rinse stream was pumped through the cell, stopped an operational cycle and started a rinse cycle. Conductivity probes at the cell inlet and outlet ports were used to measure and record conductivity data. **Figure 4.8** illustrates a typical control system for a future industrial scale CDT™ operation. A typical industrial size plant would consist of pre-treatment, CDT™ modules, post-treatment and an overall control system.

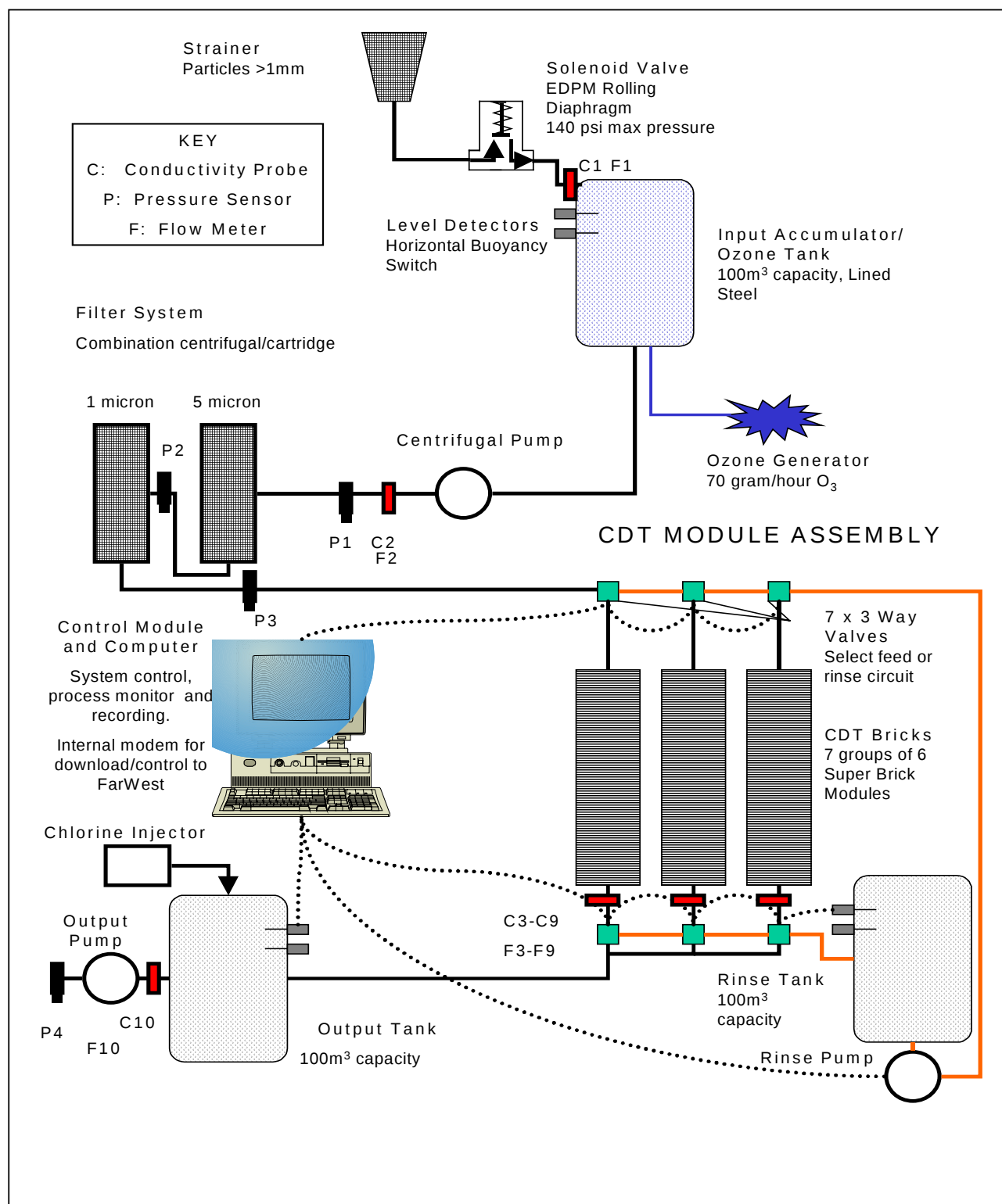


FIGURE 4.8: Typical Process Flow/Control Diagram of a Future Industrial Scale CDT™ Plant

CHAPTER 5

TEST METHODOLOGY, RESULTS AND DISCUSSION

5.1 LABORATORY FACILITIES

The laboratory test work conducted for this dissertation was performed in two locations. The main laboratory was in Tucson, Arizona (USA) and a second laboratory in Carlsbad, California (USA). During this phase, AirWater, Inc. in Otsuka, Japan conducted some supporting test work, under the guidance of the CDT Systems, Inc. research and development team. Results obtained from test work conducted in Japan, are referenced accordingly.

Laboratory test results can be divided into two main categories. Results obtained from developing the industrial prototype bench scale unit, and results from evaluating the prototype as a potential alternative desalination technology. Test work during the developmental stages mostly focused on electrode quality control and optimization of electrical connections and energy efficiency. After the development of an optimum prototype unit, the test work focused on evaluating capacitive deionization as a potential industrial scale desalination technology.

5.2 METHODOLOGY

Figure 4.6 in Chapter 4 illustrates the typical set-up for test work during the module development and technology evaluation phases. Conductivity probes in the inlet and outlet lines were used to measure solution conductivity. A volt and an amp meter were used to measure the electrical data required to determine energy consumption. A control console allowed for rapid change from a production/charge cycle to a regeneration/discharge cycle. Electronic wiring of the control console also allowed for automatic data logging of time, conductivity, bus voltage and current supplied during each test run. Graphical interpretations of typical capacitive deionization test data always have two main cycles.

Outlet water stream conductivity is decreased to below the inlet conductivity during the operational cycle, which is a result of ions being adsorbed into the electric-double layer on the electrode surface. The outlet water conductivity increases to above the inlet conductivity during the regeneration cycle, as the adsorbed ions are removed (washed-off) from the electrode surface. Rate of ion adsorption, associated energy consumption, overall water recovery and general operations & maintenance requirements, were used as the fundamental comparative factors in comparing capacitive deionization to other existing desalination technology's.

The following two sections in this chapter present and discuss the typical test results obtained during the prototype development and evaluation phases. During the development phase various tests had to be conducted to come-up with an optimum prototype design. Once the development phase results researched set criteria of performance, the optimum prototype was further tested and evaluated in more detail to determine the technologies potential as an industrial desalination technology.

Electrical conductivity probes were used to determine salt content. However for the purpose of comparison the following conversion factor can be used to convert conductivity to TDS in mg/l. Salt content as a conductivity reading in $\mu\text{S}/\text{cm}$ (micro-siemans per centimeter) can be converted to TDS in mg/l by multiplying by 0,7. It must be noted that this factor will differ between source water's, but for most source water's tested during this research project it proved accurate enough.

5.3 RESULTS – PROTOTYPE DEVELOPMENT PHASE

The main objective of this phase was to develop a prototype, which could be manufactured and operated cost effectively on an industrial scale. Tests on the manufactured aerogel for quality control purposes were already discussed in Chapter 4. Results discussed here focus more on the quality control of the overall module development. **Appendix's A and B** contains detailed data and calculation methods used to produce graphical results discussed in this section, as well as applicable additional data.

One of the main challenges during the development phase was to ensure optimum electrical connection between the aerogel electrodes and their associated bus connectors. Various materials were tested for use in the manufacturing of the bus connectors. **Figure 5.1** illustrates the effect of changing the bus connection material from nickel-plated stainless steel (metallic) to graphite.

Similar **Figure 5.2** illustrates the ion adsorption improvement of the prototype by changing from a metallic to a graphite bus connector. A once-through system set-up conducted test runs for both **Figure 5.1 and 5.2**, with conductivity of the output water measured.

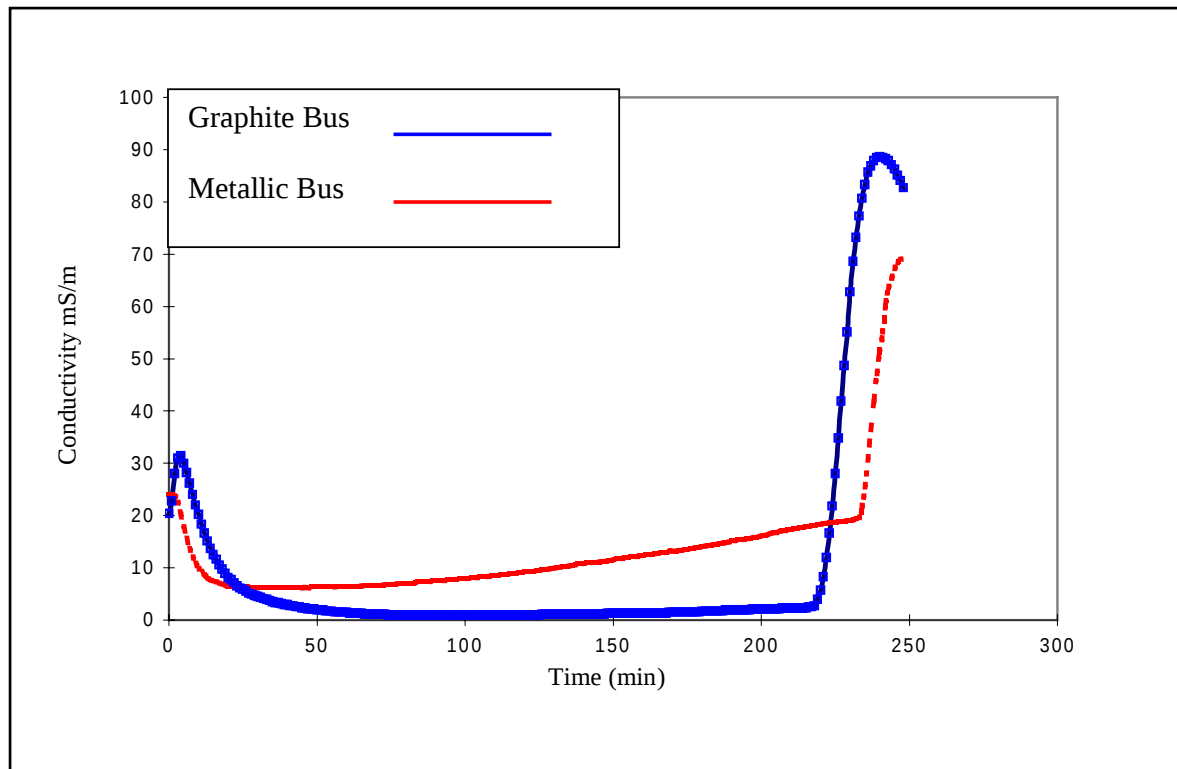


FIGURE 5.1: Nickel Plated/Stainless Steel vs. Graphite Bus Connections - A

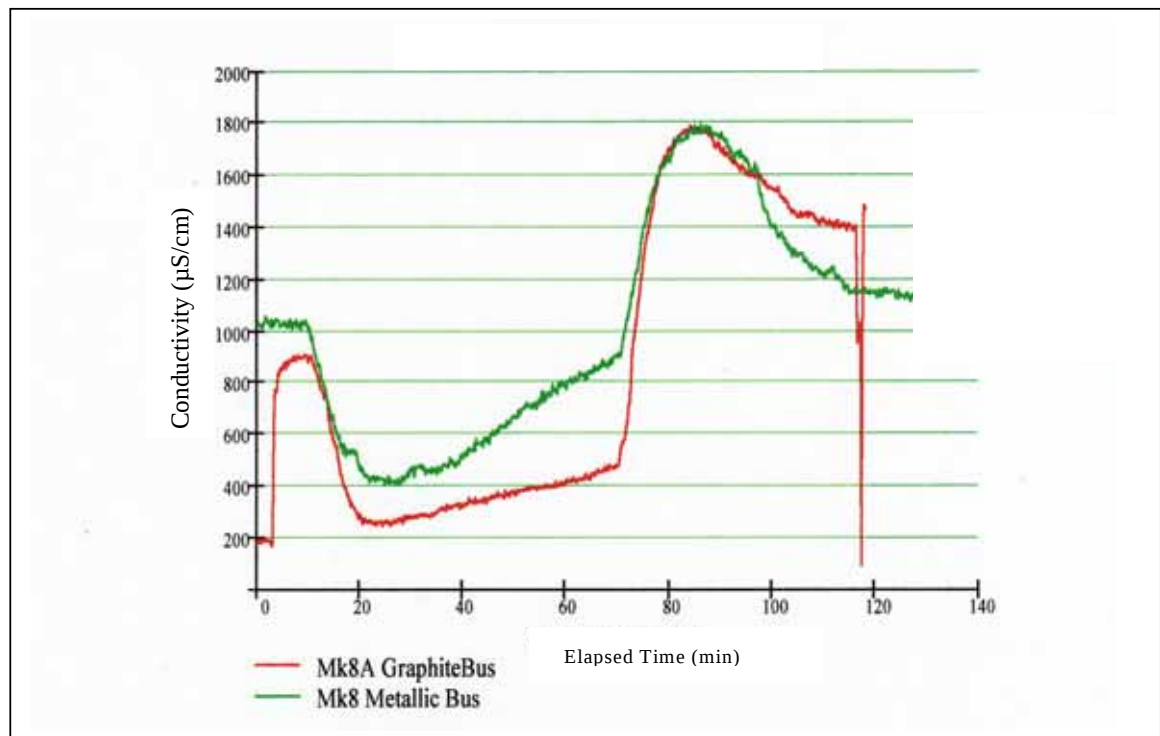


FIGURE 5.2: Nickel Plated/Stainless Steel vs. Graphite Bus Connections - B

Data presented in **Figure's 5.1** and **5.2** were generated by using a MK-8A prototype at a constant flow rate of 50 ml/min. The usage of graphite instead of stainless steel/nickel-plated bus connectors had an improved ion adsorption effect. It is noted that by the time the regeneration cycle was started (around 72,5 minutes), that the MK-8A prototype was not fully saturated as was the case for the metallic bus connector prototype (MK-8).

The next step of comparing bus connector efficiencies was to conduct continuous cyclic tests. **Figure 5.3** illustrates the results obtained from repetitive long term testing of two prototype modules, one containing stainless steel nickel plated bus connectors and the other the more efficient graphite connectors. The feed water conductivity was 22 mS/m (220 µS/cm).

Cyclic tests were conducted by measuring the prototype output conductivity and by switching between charge and discharge cycles. Adsorbed ions are washed off the electrode surface during the discharge cycle, therefore the increase in conductivity to above the feed conductivity.

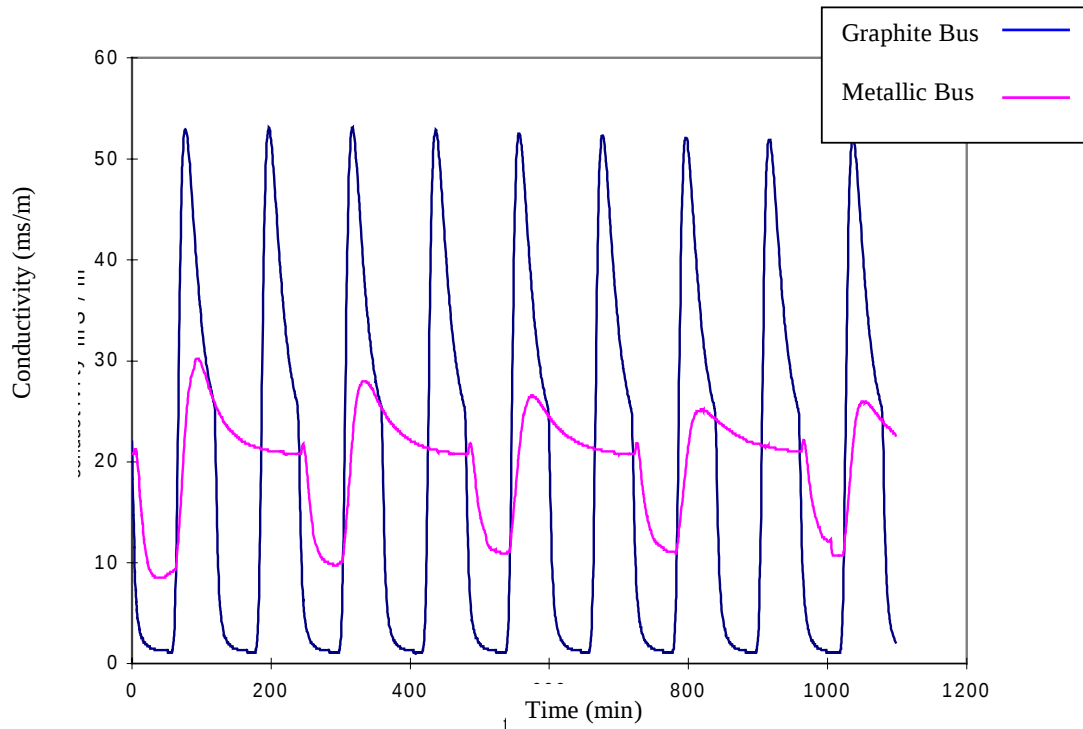


FIGURE 5.3: Repetitive Cycle Testing: Bus Connector Optimization

The higher peaks and deeper valleys of the graphite bus connector prototype, indicate more efficient ion adsorption and regeneration per unit time. **Figure 5.4** illustrates the typical charge and discharge cycles used in CDTTM. The flow rate used to generate the data for **Figure 5.4** was 50 ml/min through the MK-8A prototype.

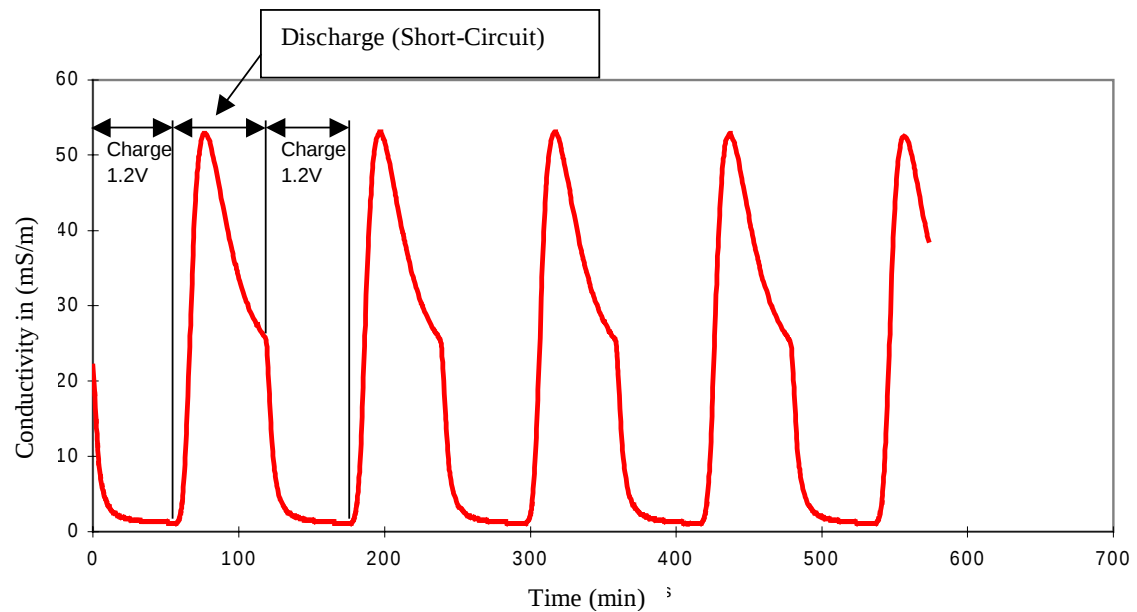


FIGURE 5.4: Production/Charge and Regeneration/Discharge Cycles

After the bus connector design had been optimized, the next step was to determine the prototypes optimum flow rate and hydraulic design for the desalination evaluation tests, to follow. **Figure 5.5** illustrates two test runs conducted on the same MK-8A prototype. For the test in **Figure 5.5** the feed water quality was the same; however the once-through test runs were conducted at two different flow rates, one at 52 ml/min and the other at 157 ml/min.

As expected, the higher flow velocity produced more rapid ion removal during the rinse phase. At around 100 minutes, the 157 ml/min flow conductivity started to fall as a second cycle was initiated. The sharp spikes on the graphs have been due to instrumentation and have no relevance on the overall experiment. Due to the low-pressure requirement for CDT™, optimization of head loss through the prototype was not of primary concern. However the manufacturer plans future hydraulic optimization to ensure lowest head loss possible.

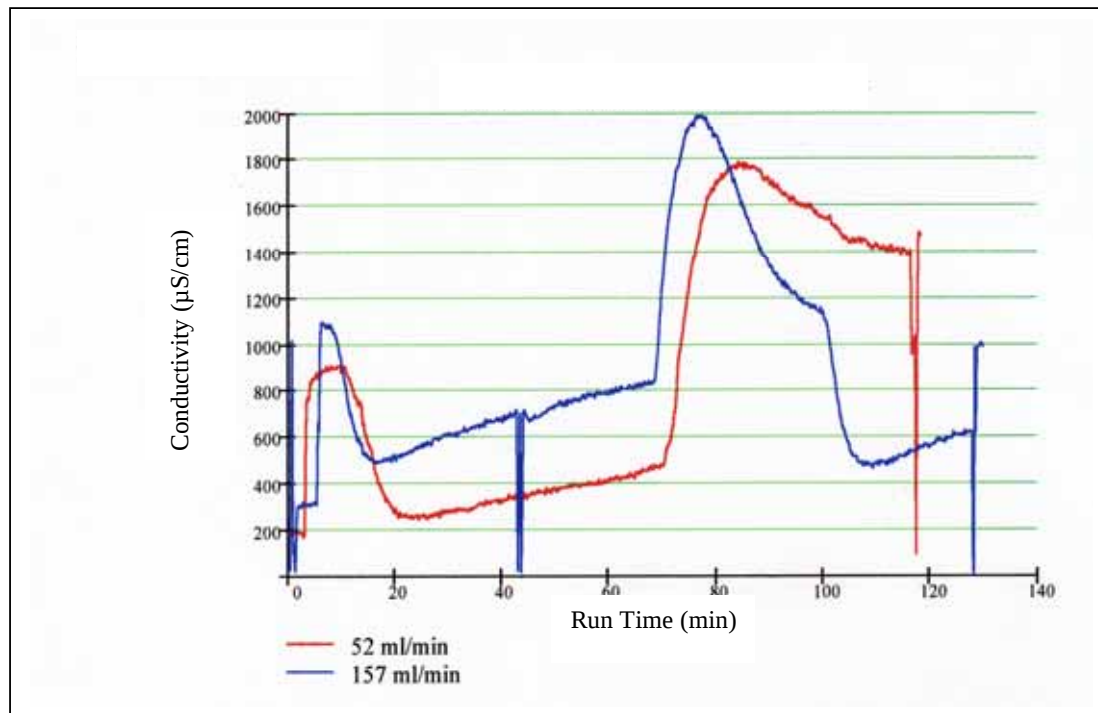


FIGURE 5.5: Effect of Flow Rate on Prototype Performance

Ion Adsorption

The final decision on which prototype design to use in further desalination efficiency testing was made after an ion adsorption test run was conducted on the two main prototype alternatives. **Figure 5.6** illustrates the ion adsorption capacity per prototype as a function of time.

Figure 5.6 represents the cumulative ion adsorption for a single charge/discharge cycle on each prototype alternative. The feed water was a 1 032 $\mu\text{S/cm}$ NaCl solution at a flow rate of 52,6 ml/min. A potential difference of 1,3V was used on both alternatives. The MK-8A (graphite bus connectors) prototype adsorbed around 1,6 times more ions at the same energy consumption, as compared to the metallic bus connector prototype.

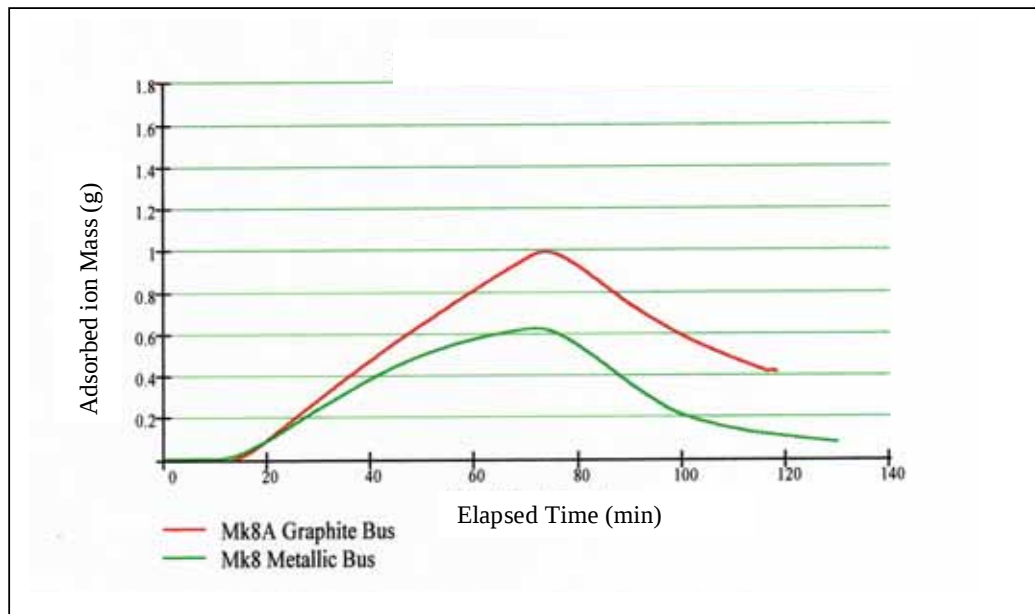


FIGURE 5.6: Ion Adsorption: Metallic vs. Graphite Bus Connectors

Energy Requirement

Figure 5.7 illustrates a comparative power use/energy requirement test run. The energy/power was calculated by multiplying voltage and current data. Flow was constant at 52,6 ml/min and the feed conductivity was 1 032 $\mu\text{S}/\text{cm}$. In this test run the MK-8 (metallic bus connector) prototype developed an increased current draw at approximately 12 minutes, this was not due to a direct short as the module voltage was maintained at 1,3 Volts by the power supply. The energy requirement graph of the MK-8A prototype (red line) would be typical of a CDT™ industrial module, due to the capacitive behavior of a module. As the capacitors charge up, less and less current is allowed to flow through the capacitors, resulting in the typical exponential decrease of the required energy. Saturation of the electrode surfaces are directly proportional to the over-all “charged state” of the various capacitors making-up a CDT™ module. Therefore a fully charged CDT™ module indicates a saturated electrode condition and visa versa.

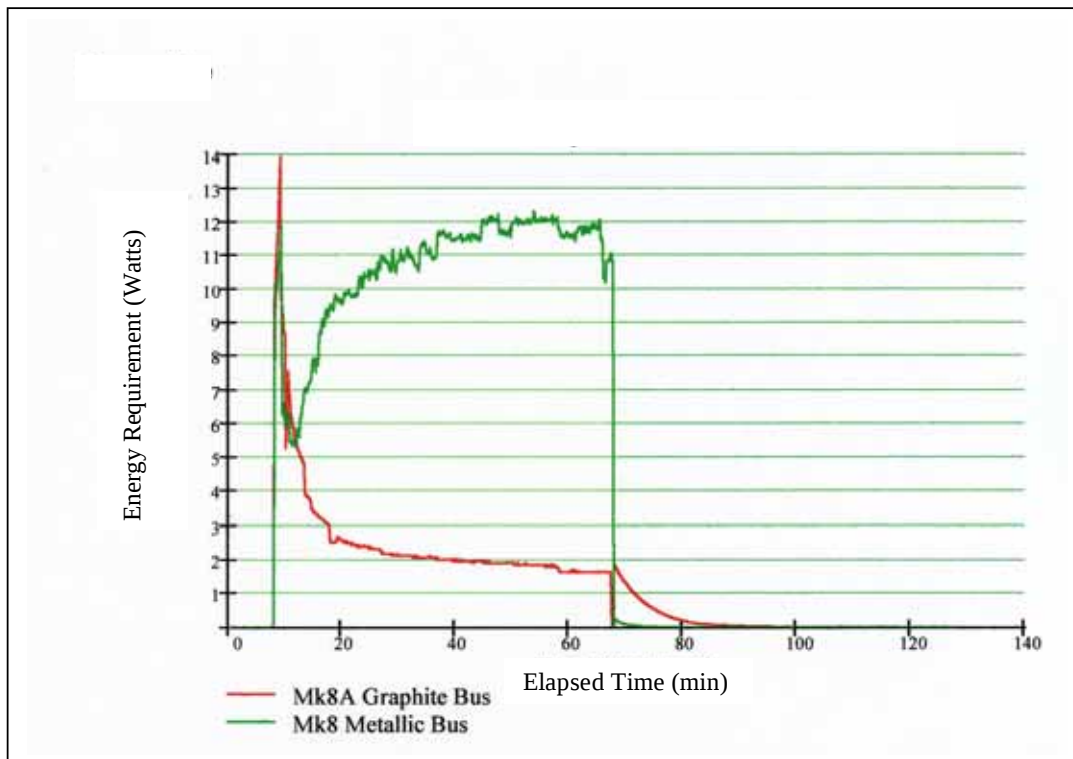


FIGURE 5.7: Energy Requirements : Metallic vs. Graphite Bus Connectors

The prototype developmental phase was concluded for research conducted in this dissertation, once the carbon aerogel electrode manufacturing process, design of electrical bus connectors and the module hydraulic design had been successfully integrated into a single industrially reproducible module. The MK-8A prototype was chosen as the optimum alternative, to be used in the following evaluation phase. During the next evaluation phase, CDT™'s overall potential, to compete on an industrial scale with existing desalination technologies was evaluated.

5.4 RESULTS – PROTOTYPE DESALINATION TESTING PHASE

This section discusses the results obtained from the following two final overall testing phases:

- General Prototype Performance Testing, and
- Brackish Water: Application Specific Testing

5.4.1 GENERAL PROTOTYPE PERFORMANCE TESTING

In order to realistically evaluate capacitive deionization as a potential alternative to existing industrial scale desalination technologies, two main parameters need to be investigated (1) ion adsorption per electrode surface area (percentage water recovery), and (2) energy required to facilitate adsorption. With regard to electrical energy, the typical operational mode of a CDT™ plant would be to switch between charging the cells (ion adsorption) and discharging the cells (ion removal). **Figure 5.8** illustrates a typical continuous/cyclic once through test run used during this phase of testing, which would also be the typical continuous scenario for a module as part of an industrial size application.

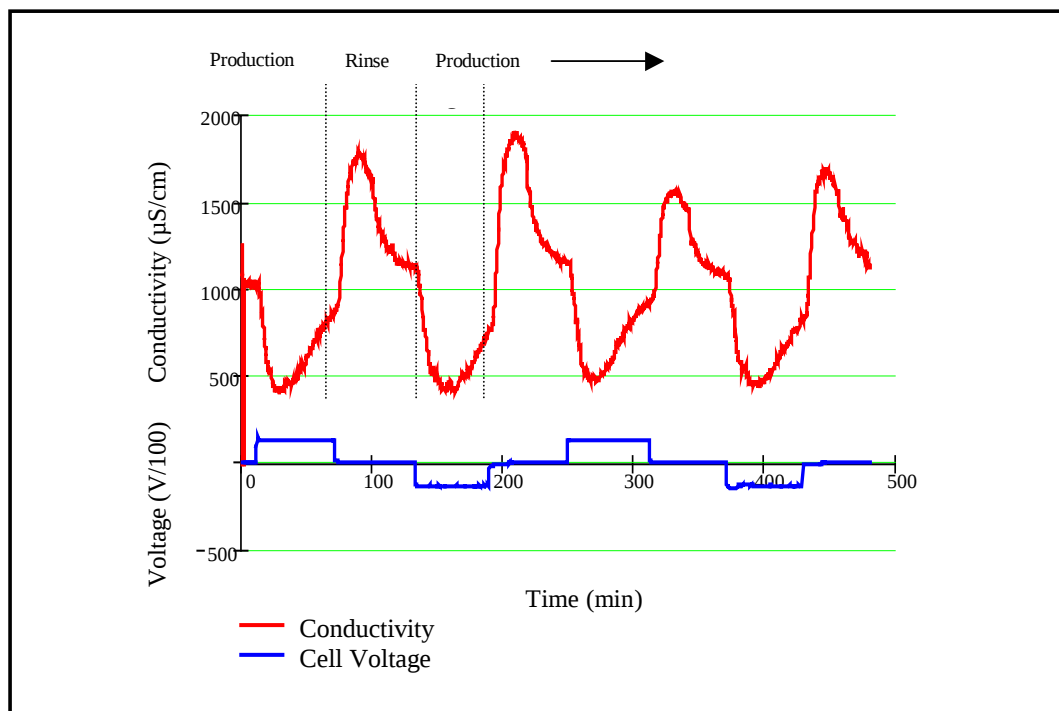


FIGURE 5.8: Typical Continuous CDT™ Desalination Evaluation Test Run

Figure 5.8 further illustrates the typical graphical interpretation of time, outlet conductivity and bus voltage/supply current data collected at each test run in this phase.

The feed NaCl solution conductivity for this specific test run was 1 088 $\mu\text{S}/\text{cm}$ through a MK-8A prototype module. The blue trace shows the applied voltage as it was switched from +1,3v to 0 v to -1,3 v. Switching the polarity after each cycle, assists with the regeneration phase. During the production cycle, with a direct current voltage applied to the module, ions are removed from the water passing through the system; conductivity is reduced below the input level. Conductivity drops for about the first $\frac{1}{4}$ of the production cycle, then increase to again to close to the starting value.

During the regeneration cycle, with the module electrical connections grounded (energy can be recovered here in full scale systems), ions are released into the water and the output conductivity is increased above input level of 1 088 $\mu\text{S}/\text{cm}$. By integrating the TDS removal for the production cycle, the overall mass of ions removed, can be determined. Voltage and current data automatically collected during a test run is used to determine how much energy is required per volume of water.

Figure 5.9 illustrates the data from repetitive test runs done on the MK-8A prototype module.

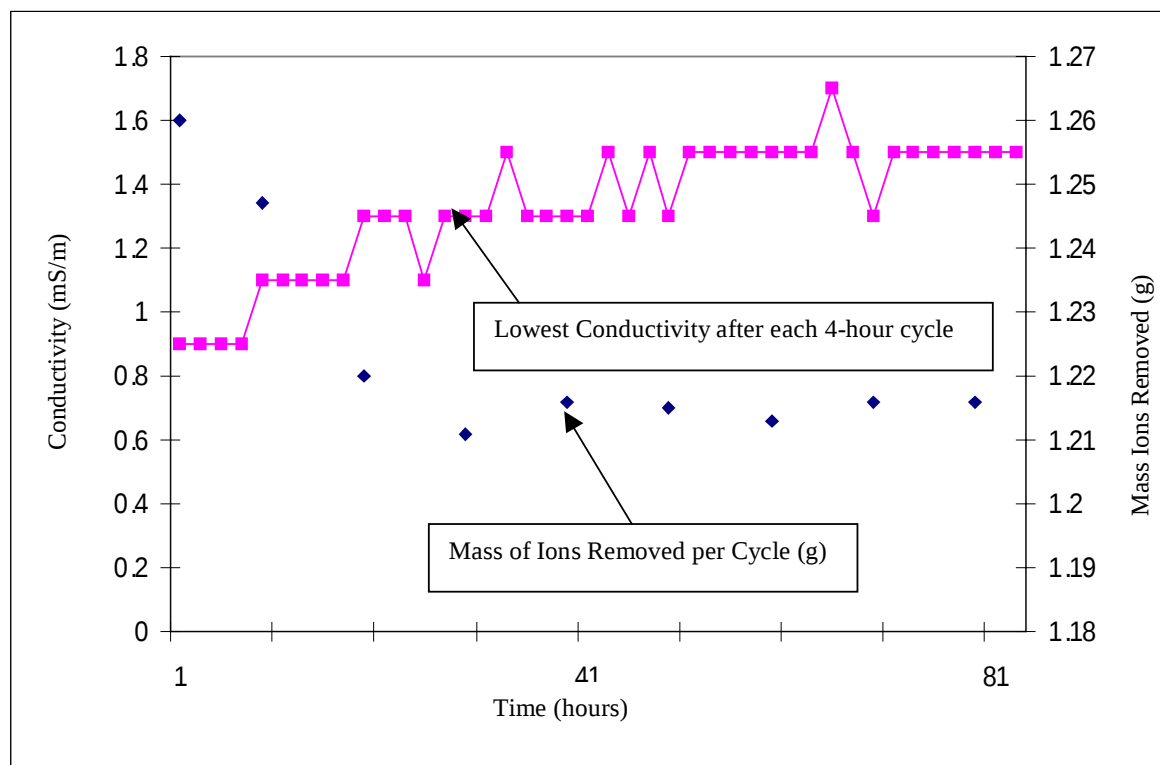


FIGURE 5.9: Ion Adsorption Repetitive Tests on MK-8A Prototype Module

A 20 mS/m (200 μ S/cm) NaCl solution was continuously treated for 100 cycles (4 hour charge vs. 2 hour discharge) at 50 ml/min at the Air Water, Inc laboratory. Results indicated a 66% recovery rate, as the flow rate stayed constant. In **Figure 5.9** each cycle consisted of a 4-hour charge (operational) period, and a 2-hour discharge (regeneration) period. The graph shows the lowest conductivity recorded for each charge cycle, as well as the calculated mass of NaCl removed.

The ion adsorption capacity for the prototype stabilized at about 1,215 g per charge cycle. The overall ion removal decreased and then stabilized. This phenomenon could be due the physical adsorption that took place at the start of a test series. Ions that are physically adsorbed are not so easily removed as compared to ions electrically adsorbed. Next ion adsorption capacity, as a function of flow rate was evaluated for the MK-8A prototype. **Figure 5.10** illustrates the difference in cumulative ion adsorption capacity of the same prototype, but two different flow rates.

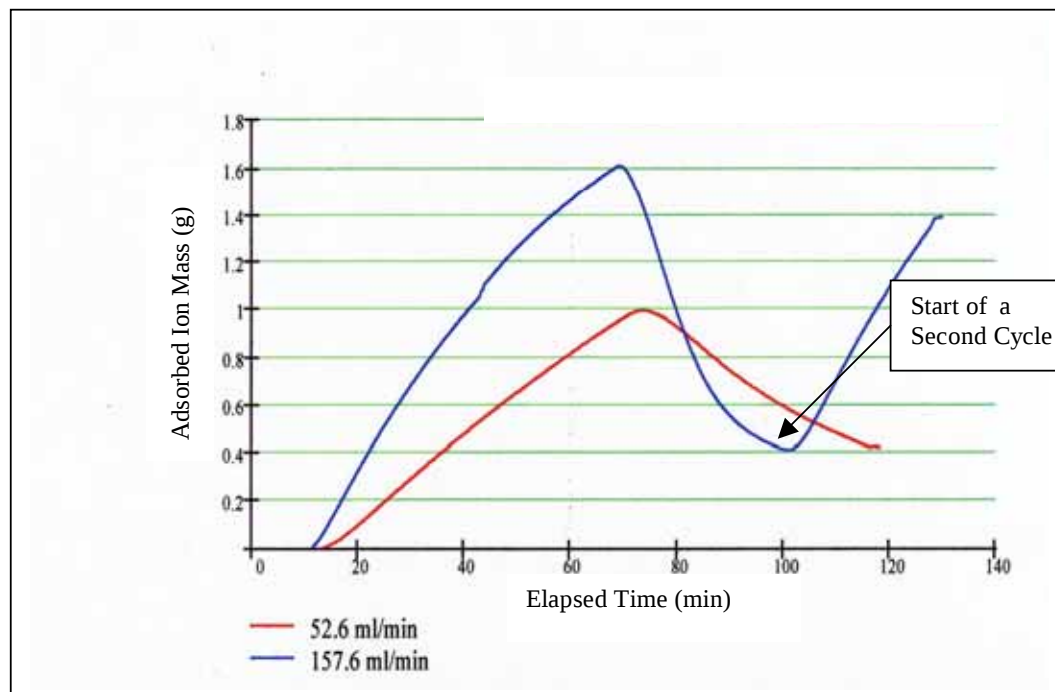


FIGURE 5.10: Effect of Flow Rate on Ion Adsorption Capacity for the MK-8A Prototype

Data in **Figure 5.10** indicate that an increase in flow rate improves ion adsorption and reduces regeneration time. This phenomenon was earmarked for further investigated in future research.

5.4.2 BRACKISH WATER: APPLICATION SPECIFIC TESTING

Table 5.1 summarizes the pre- and post treatment results on diluted artificial seawater (sea water intrusion scenario). A MK-8A capacitive deionization prototype module was used to generate data for **Table 5.1**. A feed stream of diluted artificially generated seawater at 1 000 $\mu\text{S}/\text{cm}$ was treated to produce a product stream of 23.4 $\mu\text{S}/\text{cm}$ at 50 ml/min.

TABLE 5.1: Pre-and Post Treatment Results on Diluted Artificial Seawater

		Feed Water	Product Water	Reduction %
Cation	Sodium as mg/l Na^+	180	39	78,33%
	Magnesium as mg/l Mg^{2+}	20	3.9	80,50%
	Calcium as mg/l Ca^{2+}	4.7	1.1	76,60%
	Potassium as mg/l K^+	16	2.6	83,75%
	Zinc as mg/l Zn^+	0.17	0.14	17,65%
	Boron as mg/l B^+	0.09	0.06	33,33%
Anion	Chlorine as mg/l Cl^-	260	58	77,69%
	Sulfate as mg/l SO_4^{2-}	40	9	77,50%
	Bromine as mg/l Br^-	0.36	0.05	86,11%
	Carbonic Acid HCO_3^-	120	72	40,00%

High ionic specie reduction as shown in **Table 5.1** on artificially prepared brackish water was a good start, however in order to evaluate capacitive deionization in a “real world” scenario, testing on naturally occurring brackish water was needed. Testing on naturally occurring brackish water follows next.

In the natural gas industry, a lot of brackish water is generated during well drilling. The brackish type water generated by drilling is called “produced water”.

The first naturally occurring brackish water tested on a CDT™ industrial prototype was samples from the natural gas industry in Wyoming, USA. In these brackish water bicarbonates ($< 1\,900\text{ mg/l}$) are the main contaminant. The same test methodology was used as for the laboratory-generated solutions. During the production cycle a 1,3 Volt potential difference was generated via direct current. During the regeneration cycle the electrodes were grounded. **Figure 5.11** illustrates the desalination of coal bed methane (CBME) produced water.

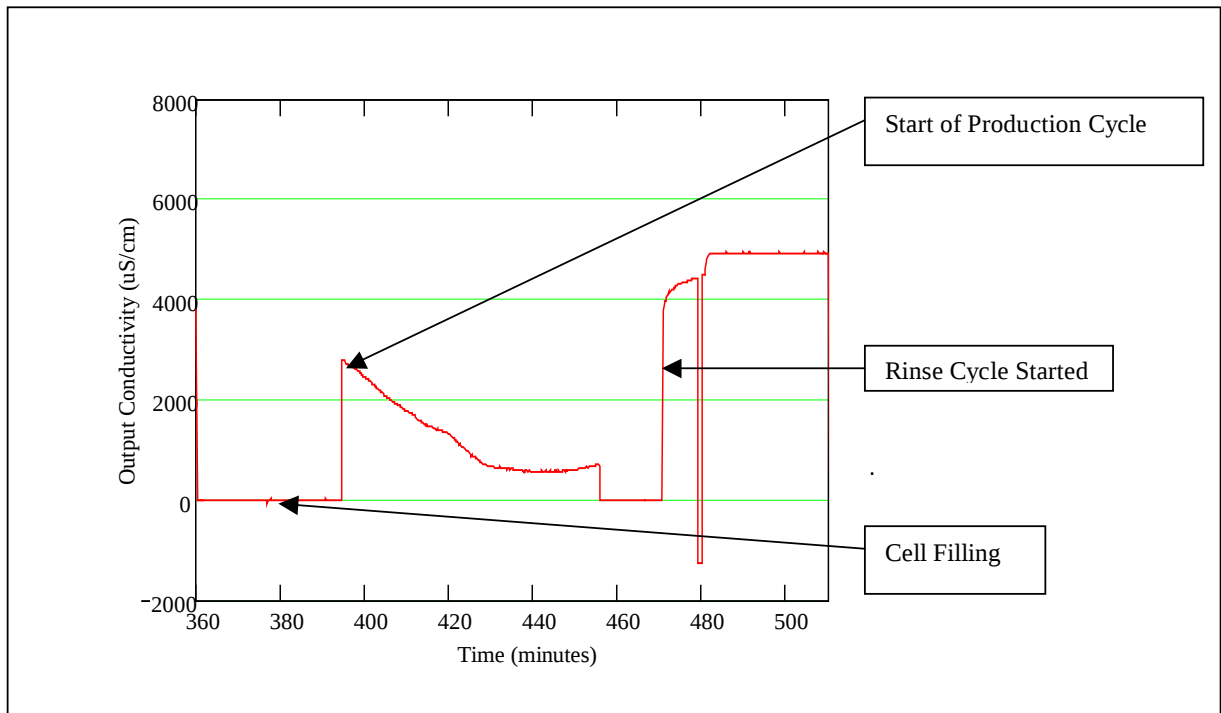


FIGURE 5.11: Desalination of CBME Produced Water

During the period from 360 to roughly 390 minutes, the module was filling, so there was no output from the conductivity probe located on the water output line. The input water conductivity was $2\,095\text{ }\mu\text{S/cm}$ at $20,5^{\circ}\text{C}$.

The output conductivity at the start of the cycle was above the input value due to residual rinse water being pushed out the system. The rinse began at roughly 470 minutes, the zero conductivity occurs during the fill time and is 1/3 the time of the production fill since the rinse flow rate was 3 times the production flow rate. Rinse conductivity saturated at 5 000 $\mu\text{S}/\text{cm}$ since this was the maximum range set on the meter. It was increased for subsequent runs. For this test run the water recovery rate was around 70% and rinse water could be re-used for at least another rinse cycle, before discarding as brine. Reducing the volume of the brine has a major cost benefit in this industry, as it needs to be trucked and pumped underground at specific brine aquifer injection points.

Voltage and current data (see **Appendix A**) was used to determine that it would take an estimated 2,25 kWh to treat 1 000 gallons (3 785 liters) of the produced brackish water to below reinsertion/reuse limits ($< 1\,000\text{ mg/l}$). This result is significantly higher than the 0,36 kWh per 1 000 gallons (3 785 liters) predicted by earlier research work from LLNL, however by including energy recovery and improved electrical connection, future industrial modules could approach the laboratory benchmark.

Carlsbad Pilot Plant

Next in the evaluation process was the design, construction and operation of a CDT™ pilot plant. A CDT™ pilot system was constructed and operated at the Encina Water Pollution Control Facility in Carlsbad, California (2000 to 2001). This specific wastewater treatment facility produced two streams of brackish source waters. The first is a brackish ground water stream, generated by the daily pumping down of the water table, under the secondary settlers. The second brackish water stream is the secondary effluent from the plant (Avg. TDS $> 1\,100\text{ mg/l}$).

A small percentage of the secondary effluent is further treated and recycled as irrigation water. However the majority is disposed of via a dedicated sea outfall.

Figure 5.12 illustrates the control panel of the demonstration unit at the Encina Water Pollution Control Facility.

Behind the control panel source water was directed via a series of pumps to $\frac{1}{4}$ scale (250 ft²) CDT™ cells. These cells were constructed as per the manufacturing process developed for the smaller MK-8A prototype.

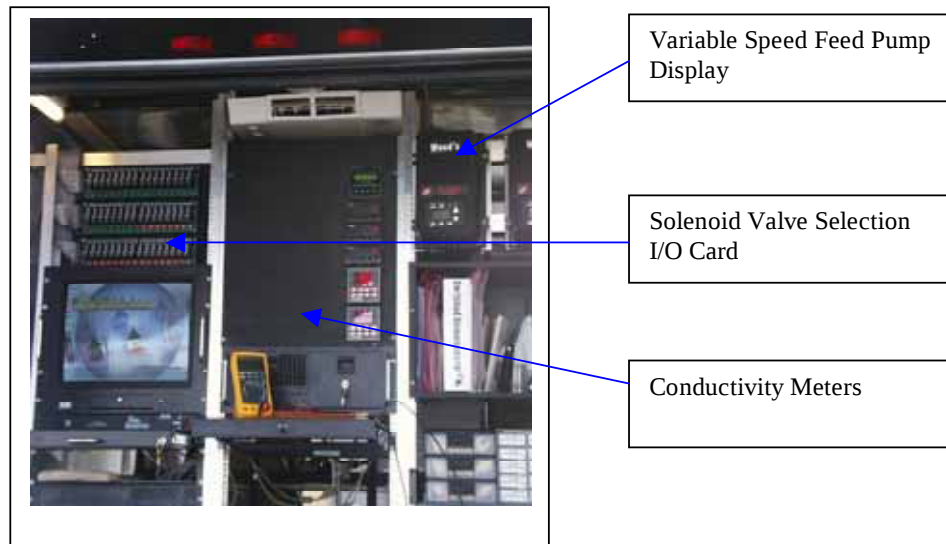


FIGURE 5.12: CDT™ Pilot Plant Control Panel at the Encina Water Pollution Control Facility

A test run was conducted at the pilot plant to determine the ion storage capacity of a larger industrial prototype type unit. A recirculation test was conducted on the brackish ground water. The purpose of the test work was to provide insight into the operating scenario's best suited to an industrial type unit. **Table 5.2** lists an analysis of the Encina brackish groundwater chemical specie composition, which constituted the feed water to the CDT™ pilot plant for this specific test run.

TABLE 5.2 : Encina Ground Water Chemical Analysis

Analysis	Results	US Analysis Method #
Alkalinity, as mg/l CaCO ₃	283 mg/l	SM2320 B
Ammonia N	0,44 mg/l	SM 4500 NH C
Boron	0,6 mg/l	SM 4500 B-B
COD	86,2 mg/l	HACH 8000
Chloride	1 722 mg/l	SM 4500 Cl B
Total Hardness, as mg/l CaCO ₃	1 440 mg/l	SM2340 C
Nitrate N	7,38 mg/l	USEPA 352.1
Nitrite N	< 0,1 mg/l	SM 4500 NO-B
Grease & Oil	0,2 mg/l	SM 5520 B
pH	7,20	
o-Phosphate	0,063 mg/l	SM 4500 E
t-Phosphate	0,067 mg/l	HACH 8190
TDS	4 598 mg/l	SM2540 C
TSS	1,9 mg/l	SM2540 C
VSS	1,3 mg/l	SM2540 E
Specific Conductance	6 370 µs/cm	SM2510 B
Sulfate	630 mg/l	USEPA375.4
Temperature	25,2 °C	SM2550
Turbidity	0,194 NTU	SM2130 B
Aluminum	0,18 mg/l	USEPA 6010 B
Antimony	0,002 mg/l	SM3113B
Arsenic	0,003 mg/l	SM3113B
Barium	0,073 mg/l	SM2130B
Beryllium	< 0,0005 mg/l	SM3113 B
Cadmium	0,006 mg/l	SM3111B
Calcium	70,8 mg/l	SM3111B
t-Chromium	<0,1 mg/l	SM3111B
Copper	<0,05 mg/l	SM3111B
Iron	0,093 mg/l	SM3111B
Lead	0,1 mg/l	SM3111B
Magnesium	177,8 mg/l	SM3111B
Manganese	0,109 mg/l	SM 3111B
Mercury	0,0004 mg/l	SM3112B
Molybdenum	<0,01 mg/l	SM3113B
Nickel	0,056 mg/l	SM3111B
Potassium	15,4 mg/l	SM3500D
Selenium	<0,015 mg/l	SM3113B
Silver	<0,025 mg/l	SM3111B
Sodium	977 mg/l	SM3500 D
Thallium	< 0,005 mg/l	USEPA 279.2
Zinc	0,046 mg/l	SM3111B

Heterotrophic Plate Count	7 700 cfu/ml	SM9215D
Total Coliform m-F	8 800 cfu/100 ml	SM9222B
Fecal Coliform m-F	<10 cfu/100 ml	SM9222D
Enterococcus m-F	140 cfu/100 ml	SM9230C
Color	2,0 color units	SM 2120B
Odor	2,9 TON	SM2150B

**Source : Encina Wastewater Authority Laboratory (Certification No. 1441) – Sample 5
September, 2000 @ 10:10 am – East Well.**

By using a direct conversion from conductivity to mg/l for TDS, the estimated mass of contaminants adsorbed and released can be predicted.

Feed water Conductivity : 6 370 μ S/cm

Feed Water TDS : 4 598 mg/l

The volume of water treated for the test run was 50 liters. **Figure 5.13** illustrates the main variables, output conductivity, bus voltage and current as measured during this test run of the pilot plant.

Pilot Plant Test Run Notes:

- Maximum Bus Voltage: 1,2 V
- Maximum Current Required: 110 A
- Bus connections shorted after 40 min to simulate regeneration cycle.
- Voltage not recorded during minutes 41 to 46, therefore dip in graph.
- Capacitor discharge current not measured.
- Total Electrode Surface Area: 23,23 m² (250 ft²)

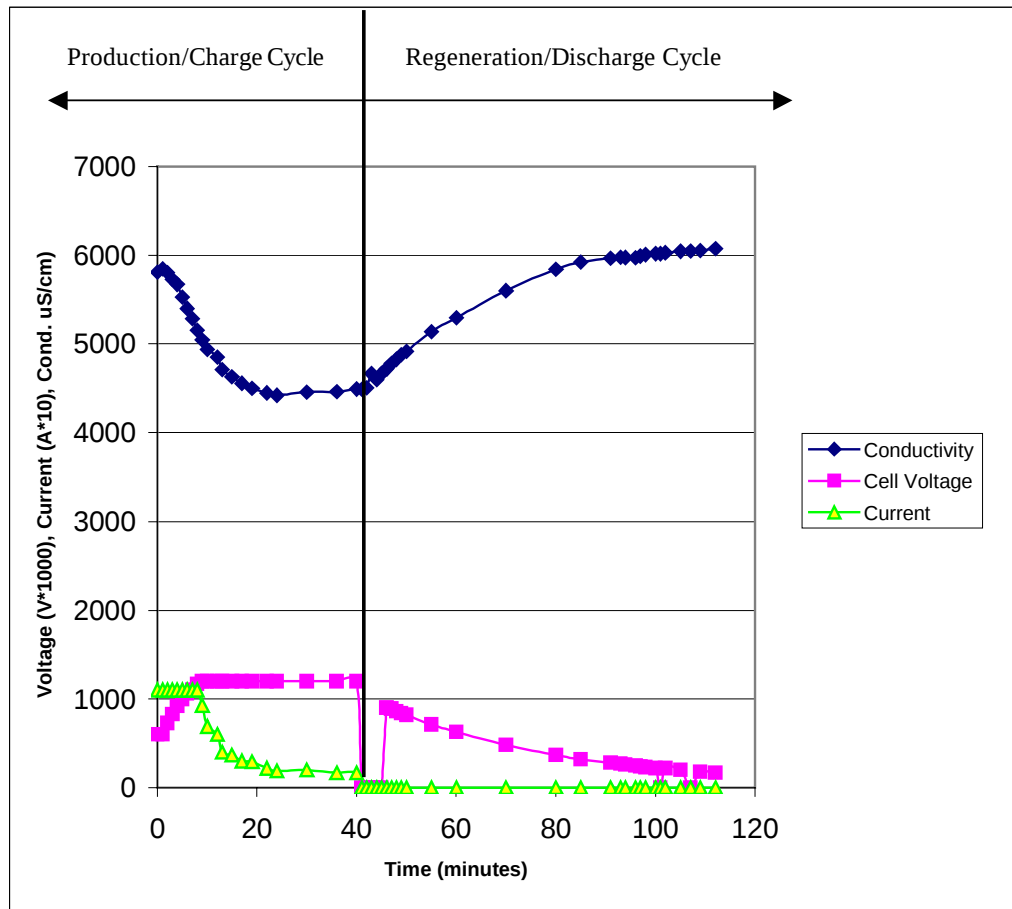


FIGURE 5.13: Pilot Plant : 250 ft Industrial Cell : Ion Storage Test Run

The approximate mass of ions adsorbed can be calculated by looking at the change in conductivity of the output stream.

$$\text{Conductivity Reduction} = 6\,075\ \mu\text{S/cm} - 4\,421\ \mu\text{S/cm} = 1\,654\ \mu\text{S/cm}$$

By using a conductivity to TDS conversion factor of 0,722 $\{4598.10^{-6} / 6370.10^{-6}\}$ it is estimated that 59,695 grams of ions had been removed by the operational cycle of the cell. Therefore the carbon aerogel electrode ion adsorption capacity for specifically brackish groundwater as per **Table 5.2** is 2,5697 g/m² (0,2388 g/ft²).

Due to practical size and weight considerations the original bench mark for a full size industrial cell was set at 92.90 m² (1000 ft²). Laboratory test work at LLNL indicated that this surface area should be able to remove 1 000 mg of TDS per 24 hours. The full cycle (charge and discharge) for the pilot plant test run took 110 minutes and 50 liters of brackish water was treated during this period. A scaled daily production for the pilot plant could be estimated by using the equation 5.1.

$$\text{Scaled_Daily_Production} = (24 \text{ hrs/Cycle Time}) \cdot (M_{\text{ions}}) / (10^{-3} \cdot \rho_{\text{water}}) \cdot (1/\text{Cell Scale}) \quad (5.1)$$

- Scaled_Daily_Production = Volume of brackish water treated by a singly CDT™ cell (1 000 ft² electrode surface) per day
- Cycle Time = 110 minutes = 1,833 hours
- M_Ions = Mass of TDS Removed = 59,695 g = 59 695 mg
- ρ_{water} = 1 kg/liter
- Cell Scale (as compared to full size unit) = 0,25

By using the scaled production equation 5.1, it can be calculated that in a 24 hour period the cell would reduce the TDS of 825,76 gallons (3 125 liters) of brackish water by 1 000 mg/l. Additional experimental results obtained during pilot scale testing are contained in **Appendix B**. The testing phase for this research was thus successfully concluded, with test results on actual industrial type CDT™ prototypes coming close to laboratory scale test results. Test results achieved in this research will serve as a benchmark for an ongoing research and development program on Capacitive Deionization Technology™.

CHAPTER 6

COST: EVALUATION AND COMPARISON

6.1 BASIS OF COST EVALUATION

At the time of this research, technology license agreements limited manufacturing to the USA and as the majority of research for this dissertation was conducted in the USA, the currency used in this chapter is the US Dollar. In order to compare “apples-with-apples” a reference design will be used to compare the costs (capital and operational) of a 3,78 ML/d (1 mgd) low-pressure brackish groundwater RO desalination facility to a 3,78 ML/d (1 mgd) CDT™ brackish water facility treating a brackish feed water (TDS: 2 000 mg/l) to potable standards. **Table 6.1** summarizes the reference design conditions.

TABLE 6.1: Reference Design Parameters

Parameter	Value
Water Supply Source	Groundwater
Source Water TDS, mg/l	2 000
Required Produced Water TDS, mg/l	500
Finished Water Quantity, ML/d (mgd)	3,78 (1)
Brine Concentrate Disposal	Surface Water Body
Intake Type	Well Feed pump

Data Source : AWWA M46: p 93

Section 6.2 discusses more specifically cost projections applicable to CDT™ capital, operations and maintenance requirements. A cost comparison, between the RO and CDT reference designs, follows in **Section 6.3**.

6.2 CDT™: COST PROJECTIONS

Capital and O&M cost projections for CDT™ are discussed in the following two sections.

6.2.1 CAPITAL COST PROJECTIONS FOR CDT™

During the CDT™ prototype developmental phase, the manufacturing cost of industrial size modules was estimated by using the pilot manufacturing process as a model. Acquisition of land, factory space, and machinery costs were taken into account. Like most new technologies, evolving from a laboratory to an industrial level, the initial manufacturing costs per module would be higher than manufacturing costs a few years down the full scale industrial manufacturing road. It is estimated by CDT Systems, Inc. that the initial purchase price per industrial size module, producing 3 785 liters/day (1 000 gpd) and removing 1 000 mg/l, would be in the range of US \$1 000 to US \$1 500. However based upon volume manufacturing and continuous electrode material improvements (Dietz, 2004), CDT Systems, Inc. estimates that they can reduce the purchase price to between US \$600 and US \$800 within the first three years of volume production. These estimates are based on manufacturing costs in the USA.

Table 6.2 illustrates the improvements made during the development process in reducing the cost to manufacture an industrial CDT™ module, as compared to initial laboratory scale test work and estimates.

TABLE 6.2: Reduction of CDT™ Module Manufacturing Costs

Development Stage	US\$ Cost/ft ² Aerogel	Module Sales Price in US Dollar
Technology Licensed from LLNL at Jan. 1997	75	75 000
Projected Cost by LLNL for 2004	30	30 000
CDT Systems, Inc at 1998	5	5 000
CDT Systems, Inc at 2000	3	3 000
CDT Systems, Inc at 2002	2.5	2 000
CDT Systems, Inc 2004	1.6	1 000
CDT Systems, Inc 2007 (projected)	1	600

Source: CDT Systems, Inc Dallas, Texas - 2004

It must be noted that **Table 6.2** includes the following changes to the manufacturing of a full size industrial CDT™ module.

- 1997 to 2000: 1 000 ft² per industrial size module
- 2000 to 2004: 500 ft² per industrial size module

Current advances in material sciences indicate that future electrode efficiencies would reduce the required electrode surface area, without sacrificing the overall treatment capacity. Depending on the volume and level of treatment required, modules will be stacked in either parallel or in series. **Figure 6.1** illustrates the typical layout of an future industrial type capacitive deionization plant (See **Figure 6.3** for a process flow diagram of a typical CDT™ system).



FIGURE 6.1: Typical Industrial Scale Capacitive Deionization Treatment Plant

To determine how many modules in series or parallel will be needed, a simple linear method can be used.

$$\text{Number of Modules} = [\text{Flowrate (gpd)} \times \text{Required TDS reduction (ppm)}] / 1\,000\,000$$

For example an industrial size treatment plant has the following basic design criteria. Produce 1 000 000 gallons per day ($3,8 \times 10^6$ liters per day) of potable water at 500 mg/l TDS from a brackish source water at 2 000 mg/l TDS.

Number of Modules = $(1\,000\,000 \times 1\,500) / 1\,000\,000 = 1\,500$ modules

Total estimated capital cost could then be calculated by including site-specific civil, electrical, instrumentation and mechanical costs. For brackish type water treatment, a good starting point for the calculation of power required is 100 watts per module. Thus for the above-mentioned scenario, around 150 kW would be the maximum power needed to operate the plant at full capacity.

6.2.2 OPERATIONAL COST PROJECTIONS FOR CDT™

Test work conducted by using CDT™ on “real world” brackish water (Chapter 5) and laboratory samples indicated that the energy requirement to treat a brackish type water (2 500 to 3 000 mg/l TDS) to potable standards below 500 mg/l TDS, would be 2,25 kWh per 1 000 gallons or 0,594 kWh/m³. These energy consumption rates do not include further potential energy savings by energy recovery due to the capacitor type operation.

CDT Systems, Inc. believes that with energy recovery, these energy consumption rates can be 20% to 50% lower. An industrial size treatment plant will not require a large operational staff contingent, as a centralized control room would be able to monitor/control of the entire plant. Module replacement (if necessary) would be like changing the batteries in a flashlight. Carbon aerogel is extremely durable and the minimum lifetime of a module is estimated to be approximately 10 years. **Table 6.3** summarize the estimated costs to produce potable quality water from various source waters at a flow rate of 3 785 411 liters per day or 1 000 000 gallons per day.

TABLE 6.3: Estimated CDT™ Costs for Reference Design

ITEM	VALUE
Feed Salinity Content, TDS in mg/l	2 000
Flow Rate in mgd (Ml/d)	1 (3,785)
Number of CDT Modules	1 500
Capital Cost (Modules + 30% for Other Direct and Indirect Costs)	\$1 560 000
Annual Energy + O&M	\$52 500
15-Year Capital Amortization	\$93 600
Total Annual Costs	\$146 100
Cost per 1000 gallons	\$0,40
Cost per 1000 liters	\$0,11

Data Source : CDT Systems, Inc 2004

Assumptions used in **Table 6.3:**

1. CDT Module/Cell Performance:
 - One module reduces TDS by 1000 mg/l per 1000 gpd.
 - Aerogel Material in one module 500 ft²
 - Average sales price per module: US \$800
2. Annual Energy consumption per module is \$0.066/kWh + add 10% for general operations and maintenance costs.
3. Energy Recovery: 50%
4. 15 year Amortization with 10% residual.
5. Cost per 1 000 gallons (1 000 liters) is based on 1 000 000 gpd (3 785 411 lpd) x 365 days of operation per year divided into annual costs.

6.3 COMPARATIVE COSTS

Membrane technologies (low pressure RO and ED/EDR) are leading the existing desalination race for brackish water applications and it was therefore decided to

compare capacitive deionization against low pressure RO with regards to capital and operations/maintenance costs.

Table 6.1 illustrates the reference design parameters. **Figure 6.2** illustrates a process flow schematic of a typical low-pressure RO system used for cost comparative purposes.

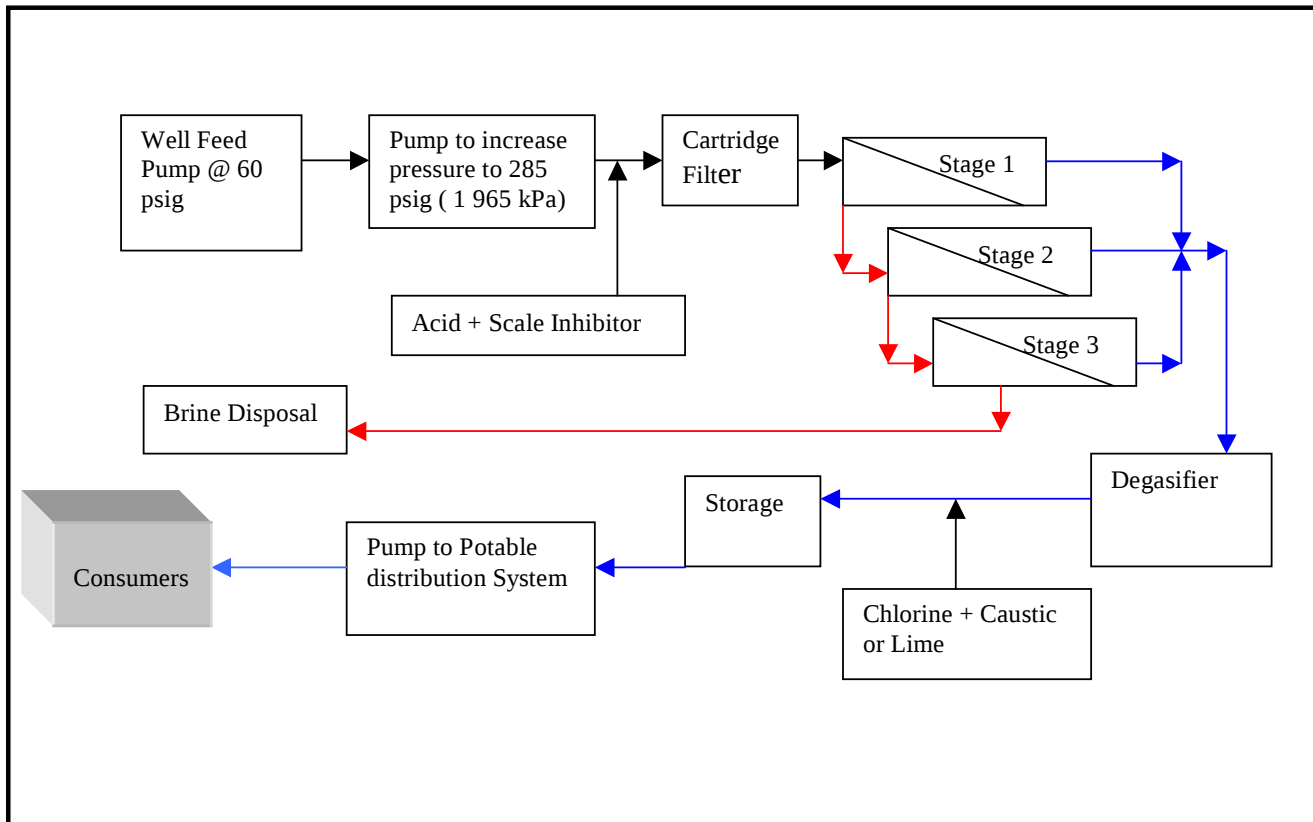


FIGURE 6.2: Typical Low Pressure RO Brackish Water Process Flow Schematic

Figure 6.2 illustrates a typical three stage low-pressure RO system used to achieve a recovery of 80%. **Figure 6.3** illustrates a typical CDT™ process flow schematic for treating the applicable brackish feed water to potable standards. A cost breakdown (capital and O&M) for this scenario is presented in **Table 6.3**.

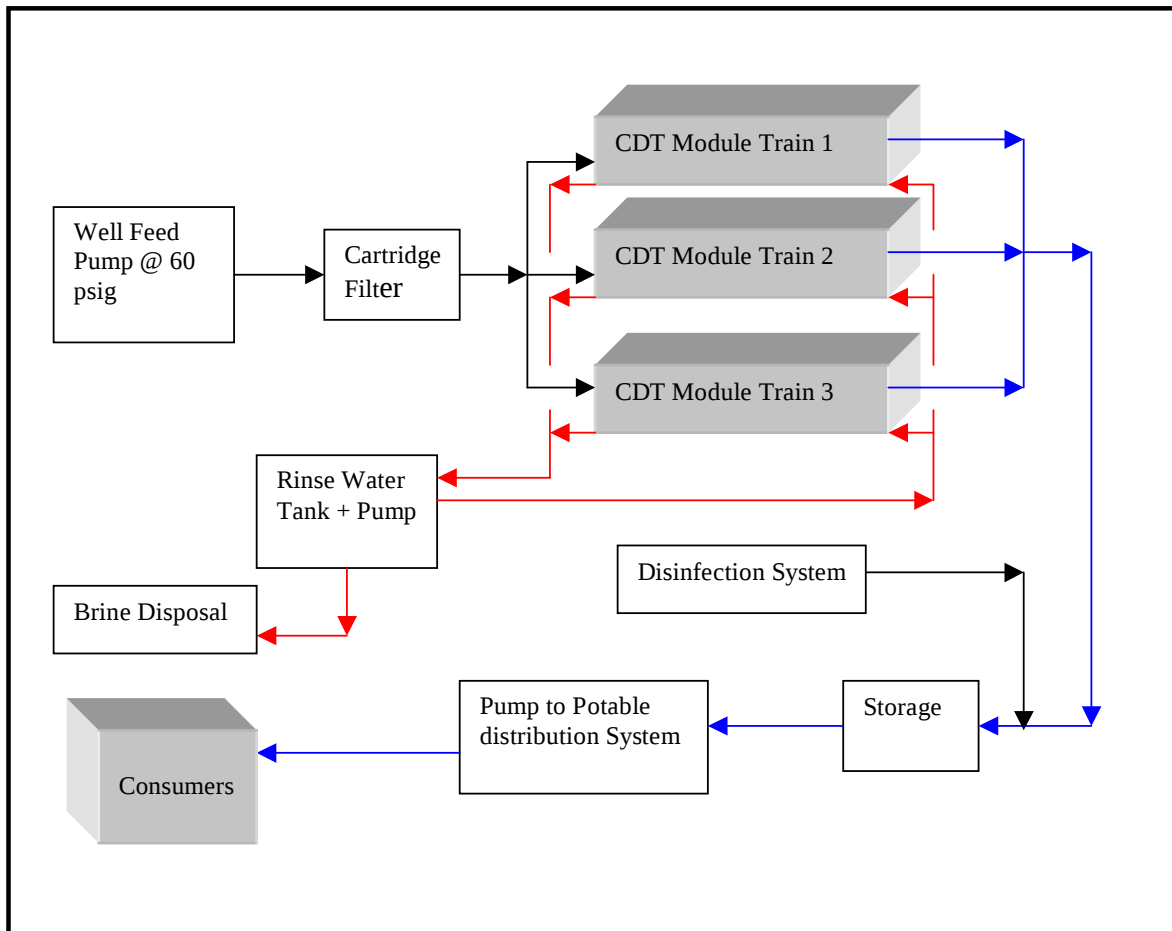


FIGURE 6.3: Typical CDT™ Brackish Water Process Flow Schematic

It must be noted that various site-specific factors could influence the final construction costs for both a RO and CDT™ facility. However for comparative purposes in this research it is assumed that both plants are to be constructed on similar sites, as described in the reference design (**Table 6.1**). **Table 6.4** presents a cost breakdown for the low-pressure RO system as illustrated in **Figure 6.2**.

TABLE 6.4: Estimated RO Costs for Reference Design.

ITEM	VALUE
Feed Salinity Content, TDS in mg/l	2 000
Flow Rate in Ml/d (mgd)	3 785 (1)
Capital/Construction Costs* (Direct and Indirect Costs)	\$3 139 000
Annual Energy + O&M**	\$296 535
15-Year Capital Amortization + 10% Residual	\$188 340
Total Annual Costs	\$484 875
Cost per 1000 gallons	\$1,33
Cost per 1000 liters	\$0,35

* See AWWA, M46 : p94 for a detailed breakdown of construction costs.

** Energy @ 3.83 kWh/1000 gal (AWWA, M46: p 98) typically is 33% of a RO facility's O&M costs (AWWA, M46: p 5). No Blending.

Table 6. 5 summarizes the costs as broken down in **Table 6.3** and **6.4**, for both CDT™ and a low pressure RO system, using the same reference design.

TABLE 6.5: Comparative Cost for Reference Design

CDT™			RO		
Capital	O&M	Total	Capital	O&M	Total
\$0,26	\$0,14	\$0,40	\$0,52	\$0,81	\$1,33
\$0,11/1000 liters or \$0,40/1000 gal			\$0,35/1000 liters or \$1,33/1000 gal		

Data Source:

CDT Systems, Inc for CDT data.

(AWWA M46, 1999) and (Gomez, 2004) for RO data.

As indicated in **Table 6.5**, significantly lower estimated capital cost of the CDT™ system and its lower energy consumption (including an assumed 50% energy recovery) mean that that this system could be cost competitive compared to RO for brackish water applications (TDS < 10 000 mg/l). However, reverse osmosis would be more cost effective for the higher salinity waters and only by reducing the capital costs for the production of CDT™ modules, would capacitive deionization become a serious competitor for reverse osmosis in higher salinity brackish or seawater applications.

EDR is another competitive brackish water desalination technology. Without energy recovery test work on an industrial type CDT™ module indicated an energy requirement of 2,25 kWh/1000 gallons and EDR utilizes 7,7 kWh/1000 gallons (AWWA M46, 1999) for typical brackish water conditions. It is thus possible for future CDT™ plants to cut the costs to produce desalinated brackish water by 70%, as compared to existing EDR data.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The following conclusions can be made regarding the research conducted for this dissertation:

- **Aerogel manufacturing.**

It is possible to cost effectively manufacture the carbon aerogel electrodes on a large/industrial scale, by designing and constructing a small model of a potential future manufacturing facility. To summarize, carbon aerogels are manufactured by poly-condensation of resorcinol and formaldehyde in a slightly basic medium, followed by supercritical drying and pyrolysis in an inert atmosphere. The impregnation of carbon cloth with the resorcinol-formaldehyde resin generates monolithic sheets. These monolithic sheets can easily be trimmed to produce the electrode sheets used in module assembly. Future carbon aerogels will be even more human and environmental friendly as material sciences advance.

- **Simple construction of industrial modules**

CDT™ only requires simple double-sided planar electrodes, which can be stacked in a low-pressure housing (Plate-and-frame type module).

- **Enhanced energy efficiency for treatment of brackish water.**

CDT™ can be used to treat brackish water (800 to 10 000 mg/l). The desalination of brackish source water is becoming increasingly more important.

Competing technologies for this application are electrodialysis 2,03 Wh/liter (7,7 Wh/gal) and reverse osmosis 2,25 Wh/liter (8,5 Wh/gal). CDT is more energy efficient at 0,13 to 0,59 Wh/liter (0,5 to 2,25 Wh/gal) depending on energy recovery and operation.

- **Elimination of wastes from chemical regeneration.**

CDT™ uses electrical regeneration, thereby eliminating the need for handling secondary chemical wastes streams. A highly concentrated brine stream is the only waste stream produced.

- **Carbon Aerogel is resistant to chemical attack.**

Aerogels are resistant to aggressive chemicals like HCl and resistant to oxidizing agents, should de-scaling or de-fouling be required in CDT™ desalination facilities.

- **Industrial treatment plants would be fully automated.**

The capacitive deionization process is fully automatic. A typical industrial size plant would require a minimum of two treatment trains for continuous operation. While the one train produces desalinated water, the other would be regenerating. Energy captured from the regenerating train could be supplied to the train in production mode.

- **Potential to reduce treatment plant disposal costs.**

Old membrane modules have no recycle value and thus present a disposal problem. CDT™ has the potential to reduce the overall disposal costs to a treatment plant, as the carbon aerogel electrode lifetime is conservatively estimated in excess of 10 years by LLNL.

In summary, simple design requirements and low energy costs could make CDT™ very competitive to existing membrane technologies such as reverse osmosis and electrodialysis for brackish water applications in the immediate future.

To be competitive for seawater applications, the production costs per capacitive deionization module needs to be reduced before the technology can cost effectively compete with reverse osmosis on such applications. CDT™ is a young, but very promising technology for the desalination of brackish and seawater sources.

7.2 RECOMMENDATIONS

Ongoing CDT™ industrial bench scale studies are important, however in order to prove long-term industrial scale operational effectiveness, it is vital to get a capacitive deionization industrial scale plant in operation. It is recommended to first use a pilot plant to verify design requirements for the larger industrial size plant.

Currently there are various ongoing research projects in the USA and Japan. The data from these projects would greatly accelerate the design and construction of industrial scale manufacturing plants. However, before an industrial size treatment plant can be built, an industrial scale manufacturing facility would be needed. CDT Systems, Inc is in the process of establishing such a facility.

With a manufacturing facility in place, this and LLNL research clearly indicates that CDT™ could cost effectively compete with existing industrial scale desalination technologies. Dedicated long-term planning, material science research and continued pilot scale testing will take this exciting water treatment technology to the industrial level. CDT™ has the potential to provide an order-of-magnitude step reduction in desalination costs and thus has the potential to provide not only potable water, but also agricultural and industrial water, from saline sources.

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