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Water Contaminants and Their Removal

1.1 Introduction

This book is intended both as a tutorial presentation of basic principles of electrochemical water processing as well as a short working manual for the design and operation of electrochemical deposition cells and for electrodialysis devices.

Water quality for direct and indirect human uses has always been an important concern in the past, and continues on into the future. With the ever-increasing concentrations of population centers and the demands of the industry, that concern is growing continuously throughout the world.

The conditions that determine acceptable water quality are very dependent upon the use to which the water is intended. The factors involved are numerous, to say the least, and range from one high purity extreme to non-potable irrigation water. Water intended for farm irrigation, for example, can contain a high level of foreign substances at the level of thousands of parts per million as long as these are not damaging to crops. At the other end of the water spectrum is the need for super pure, or "polished" demineralized water for pharmaceutical or semiconductor production uses.

Among the more common types of foreign materials present that determine the "purity level" of water are listed below. Their removal from the body of water for each type is identified.

1. Solid matter in agitation or suspension
   Removal by: filtration, decanting
2. Dissolved organic substances
   Removal by: distillation, adsorption
3. Dissolved inorganic, ionic substances
   Removal by: distillation, reverse osmosis (RO), ion exchange resins, electrodialysis (ED)
4. Bacteria and other living organism contaminants
   Removal by: reverse osmosis, chemical addition, heating
5. Gasses present, in solution or otherwise
   Removal by: heating, ED, RO, adsorption
6. Other liquids miscible or non-soluble
   Removal by: fractional distillation, adsorption, RO, ED

The removal method selected depends upon the economics of the situation for the intended applications, the specifics of the contaminants, and other unwanted substances present in the water.

In the future, water treatment with minimal use of chemical reagents will become the goal of most processing systems. This approach is stimulated by the desire to minimally disturb the existing chemical conditions in water, and to reduce the amount of chemical correction needed as one introduces a reagent to fix one problem, only creating another problem. In some water conditioning instances, the elimination of all chemical agents is possible.

A family of systems is possible, which will provide means for controlling pH, biocide level and dissolved solids concentration in water. One such form of technology is the direct removal of dissolved, ionized materials in water via electrochemical, (electrodialysis), separation.

In the ensuing pages, one such class of processes will be described in some considerable engineering detail. In some instances the need to introduce bulk chemical agents to the water system can be eliminated entirely.

This system removes dissolved substances such as salts, mineral compounds, acids and alkalis through the application of an electric field impressed across an array of electrodes and ion selective membranes. An electric power source is only required as input to the water. No chemicals or consumable materials are introduced into the water system.

Dissolved substances that are removed from the main body or mainstream of water are carried over into a waste water stream and eventually discarded. A maximum of only a small percent of the incoming water is "wasted" in this manner, and no materials are put back into the drainage that were not present initially. The waste- water just has a higher concentration of the same dissolved materials than it had when first introduced into the systems.

There are only a limited number of other methods, which can be employed to perform this task. They are:

1. Distillation
2. Reverse osmosis, RO
3. Ion exchange resin beds

- Distillation is simply the evaporation of solvent from solids and other contaminants present in the original body of water. The disadvantages are the life of equipment, relatively high maintenance in cleaning residues from evaporating surfaces (heat exchangers), and high temperatures and high-energy consumption.

- Ion exchange resins operate on the basis of the displacement of one ionic species for another as a function of relative concentrations. A mixed resin bed (cation and anion), regenerated in the hydrogen and hydroxide forms, respectively, will remove all other species of ions upon passing through the bed, and replace them with hydrogen and hydroxide (water as net product). High quality water can be obtained via this method. However, problems include high cost of regeneration and contamination. Usually this process is suitable for bringing good quality input water to high quality (polished, ultra pure) water for pharmaceutical and semiconductor uses.
- During osmosis, solvent passes through a semi-permeable membrane separating two solutions. Solvent—or water in this case—passes from the dilute solute side to the more concentrated side. This migration of solvent molecules to the concentrated side will continue until the solute concentrations are equal on both sides of the membrane. Reverse osmosis or migration of solvent to the dilute side can occur if a sufficiently large hydraulic pressure differential is established across the membrane in the appropriate direction (see Chapter-2, Section 2-12).

RO is a system in which the water (solvent) is forced through the membrane, leaving behind ionized solutes as well as solids and organic materials. This filtration aspect of the process is an advantage in terms of ridding the water of most of the unwanted contaminants. However, the problems of membrane damage and clogging or blocking and fouling are significantly increased.

The electrodialysis, (ED), method offers some distinct advantages over all three of the above alternative methods. A comparison of attributes shows these to be some of the distinct benefits in practical use.

Problem areas with Distillation

a. Costly in energy consumption
b. Small systems are usually very inefficient
c. Maintenance and scale accumulation problems
d. Low production rate of water

Problem areas with Reverse Osmosis

a. Fouling of membranes
b. High pressure requirements for high TDS differences and their potential hazards.
c. Costly systems
d. Large size systems for large water flow rates make them impractical for many consumer applications

Problem areas with Ion-Exchange Resins

a. Resins are costly
b. Need for regeneration is inconvenient and costly
c. Two resin bed systems require use of hazardous acids and alkalis for regeneration
d. Practical considerations of these de-ionize systems render them impractical for consumer and many commercial applications

Problems and Limitations of ED Methods

1. No filtration provided for particulate matter
2. ED will separate out only ionized chemical species, no organic
3. Possible corruption of membrane by crystallizing materials within the membrane structure

The ED system employs long-term, inexpensive electrodes in conjunction with durable membranes that make for a low capital cost apparatus. The equipment operates at standard conditions of temperature and pressure, and requires no special precautions regarding quality of incoming water. The system can be designed to handle a full flow of water on a "once through" basis or it can be made very small and used in conjunction with a storage tank as a batch processor.

Because the system is very simple in structure and operates through direct input of electric power, it can be made very small for portable applications.

Surprisingly, ED is not employed in many areas where its applicability has distinct advantages. For various reasons of cost, unavailability of durable ion exchange membranes, and perhaps complex manufacturing requirements in the past, ED is not as popular for desalination and demineralizing as reverse osmosis, RO, systems. In a similar fashion, RO and cation exchange resin bed methods have been preferred for performing the tasks of water softening.

Residential water softening presents an interesting example of a use where one method almost exclusively predominates the field. Cation resin bed devices have become the primary choice of the industry. RO and ED are competing systems that offer dramatic advantages with regard to the condition of the emergent, treated water over cation resins for softening water.

Neither RO nor ED requires the consumption of sodium chloride for its operation resulting in brine waste water effluents into the ground water table. Softening by cation resins results in virtually the same concentration of dissolved substances in the treated water, except that sodium ions have been substituted for the unwanted "hardening cations" such as calcium and iron.

RO and ED systems soften and demineralize input water by the removal of both cations and anions, thus lowering the total dissolved solids concentration without ionic substitutions.

RO devices are presently available as small units for residential applications, processing a few gallons per day. A full-scale unit that has the capacity to handle peak flows of 2 to 10 gallons per minute, without storage tanks, would be too large, impractical, complex and costly for individual home use.

However, ED systems can be fabricated with high flow rate capacities that would be relatively simple and low cost. It is the intention here to review the operation of ED systems and show how economically practical ED water treatment systems might be designed to solve more problems than they are presently employed. Perhaps we can encourage a closer examination of the salient features and applicability of ED and electrochemical methods in general.

The main attractiveness of the ED approach to water treatment is its inherent simplicity and compatibility with ambient conditions of standard temperature and pressures. This simplicity of hardware is illustrated in the photograph below (Figure 1.1) of an early field test prototype water demineralizer.

The principle component parts of the system shown in Figure 1.1 are listed below.

Processing Module (ED stack of electrodes and membranes)
Processed water reservoir
Waste water reservoir
DC electric power supply
Circulation pumps (two)

We hope to accomplish our goals by going through numerous design exercises, and by establishing straightforward analytical methods, as well as describing some approaches to the practical problems of equipment life, manufacturing designs and costs.

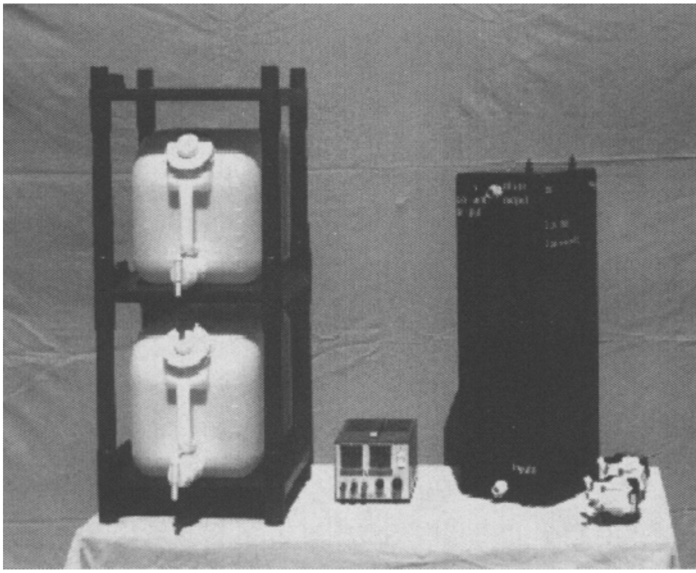

Figure 1.1 Water demineralizer system components.

We are concerned in this book only with electrochemical processes for the control of water quality. Filtration, active carbon adsorption, and reverse osmosis systems are not the subjects of this text.

Our primary purpose is to present the results of research and development conducted and some of the resultant engineering prototypes, along with some useful analytic methods for the design and performance optimization of an array of electrochemical systems. These potential systems range in function from that of demineralizing and desalting streams or bodies of water to the generation, in situ, of oxidizing agents for biocide purposes. The latter would eliminate the need for introduction of biocides from external sources.

Some basic physical chemical principles and electrochemistry are briefly reviewed in Chapter 2 to provide a convenient reference for the reader when going through the analytic portions of this book. For a thorough understanding or tutorial presentation of the physics and thermodynamics of the relationships employed in the parametric developments, it is suggested that the reader consult any of the numerous and excellent texts on the subject matter. Some suggested sources are given in the accompanying Bibliography section.

ED systems can be designed to handle full flow of water on a "once through" basis or they can be made quite small and used in conjunction with a storage tank.

Many portable applications are also possible due to the relative simplicity of its construction and the absence of any need for non-standard ambient conditions, including high pressures or temperatures.

1.2 Technology, History, and Background

TRL, Inc. is an independent Research & Development company. It was formed in Cambridge, Massachusetts in 1971 for the purpose of developing its own proprietary technology in energy conversion and storage; energy storage for utility load leveling and standby power. Most of the laboratory work over the years has been in the area of electrochemical processes, electrode development for Redox and halogen batteries, along with research in the physics of surfaces and transport phenomena.

During the 25 years of applied research and prototype designing, a body of electrochemical technology was developed that lends itself to many applications totally unrelated to energy storage, batteries or fuel cells.

Figure 1.2 shows a typical test set up for evaluating single cell electrodialysis systems for either pH control or de-ionization applications. Pictured are power supplies, timers, TDS and pH meters along with small fluid pumps and data acquisition connections for computer filing.

A resulting potential application for some of the developmental work at TRL is in the field of water processing.

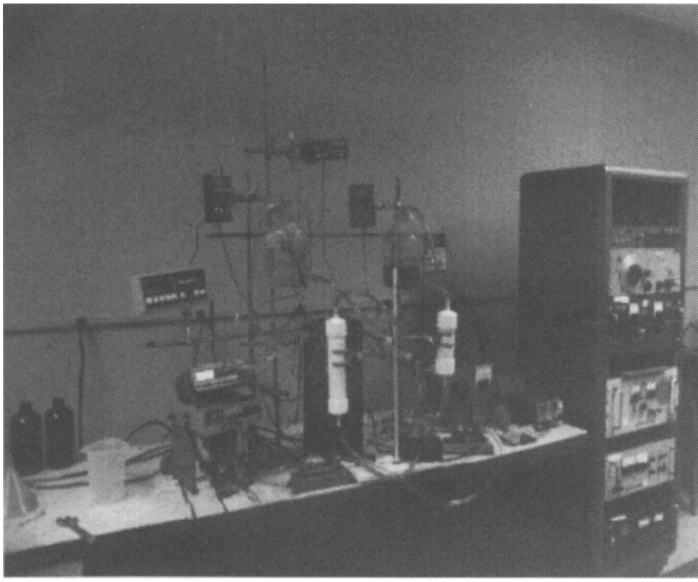

Figure 1.2 Laboratory test stand for water electrochemical studies.

Water treatment via non-hazardous methods afforded by electrochemical processes is an attractive and sensible product area possibility.

The laboratory proceeded to develop, field test and engineer a class of new products for pool and spa use (labeled SimPool systems), and manufactured systems for field testing over a year.

Over that time period, systems were developed and successfully installed in over 100 pools and spas in various geographic areas of the United States.

1.3 Application Areas: Electrochemical Technology Water Processing

The following is a list of some immediate areas of application, which are possible with ED and electrochemical technology. These product applications would make use of well-established hardware designs and know-how.

1. Electrochemical Generation of Free Halogen (chlorine or bromine) in "salted" water for the purpose of disinfection. Product types are:

   1. Swimming pool and spa halogenators
   2. Water cooling tower processing
   3. Potable water supply treatment

2. Free Halogen, Hypochlorous or Hypobromous Acid Injection

   Electrochemical generation of halogens and halogen acids via concentrated salt solution are injected into electrode reaction chambers. "Salting" an entire body of water to be treated is thus avoided. This method is particularly suited to large bodies of water and in evaporative cooling water systems, which require frequent "blow-down".

3. pH Control of bodies of water without the addition of acids or bases from an external chemical source. Only electrical power input is required to perform the conversion process instead of introducing additional chemical species. Handling, transporting, and storing corrosive and hazardous chemicals is eliminated. This is suitable for:

   1. Swimming pools and spas
   2. Industrial water supplies for the process industry
   3. Cooling water for machinery
   4. Reverse osmosis system pH control

4. Water Softening

   1. Residential and commercial water softening systems use the precipitation of dissolved minerals as scale on the negative electrode surfaces.

A system employing a membrane separator will perform this function without the introduction of sodium ions into the water stream, as is presently done.

2. A counter top version of this system is possible, which would "purify" a small quantity of water at a time (perhaps 1 qt. to 1 gal.). The design may resemble that of a typical drip-type coffee maker.

5. Oxygenation

Oxygen bubbles can be generated for the purpose of replenishing the supply in relatively confined and stagnant bodies of water, including aquariums. Such a unit would have no moving parts, generate no noise or vibrations, last indefinitely and be quite inexpensive. Electrolysis of the water produces the needed oxygen. "Starved" electrode designs would have to be employed in this instance to guard against production of free halogens.

6. Ion Exchange Resin Regeneration

1. Regeneration of resin beds normally employed in residential and commercial water softeners requires the periodic replenishment of salt (sodium chloride) in a reservoir. Frequently unwanted sodium ions are then substituted for the heavy, hardness producing metals, which are removed from the water. An ED system can be substituted for the salt reservoir and hydrogen ions used to regenerate the resin instead of sodium. Electrolysis of the water through an ED unit produces the H^+ ions. Normal pH is restored by the proper use of the staged electrolytic unit. In this approach, no salt is needed and no sodium ions are produced in the water.

2. Regeneration of de-ionizer resin beds at the operating site via electrochemical means. This would eliminate the need to remove equipment and transport it to service depots. Costs would be reduced and operational interruption minimized; plus, there would be no handling of hazardous chemicals, such as concentrated acids and alkalis.

7. Organic Contaminant Control

In some cases where unwanted organic molecular structures can be altered and rendered acceptable via high acid or alkali exposure, a pH control cell may provide a "local" environment to achieve the needed reaction without the introduction of chemical reagents.