

**Advanced Water and Wastewater Treatment: Implications and Prospects for the  
Construction Industry**

by

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**Submitted to the Technology and Policy Program and the Department  
of Civil and Environmental Engineering  
in Partial Fulfillment of the Requirements for the Degrees of**

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and

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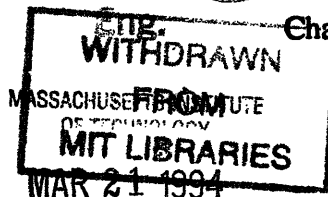
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**ABSTRACT**

Water pollution control is largely driven by two pieces of federal legislation: the Clean Water Act and the Safe Drinking Water Act. Compliance with these two acts and their subsequent amendments has resulted in tens of billions of dollars being spent by industry, municipalities, states and the federal government. The construction industry, however, has largely benefited from this outpouring of money.

This thesis examines the use of certain water pollution control technologies from the point of view of the construction industry. This is accomplished by looking at, for each technology or technology group, the individual technologies; the market characteristics; the regulatory, legal and social environment; the market attractiveness to the construction industry; and the investment requirements. Lastly, within each technology group, a case study illustrates an example of the implementation and use of a given technology.

In particular, the issue of wastewater recycle and reclamation, and certain technologies associated with providing advanced levels of treatment, is examined. Second, ion exchange—used to remove nitrates, radionucleotides, and heavy metals from drinking water and municipal and industrial wastewater—is analyzed. Lastly, emerging chemical oxidation technologies are examined.

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## Chapter 1 Introduction

The planet earth is blessed with the gift of water and from this water life. Somewhere in the great seas of the past, the inorganic was transformed to the organic, the first premonition of life on this planet. Over four billion years ago, the seas were home to the simplest of all living things; as time passed, slowly transformations occurred and life expanded to include single-celled organisms and much later multi-celled organisms. Some of these in turn progressed into plants and then into animals. Seeking something else, some of these animals eventually left the ocean. From that moment when those first animals dragged themselves out of the sea and onto the beaches, there has been a quest for fresh water: Eons later, man would share this quest with others of the animal kingdom. Man's earliest ancestors roamed, hunted and finally settled near sources of water. The development of water resources technology—canals, aqueducts, levees, dikes and reservoirs—fostered civilizations and allowed for empires. Babylon, Egypt, China, Rome and Hitti were all dependent on such technologies<sup>1</sup>. While these civilizations rose and fell, the technology advanced, surviving the passage of time and the lives and deaths of individual engineers, kings and peasants. Some early innovations, like the large-scale irrigation project in Sichuan Province in China, are still in use after 1800 years; many other irrigation schemes failed to drain properly and were doomed by salt buildup in the soil. Other types of projects had their individual successes and failures, like the construction of lead drinking water pipes in the ancient city of Rome<sup>2</sup>. For better or worse, water resource technology helped transform the landscape and history alike; people were able to congregate in large numbers and live in close confines. Rivers, lakes and oceans—giant trash receptacles for centuries—were considered ideal for washing away wastes.

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<sup>1</sup> Vujica Yevjevich, "Water and Civilization", *Water International*, Vol. 17, 1992, p. 164.

<sup>2</sup> Vujica Yevjevich, *Ibid.*, p. 165.

Somewhere along the way, these large bodies of water were no longer able to withstand the pressures put on them by humans and became polluted by disease-bearing microorganisms, metals, radioactive waste, and recalcitrant organics.

Approximately 9 million cubic miles or one percent of all the water on this planet is freshwater. This must be shared amongst the five and a half billion people living on this planet<sup>3</sup>, allowing for over 240 million cubic feet per person. Were it ever that simple! Sixty-five percent of the fresh water is tied up in the Antarctic Icecap<sup>4</sup>, still leaving 84 million cubic feet per person. However, in the last hundred years, the technological era has taken its toll on the world supply of fresh water. All over the world, chemicals and petroleum products are synthesized and produced zealously. The per capita use of water has increased. As the population grows, the demands on water as a natural resource only rise. People depend on more and more water to accommodate a modern lifestyle; to irrigate rice fields in the middle of deserts; to turn their cities from a lifeless brown to a bright chipper green; to flush household sewage out of the home, out of sight, and out of the mind. Fresh, clean water becomes a distributional issue; it must be transported from a natural source, treated and finally conveyed to the user. The City of Los Angeles is only able to exist because rivers have been diverted and their water transported across the desert, a monumental achievement of civil engineering, illustrating what any thirsty person knows: high quality water is only useful if it can reach the user. The 84 million cubic feet of freshwater that exists for each person on this planet is as elusive to the average person as the small drink of water from the desalination plant.

Estimates on the US average per capita use of water vary according to the method of accounting. Personal water use amounts to about 60 gallons per day, with a range of

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<sup>3</sup> 1992 Information Please Almanac, Houghton Mifflin Company, Boston, 1992, p. 137.

<sup>4</sup> 1992 Information Please Almanac, Ibid., p. 137.

40–130<sup>5</sup>, while municipal water produced per capita is 160 gallons per day, second worldwide only to Australia. However, in terms of total use— including industrial, agricultural and municipal use—1400–1600 gallons per day per person is the norm<sup>6</sup>, and the US is the world leader<sup>7</sup>. In stark comparison, the country of Malta only has a per capita total usage of 43 gallons per day<sup>8</sup>. If every person on the planet consumed as much as a typical American, 330 billion gallons or 0.3 cubic miles would be required for personal use. Finally, if the world industrialized to the current level of the United States and mimicked the US in terms of water usage, 7.5 cubic miles would be used every day.

In the United States, the primary sources of water are fresh surface water (65%), fresh groundwater (18%) and saline surface water (15%), although saline groundwater (0.2%) and reclaimed wastewater (0.2%) do supply a small fraction of the total. Of the 400 billion gallons used daily in the US, less than 10% is used for municipal water supply, and an additional 2% used for rural water supply. The remainder is used to provide cooling water for thermoelectric power (48%), irrigation (35%) and industrial usage.

When settlers first came to this country, water was a precious resource, difficult to come by and sparingly used. In the first few centuries, any sewage produced was disposed of directly into a nearby river. As the country industrialized, people left the farms in ever-increasing numbers and headed to the cities, taking jobs in shops and factories. Water was needed to run the homes and industries. Using a technology that was first

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<sup>5</sup> George Tchobanoglous and Franklin L. Burton, Wastewater Engineering: Treatment, Disposal, and Reuse, Third Edition, Metcalf & Eddy: New York, 1991, p.17.

<sup>6</sup> W.B. Solley, C.F. Merk and R.R. Pierce, *Estimated Water Use in the United States in 1985*, U.S. Geological Survey Circular 1004, 1988 in Fritz van der Leeden, Fred L. Troise, and David Keith Todd (eds.), The Water Encyclopedia, 2nd Edition, Lewis Publishers, Chelsea, Michigan, 1990, p. 302–305.

<sup>7</sup> Organization for Economic Cooperation and Development, *Environmental Data Compendium 1987*, in Fritz van der Leeden, Fred L. Troise, and David Keith Todd (eds.), The Water Encyclopedia, 2nd Edition, Lewis Publishers, Chelsea, Michigan, 1990, p. 311.

<sup>8</sup> Water Resources Institute, *World Resources, 1986* in Fritz van der Leeden, Fred L. Troise, and David Keith Todd (eds.), The Water Encyclopedia, 2nd Edition, Lewis Publishers, Chelsea, Michigan, 1990, p. 311.

implemented by the Ancient Romans and later updated in 17th century London<sup>9</sup>, water was piped into the major American cities. In 1802, Philadelphia was the first city to build a waterworks; and within the next six decades, the sixteen largest cities in the United States had constructed systems of waterworks<sup>10</sup>. With a ready supply at hand, the per capita use of water began to increase steadily. The water closet, the precursor to the modern-day toilet, was first patented in 1833<sup>11</sup>, and was by the mid- to late- nineteenth century a common feature in affluent homes<sup>12</sup>. This only helped to further increase the pollutant load as more and more raw sewage from individual households and factories was dumped into the nearest body of water. Continuing through the early 1900s, most sewage and wastewater from individual households and factories was discharged directly to the environment via the storm sewer systems<sup>13</sup>. This, however, was not without its problems: the accumulation of sludge in the sewers, severe odor problems and danger to public health. Separate sewers and wastewater treatment facilities were constructed in response to these problems. Later, these systems were updated to reflect increases in knowledge and technology.

### 1.1. Water Pollution and Environmental Legislation

Originally, pollution and industry were thought to go hand and hand: where there was one, there was the other. If this wasn't liked by everyone, it was at least generally accepted. Over the last twenty-five years, the mindset of the American populace has changed. From pliantly accepting industrial and municipal pollution, the average American has become more informed about the environment, more cynical about the wonders of

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<sup>9</sup> Joel A. Tarr, "Water and Wastes: A Retrospective Assessment of Wastewater Technology in the United States, 1800-1932", *Society for the History of Technology*, 1984, p. 226-263.

<sup>13</sup> Joel A. Tarr, *Ibid.*, p. 226-263.

<sup>11</sup> Joel A. Tarr, *Ibid.*, p. 226-263.

<sup>12</sup> Joel A. Tarr, *Ibid.*, p. 226-263.

<sup>13</sup> George Tchobanoglous and Franklin L. Burton, *Ibid.*, p. 8.

industry, and more vocal in her or his demands of a clean, green place to live and breathe<sup>14</sup>. Collectively, public pressure was placed on Washington.

This resulted in a piecemeal series of legislation, each designed to protect a small part of the whole. Lacking a holistic approach, each media—the air, the water, the land—was protected under a different, often conflicting piece of legislation, each with a name longer and more grandiose than the next. This was the era of acronyms: CERCLA and RCRA, CAA and FWPCA, FIFRA and SDWA, TSCA and OSHA<sup>15</sup>. Of all these pieces of federal legislation, two in particular, and their subsequent amendments, have shaped the water pollution control industry. These are the Federal Water Pollution Control Act of 1972 and the Safe Drinking Water Act of 1974.

The Federal Water Pollution Control Act of 1972 was designed to protect the nation's surface waters: the lakes and rivers that crisscross the United States. Colloquially known as the Clean Water Act and officially as Public Law 92-500, this piece of legislation had a stated "national goal that the discharge of pollutants into the navigable waters be eliminated by 1985"<sup>16</sup>, and sought to legislate the burgeoning environmental concerns of the American public about the waterways of this country. Principally, it sought to reduce the pollutant load on the nation's waterways by employing two main strategies. First, the act required that all wastewater, municipal and industrial, be treated prior to discharge. The US EPA then established municipal and industrial effluent limitations, which defined the amount and concentration of specific pollutants that could be discharged by municipalities and industries. Each facility then had to be permitted by the state under the National

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<sup>14</sup> Thomas Kvan, "Environmental Market Is Growing Here and Abroad", *American Consulting Engineer*, p. 17.

<sup>15</sup> These are, respectively, Comprehensive Environmental Response, Compensation and Liability Act; Resource Conservation and Recovery Act; Clean Air Act; Federal Water Pollution Control Act; Federal Insecticide, Fungicide, and Rodenticide Act; Safe Drinking Water Act; Toxic Substances Control Act; Occupational Safety and Health Act.

<sup>16</sup> Federal Water Pollution Control Act, Subchapter 1, section 1251, part a.

Pollutant Discharge Elimination System (NPDES), with all discharges falling within the effluent limitation levels. Second, in order to help communities finance the construction of new or upgraded sewage treatment facilities, a large federal grant program was established<sup>17</sup>. These grants were to help cities of all sizes come into compliance without undo financial burden.

Twenty years and three revisions of the Clean Water Act later, this goal of zero discharge has yet to be achieved. However, the noose, once slack and forgiving, is tightening around point-source dischargers. As of January 1, 1988, 89 percent of all municipal wastewater was receiving at least secondary treatment before discharge<sup>18</sup>. Secondary treatment standards are defined as an 85% reduction in Biological Oxygen Demand (BOD) and Total Suspended Solids (TSS), with effluent concentrations no higher than 30 mg/L for both BOD and TSS. Fifty-one industrial Best Available Technologies (BAT) standards have been established on an industry-by-industry basis to control discharges of 126 toxic pollutants. These standards mandate effluent concentrations based on the Best Available Technologies commercially available for a given industry. Furthermore, under NDPEs, all permits for discharging wastewater and industrial discharges have become increasingly technical and quite costly, requiring very stringent monitoring and record keeping on the part of the discharger. As the costs of effluent discharges increase, there is a direct economic incentive to reduce both the volume and toxicity. This can be achieved by building on-site a system to pretreat the waste, entirely redesigning the various processes to minimize inputs of the most virulent chemicals, or incorporating elements of reuse and recycle of water.

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<sup>17</sup> Steve Daniels, EESC Issue Paper on the Clean Water Act, 1993 Briefing Book on Environmental and Energy Legislation, The Environmental and Energy Study Institute, Washington DC, 1993, p. 13.

<sup>18</sup> Steve Daniels, *Ibid.*, p. 13.

One definite limitation of the Federal Water Pollution Control Act as it currently stands is its focus on point-source discharges. Most non-point source discharges— industrial, urban and agricultural runoff—are not permitted under ND PES and are, according to the EPA, currently the source for more than half the nation's water quality problems<sup>19</sup>. It stands to reason then that by only looking at point sources, the United States Environmental Protection Agency might be missing the point. The non-point sources eventually will have to be dealt with, which, indirectly, the American public is already dealing with. Due to contamination of surface and ground water sources, water bills are higher, reflecting more advanced levels of treatment required to make the water potable. Furthermore, environmental contamination leads to rivers and lakes that are not swimmable, fishable or both, decreasing the enjoyment and use the public has of these natural resources. The great aquifers of this country could become as a recalcitrant a supplier of water as the ocean is today, but for very different reasons. Currently, aquifers supply slightly over fifty percent of the water used each day in the United States; in some areas, this increases to nearly one hundred percent. Due to residence times orders of magnitude longer, aquifers aren't as tolerant of abuse as rivers and streams. For instance, in both industrial and rural locations, organics such as solvents and pesticides have percolated through the soil and into local groundwater supplies. Overdrawing aquifers near the ocean has lead to saltwater intrusion; while in inland areas this has caused the permanent collapse of certain aquifers. Aquifers under dense agricultural centers have become contaminated with nitrates. Whereas natural processes—light, biological activity, flow—can help disperse, eliminate or degrade contaminants in other fresh water systems, these are usually insignificant processes in aquifers. Without the natural self-cleaning processes, the aquifer remains quite contaminated and the water requires treatment before it is potable. The United States Environmental Protection Agency estimates that 57 percent of

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<sup>19</sup> Steve Daniels, *Ibid.*, p. 13.

rural wells and 52 percent of wells for wells used for drawing community water are contaminated to some extent by nitrates, almost entirely from non-point sources. An estimated 4.5 million Americans—including 600,000 infants, or those most likely to be injured by elevated nitrate levels—get their drinking water from wells with nitrate concentrations at levels considered unsafe<sup>20</sup>.

The other main piece of federal legislation driving the water pollution control industry is the Safe Drinking Water Act (SDWA). This act, Public Law 93-523, was signed into law by President Gerald Ford in 1974 and mandates the maximum concentrations of various organic, inorganic and microbial contaminants allowable in the drinking water supply. Originally designed to protect the public from the outbreak of infectious diseases from waterborne bacteria, viruses and other microorganisms, the 1986 amendments incorporated concerns about other contaminants such as metals and organics. The 1986 amendments, Public Law 99-339, required EPA to promulgate standards for 89 contaminants by 1989 and for an additional 25 contaminants a year beginning in 1991. These are two-tiered standards, non-enforceable Maximum Contaminant Level Goals (MCLGs), set at a level to protect against health effects over an entire lifetime of exposure, and an enforceable Maximum Contaminant Levels (MCLs), which incorporate cost and technology into the standard. Conventional and advanced processes considered for Best Available Technology for water treatment under SDWA are given in Table 1.1.

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<sup>20</sup> Steve Cook, EESC Issue Paper on the Clean Water Act, 1993 Briefing Book on Environmental and Energy Legislation, The Environmental and Energy Study Institute, Washington DC, 1993, p. 31.

**Table 1.1 Water Treatment Processes Considered for Best Available Technology<sup>21</sup>**

<b>Conventional Processes</b>	<b>Advanced Processes</b>
Coagulation, sedimentation, filtration	Activated alumina
Direct filtration	Adsorption
Diatomaceous earth filtration	Granular Activated Carbon (GAC)
Slow sand filtration	Powdered Activated Carbon (PAC)
Lime softening	Resins
Ion exchange	Aeration
Oxidation-disinfection	Packed column
Chlorination	Diffused air
Chlorine dioxide	Spray
Chloramines	Slat tray
Ozone	Mechanical
Bromine	Cartridge filtration
Others	Electrodialysis
	Reverse osmosis
	Ultrafiltration
	Ultraviolet light
	UV with other oxidants

Source: J.E. Dyksen, D.J. Hildebrand, and R.F. Raczko, "SDWA Amendments: Effects on the Water Industry", *Journal AWWA*, Vol. 80, No. 1, 1988.

All water systems with more than 15 connections or 25 customers are required to test their water regularly for these contaminants and inform their customers when the SDWA standards are exceeded. Furthermore, while the US EPA has primary responsibility, states may assume primacy and adopt their own standards may be written to reflect local conditions and public concerns, as long as they are at least as stringent as the federal code. In order to provide large numbers of people with safe drinking water, a local water utility must consider a plethora of technologic, economic and regulatory issues. Enough water must be produced, or purchased, to meet the demand of residential, industrial and agricultural users; and the water must meet federal, state and local drinking water standards. Moreover, the cost must be such that the community can afford to pay for its water.

<sup>21</sup> J.E. Dyksen, D.J. Hildebrand, and R.F. Raczko, "SDWA Amendments: Effects on the Water Industry", *Journal AWWA*, Vol. 80, No. 1, 1988, in *The Water Encyclopedia*, 2nd Edition, Lewis Publishers, Chelsea, Michigan, 1990, p. 489.

## **1.2. Pollution Control and the Construction Industry**

While the blossoming of pieces of environmental legislation may worry the heads of affected industries and municipalities, to those in the construction, consulting and environmental services industry this means more contracts up for the coming. In 1992, the federal government allocated more one billion dollars for environmental restoration programs, or approximately 1.5% of the Gross Domestic Product (GDP)<sup>22</sup>. State and local contributions push this value even higher. This money will likely be spent in both the traditional specters of environmental remediation—the design and construction of wastewater, drinking water, and solid waste facilities and facility upgrades and air emission control devices—and in the emerging areas of site investigation and remediation, environmental audits and preventative services<sup>23</sup>. An October, 1992 EPA estimate of the cost of upgrading all of the nation's wastewater treatment facilities put the amount at \$80.4 billion, or equal to the design year estimate for such treatment made a year earlier. According to a December, 1992 National Water Education Council report, the cost of repairing and replacing the sewer and water infrastructure over the next twenty years will reach \$400 to \$500 billion, or approximately \$20 to \$25 billion per year<sup>24</sup>. Whichever of these proves more accurate, there can be no dispute that water pollution control is an enormous market.

Part of the reason for such a continued need for money is simply to come into compliance with the Clean Water Act and the Safe Drinking Water Act. Furthermore, in certain areas of the country it is necessary to further treat the effluent in order to reduce

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<sup>22</sup> Thomas Kvan, *Ibid.*, p. 17.

<sup>23</sup> Thomas Kvan, *Ibid.*, p. 17 - 18.

<sup>24</sup> Allen Hammond (ed.), 1994 Information Please Environmental Almanac, World Resources Institute, Houghton Mifflin Company, Boston, MA, 1993, p. 38.

concentrations of nutrients that are causing eutrophication, such as in the Chesapeake Bay and Great Lakes areas. Finally, in arid regions of the country, water planners are beginning to view wastewater effluent as an increasingly important part of the overall water budget, instead of as a nuisance that has to be permitted and disposed of. In these areas, wastewater effluent is being used for everything from irrigation of crops and recreational facilities to snow making to aquifer replenishment. Due to state and federal standards, though, it is necessary to treat wastewater quite extensively before it is reclaimed, or used for any purpose besides simple discharge into a nearby body of water. As the need for water in a given region becomes even greater, new allowances for treatment center upgrades are being included in local and state budgets.

As may be expected, pollution control and the construction industry are complementary. Controlling pollution can be achieved in two ways: altering behavior or adding a device to remove the pollutant. Whereas in the long run it might make more sense to alter practices to reduce the amount of pollutant being produced, it has long been the practice to design processes to remove the contaminant either at the source or down the stream. This is especially true in the case of water pollution, where most end-of-the-pipe solutions to water pollution are corrected by water treatment facilities, at either the industrial or the municipal level; and the technology exists to decontaminate completely even the most heavily contaminated water. These treatment facility construction and upgrades are large-scale public-works construction projects, involving millions of dollars. During the initial stages of the implementation of the Clean Water Act, Congress allocated billions of dollars in federal grant funds for the design and construction of wastewater treatment facilities were available to construct or upgrade existing facilities. Such money is no longer available, but the needs of communities are far from met. In many areas of the South, Southwest, and West, water needs are not being adequately met with the existing infrastructure. In agricultural areas, nitrates contaminate water supplies, putting the health of infants at extreme risk. In other locales, uranium and heavy metals are a concern. The

removal of long-stream organic micropollutants—those not broken down by conventional biological treatment methods—is a concern to water treatment facilities, wastewater treatment facilities, groundwater treatment projects, and industrial facilities.

### 1.3. Thesis Objectives

This thesis will analyze three segments of the American water and wastewater treatment market in terms of the construction industry. The three areas are water and wastewater reuse and recycle; the use of ion exchange for nitrate, ion and heavy metal removal from wastewater and water streams; and advanced oxidation systems for the removal of organic micropollutants. Water and wastewater reuse and recycle is further subdivided into aquifer storage recovery (ASR), natural treatment methods and membrane separation devices. These subcategories illustrate the various ways of thinking about and solving the problem of meeting water demands with wastewater. ASR is a method to balance out temporal fluctuations in the supply and demand of water, natural treatment mimics nature; and membrane separation technologies represent the high-tech solution. Advanced oxidation systems are similarly subdivided in order to adequately represent the range of technologies available or being developed.

These areas were selected from a larger pool of potential problems and technologies by a method of weighing certain attributes in terms of their potential attractiveness to the construction industry. These attributes included initial assessments of the appropriateness of the technology for addressing a given problem, immediacy of the problem, current and potential market size, appropriateness for the construction industry, status of development, investment requirements and potential liabilities.

This thesis expands on these themes, and by doing so, analyzes these three areas in terms of the construction industry. In particular, assessments of the technologies are given as well as examples of use in the water and wastewater industry. The regulatory

environment is examined; legal, political, social and regulatory acceptability are looked at, along with any related public health and environmental issues associated with the technologies. The current and future market in general is analyzed. Furthermore, the market attractiveness to the construction industry is examined, by looking at the strategic attractiveness of each technology, the suitability to the construction industry and the cost effectiveness of the technology to the customer. Investment requirements, including status of development, are noted. Case studies for each technology or problem illustrate examples of the technology in use. Lastly, a policy analysis of water reuse and recycle is included in the water reuse chapter.

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## **Chapter 2 Wastewater and Water Recycle and Reclamation**

### **2.1. Introduction**

Broadly defined, wastewater recycle and reclamation is the process encompassing the treatment and use of wastewater as a natural resource. Recycling can be accomplished on any scale from the very small, as on board a ship or spacecraft; to the small, such as in commercial buildings; to the large and very large, as in the case of on-site industrial water recycling and at Publicly Owned Treatment Works (POTWs). In this status, the wastewater is not disposed of as a mere byproduct of the treatment process. Instead it is used for select purposes as a substitute for potable water. Recycling and reclaiming water can have substantial implications at any of these levels toward the meeting of water budgets and the production of potable water, preservation of the environment and reduction in disposal and discharge fees.

Policy issues central to the concept and practice of using and reclaiming wastewater will be addressed in the introduction, while the remainder outlines the technical, regulatory, and social issues related to reclaiming and reusing wastewater. While the focus of the report will be the reuse and reclamation of municipal wastewater from traditional wastewater treatment centers, issues concerning industrial wastewater reuse and water treatment will also be addressed. Descriptions of technologies key to this field include aquifer storage recovery (ASR), natural systems, and membrane separation technologies. The next section concerns itself with the regulatory and social acceptance of reusing and reclaiming wastewater. The following three sections will then address the market itself, the applicability to the construction industry, and investment requirements. Four case studies highlight actual examples of reclaiming and recycling wastewater. Lastly, the conclusion wraps everything together.

### **2.1.1. The Relation of Potable Water to Reclaimed Wastewater**

Each organism and ecosystem alike require a certain amount of water to survive, to function effectively, and to grow and thrive. In a similar fashion, each community, region and country needs a certain amount of water. This volume of water must satisfactorily meet the needs of the entirety of the municipal, agricultural, industrial, and electrical users. In order for the community to go about its daily business, the water supply must be of reliable quantity and quality, available around the clock, three hundred and sixty five days a year. When the water is not there, various aspects of the community—industries, utilities, social services—begin to fray at the edges and slowly dissolve or come to a halt; the social fabric unwinds.

First and foremost, without large quantities of water, food cannot be produced. This effect trickles down from the production of food to the production of goods and services to the production of electricity and other heavy industries. Chemical and pharmaceutical industries, refineries, pulp and paper manufacturers, nearly every industry relies heavily on water in order to manufacture products. Without adequate water supplies, needed directly for production and indirectly for cooling water and the production of steam, these are forced to shut down. Electrical utilities, also requiring high quality water for cooling water, are forced to curtail their production of electricity or shut down. Sanitation systems fail and with them the threat of disease skyrockets. If high quality sources of water are not available, people turn to dubious or even downright dangerous sources of water: rivers that receive raw sewage directly, groundwater wells contaminated by organic pollutants or heavy metals. However, when both money and foresight coincide, technology can take over. Whereas in the past, the technological options for acquiring safe and reliable sources of water included damming and diverting rivers, digging new wells

and building small- and large-scale irrigation systems, the technology is now available that can take the dirtiest, nastiest, most dangerous water and make it clean.

Overall in the United States, water is plentiful. However, the absolute volume of water that exists is only as important as its location. Water as a natural resource is a distributional issue; the water must be where the people and the demand are. In the arid and semi-arid heavily populated South and Southwest, the demand for fresh water far exceeds the supply. Taking over where nature left off, in the 1930s and '40s civil engineers and water planners stepped in. Large dams and canals were designed, financed and constructed to cart the water in to satisfy the demands of a growing region, and have kept the vegetables and rice growing in the middle of the desert ever since. And when there were problems as a result, new technologies came along to solve them. For instance, to meet the needs of the agricultural sector of Arizona and California, the pristine wilds of most of the Colorado River were forfeited. This 1400-mile river winds from the Rocky Mountains down to the Sea of Cortez and has experienced nearly a century of being dammed and diverted, transported, and used extensively for irrigation in two countries. This pattern of use has not left the river unharmed, nor has it left its users without additional problems. In particular, Mexican farmers, who use water from the Colorado to cultivate crops in the Mexicali Valley, received the brunt of the problems. Due to the combination of a wide variety of irrigation projects up and down the river and the natural landscape, the salinity in the lower portions of the river began to rise in the early 1960s, and within two decades it had doubled<sup>1</sup>. Irrigated with this water, wide swathes of the Mexicali valley were began to suffer from salt poisoning. Crops were unable to grow on about one eighth of the land by the early eighties and predictions suggested that should conditions continue to deteriorate unabated, by the year 2000 the entire valley would be

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<sup>1</sup> Robin Clarke, Water: The International Crisis, MIT Press, Cambridge, MA, 1993, p. 99-100.

unsuitable for agriculture<sup>2</sup>. More large-scale civil engineering projects were then needed to deal with the effects of the first round of projects. Due to the underlying bedrock in the vicinity of Yuma, Arizona, the irrigation return water—water that drains from irrigated fields—from several large-scale irrigation projects in the area became extremely saline. Coming from already elevated river concentrations of 600–800 mg/l (in comparison, the mean salinity for North American rivers is 148 mg/l<sup>3</sup>), the salinity of the irrigation return water was between 3000 and 3400 mg/l<sup>4</sup>. A 100 MGD desalination plant in Yuma, Arizona was designed and constructed to treat the irrigation return water before 72 MGD was returned to the Colorado River at a salinity of 100–400 mg/l, thus allowing the farmers in the Mexicali valley to be able to utilize the river water without further damaging their land. Finally, a canal was built to transport the remaining 28 MGD of water with a salinity ranging from 10,000–12,000 mg/l to the Sea of Cortez<sup>5</sup>. The same membrane-based technology that allowed 100 MGD of water to be desalinated is also used to reclaim wastewater. In a similar fashion to the irrigated river water becoming an integral part of the system for providing farmers downstream with water for irrigation, wastewater treatment plants can be designed and operated such that they are contributing to the solution of local and regional water needs, rather than being part of the problem.

A water supply can originate from three sources: surface water, groundwater and reclaimed wastewater. Surface water in turn can be either fresh, saline or brackish, and either domestic or imported; water transported from other locales is considered imported, and water from a source within the community domestic. Groundwater as well can be either fresh, brackish, or saline; and while it can be imported from other locations, it tends

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<sup>2</sup> Robin Clarke, *Ibid.*, p. 99–100.

<sup>3</sup> Robert G. Wetzel, *Limnology*, Saunders College Publishing, Philadelphia, 1983, p. 180.

<sup>4</sup> Anton C.F. Ammerlaan, John C. Franklin, and Charles D. Moody, "Yuma Desalting Plant. Membrane Degradation during Test Operations", *Desalination*, Vol. 88, 1992, p. 33–34.

<sup>5</sup> Anton C.F. Ammerlaan, John C. Franklin, and Charles D. Moody, *Ibid.*, p. 33–34.

to be primarily domestic. Reclaimed wastewater is the intentional or unintentional reuse of either municipal or industrial wastewater for direct or indirect consumption or environmental purposes.

Two hundred years ago, the average American utilized a couple of gallons a day; this has increased to about 60 gallons per day, with a range of 40–130<sup>6</sup>. Typical municipal water use totals around 165 gallons per day per person, or 36.4 % for domestic supply, 42.4% for industrial use, 6.0% for public service and 15.2% unaccounted for in leakage and system losses<sup>7</sup>. However, the total amount of fresh water, not supplied directly by rainfall, used each day in the United States is much higher than these numbers suggest. If all industrial, electrical, public and agricultural usages are included, the amount of water utilized per capita skyrockets to 1400–1650 gallons per day, 10% of which is accounted for by the public water supply, 11% for industrial use, 38% for electric cooling and 41% for agriculture and irrigation<sup>8</sup>. This water does not miraculously appear where it is needed; sources are taxed. Increases in the total amount utilized have progressed steadily, as Table 2.1 shows, with sources of saline and fresh groundwater and surface water, and reclaimed sewage.

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<sup>6</sup> George Tchobanoglous and Franklin L. Burton, Wastewater Engineering: Treatment, Disposal and Reuse, Third Edition, Metcalf & Eddy, New York, 1991, p. 17.

<sup>7</sup> George Tchobanoglous and Franklin L. Burton, *Ibid.*, p. 17.

<sup>8</sup> Fritz van der Leeden, Fred L. Troise, and David K. Todd, The Water Encyclopedia, Second Edition, Lewis Publishers, USA, 1990, p. 311.

**Table 2.1 Water Use in the United States, 1955–1985, in Billions of Gallons per Day<sup>9</sup>**

	Year			
	1955 <sup>1</sup>	1965 <sup>2</sup>	1975 <sup>3</sup>	1985 <sup>3</sup>
Population (in millions)	164.0	193.8	216.4	242.4
Source of water:				
Ground:				
Fresh	47	60	82	73
Saline	0.6	0.5	1	0.7
Surface:				
Fresh	180	210	260	260
Saline	18	43	69	60
<b>TOTAL<sup>4</sup></b>	<b>250</b>	<b>310</b>	<b>410</b>	<b>400</b>
Water usage:				
Public supply	17	24	29	37
Rural, domestic & livestock	3.6	4.0	4.9	7.8
Irrigation	110	120	140	140
Industrial:				
Thermoelectric power	72	130	200	190
Other industrial usages	39	46	45	31
<b>TOTAL<sup>4</sup></b>	<b>240</b>	<b>310</b>	<b>420</b>	<b>400</b>
Reclaimed Sewage	0.2	0.6	0.5	0.7

1 48 States and the District of Columbia.

2 50 States and the District of Columbia.

3 50 States, the District of Columbia, Puerto Rico, and the Virgin Islands.

4 Data is rounded to two significant digits which may lead to some discrepancies.

Source: W.B. Solley, C.F. Merk, and R.R. Pierce, *Estimated Water Use in the United States in 1985*, United States Geological Survey Circular 1004, 1988.

The resulting mixture of sources a community utilizes is a function of the water available; the total demand for water; the available infrastructure within the community and the surrounding region; the economic, environmental, and social cost and benefit of each option; and public opinion. Changing the mixture of sources can, in some cases, alleviate stress to parts of the system that are fragile, unstable or unreliable. These stresses arise from both natural and manmade causes and include overtaxing a delicate ecosystem, relying too heavily on rainfall, competing with neighboring communities for limited resources,

<sup>9</sup> W.B. Solley, C.F. Merk and R.R. Pierce, *Estimated Water Use in the United States in 1985*, U.S. Geological Survey Circular 1004, 1988 in Fritz van der Leeden, Fred L. Troise, and David Keith Todd (eds.), *The Water Encyclopedia*, 2nd Edition, Lewis Publishers, Chelsea, Michigan, 1990, p. 302.

overpopulation, over development, deforestation, overdrawing aquifers, or any other number of situations which leave the environment damaged or overtaxed.

The potential benefits of using reclaimed wastewater rather than a more traditional source of water fall into two categories: environmental and consumptive. Consumptive benefits are those in which the benefit is in having more water available with which to meet the water budget. Environmental benefits come from relieving pressure on the environment. Examples of this include preventing or curtailing salt water intrusion into a fresh water aquifer, equilibrating groundwater withdrawal and recharge, and restoring a damaged ecosystem by reducing the nutrient load onto a stream or estuary. However, if care is not taken, it is possible to damage an ecosystem by using reclaimed wastewater. For instance, the vadose zone above an aquifer can be changed due to a flourishing of microbial and algal activity if the nutrient level of the wastewater is too high. Alternately, if the concentration of total dissolved solids (TDS) is too high, the soil will become too saline to support certain types of crops, a problem common to poorly designed irrigation systems. Furthermore, unless federal or state effluent disposal fees surge, there are certain water-rich areas of the country, like in the Great Lakes region, where reclaiming wastewater will never be cost effective. This does not mean, however, that there will not be any benefits from the using reclaimed wastewater, just that the benefits will be entirely environmental rather than consumptive. In other more arid regions, both consumptive and environmental benefits are possible.

The choice of sources can be altered, due to various legal, regulatory, and economic incentives and barriers. Well-designed, consistent incentives from the relevant agencies, offices and branches of the government [e.g. the US Environmental Protection Agency (EPA) and the Internal Revenue Service (IRS)] can encourage or discourage the use or development of any of these sources, including reclaimed wastewater. For example, too

stringent environmental regulations will make reclaimed wastewater too costly to be a feasible option, whereas too if they are too lax, they will not adequately protect human health and the environment. Furthermore, each level of government, from local to state to federal, can alter the choice due to a particular agenda. This might be cleaning up a certain lake, reducing overall water consumption, increasing overall volume of water available. Similarly, regulations can be written to exploit or curtail the use of certain sources, in accordance with public policy. For instance, the State of Arizona is trying to prevent the overdraw of the aquifer from which 64% of its water is drawn. Once an aquifer is extremely overdrawn, the possibility exists that it will collapse, permanently reducing the total amount of water it can store. To achieve this goal, regulations were written on the state level to encourage aquifer recharge with the use of reclaimed wastewater, in order to bring aquifer withdrawal and recharge into balance by the year 2010.

Variable pricing, cost sharing and mandatory use are three other means to control water usage. Pricing strategies for reclaimed versus potable water vary from place to place and are designed to meet the goals and needs of a community, state or region. In water tight regions, effective pricing schemes combined with cost sharing between the user and the utility for changes in infrastructure necessary to accommodate the use of reclaimed wastewater can help increase the use of wastewater to the mutual advantage of the users, the water utilities, and the environment. The State of Florida, for example, has undergone a high rate of population and economic growth in the last two decades. Traditionally relying on groundwater for almost 90% of its potable water supplies<sup>10</sup>, Florida is looking toward the use of reclaimed wastewater to meet total demand. In parts of Florida, the use of reclaimed wastewater for certain purposes, such as watering lawns, is mandatory in various locations. This is combined with a variable pricing scheme whereas the price of

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<sup>10</sup> W.B. Solley, C.F. Merk, and R.R. Pierce, *Ibid.*, p. 317.

reclaimed wastewater varies from user to user. Large-volume agricultural users, such as citrus groves, receive the water free of charge, in return for agreeing to take a certain amount of water on a predetermined schedule. The largest of these projects—and the largest worldwide—is the Water Conserv II in Orlando, FL which supplies 4040 ha (10,000 ac) of citrus groves with 17 MGD reclaimed wastewater free of charge under a 20-year contract. The remaining 8 MGD produced by the project is used for groundwater recharge via rapid infiltration basins<sup>11</sup>. In other projects across the state, low-volume users, such as home owners, typically pay 40% the price of potable water for reclaimed wastewater<sup>12</sup>. The difference between the prices reflects the fact that high-volume users provide the utility with a guaranteed place for disposal of the water. Without this, the water would have to be disposed of by the treatment facilities in a more traditional way, requiring a National Pollutant Discharge Elimination System (NPDES) permit, at substantial cost to the utility and ultimately to the consumer. By providing the utility with a guaranteed place of disposal, these permits are no longer necessary and the utility and the consumer both save money overall. Because of this, the water is variably priced, at what is hoped is a win-win situation for all, although questions of equity do exist.

Industrial use of water can be curtailed through complete process redesign, incorporation of water recycling technology and concepts and, in some cases, simple modifications of existing processes. With more stringent mandatory industrial pretreatment required before discharge to POTWs coming on line due to recent amendments to the Federal Water Pollution Control Act, as well as increasing discharge fees through NPDES, the economic incentive towards process redesign and water recycling within a plant is becoming reality. With economic encouragement, water use can drop

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<sup>11</sup> John L. Jackson, Jr., "Citrus Trees Blossom with Reclaimed Water", *Water Environment and Technology*, February 1993, p. 27-28.

<sup>12</sup> Donald F. Newnham, "Dual Distribution Systems", *Water Environment and Technology*, February 1993, p. 60.

tremendously. For instance, in 1975, 2000 gallons of water were used to refine a barrel of oil; that amount has dropped precipitously to 90-100 gallon water/bbl oil<sup>13</sup>. Within other industries, similar strides have been made.

Reuse and reclamation of industrial wastewater can benefit the plant or company, the Publicly Owned Treatment Works (POTW), and the environment. Potential benefits to the company include forced process redesign, which may in fact do more than reduce the quantity and toxicity of the effluent. In the best case scenario, plant modernization can allow the company to compete more successfully, bring the company up to the technological leading edge of the industry, reduce the amount of water the company needs to purchase, and reduce the overall cost of production. In other factories, forced reuse and reclamation of industrial wastewater will result in more sophisticated, technologically driven, and more expensive water pollution control devices being installed at the tail-end of the processes. The same technologies that a POTW uses to remove contaminants from its feed stream are available for commercial use by industry (see Table 2.2).

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<sup>13</sup> Karen S. Elbe and Jennifer Feathers, "Characterization of Streams First Step in Reuse Scheme", *Oil and Gas Journal*, Vol. 90, No. 38, Sept 21, 1992, p. 86-92.

**Table 2.2 Possible Contaminants and Options for Treatment<sup>14</sup>**

Contaminant	Treatment Options	Notes
Aldehydes	A K	
Aluminum	B C G I J	B—requires pH adjustment
Amines	K	
Ammonia	F K I	
Arsenic	B C F H J	B—requires pH adjustment
Barium	E G I J	I—possible membrane fouling
BOD	A B D F H I	prefilter
Calcium	E G	
Chlorides	H I J	
Chlorine—residual		feed sulfite
COD	A F H I	
Conductivity	G + H I J	
Copper	B C E I J	B—requires pH adjustment
Cyanide	A K	
Fluoride	E H I J	some adsorption on CuPO <sub>4</sub> , MgOH
Total Hydrocarbons	B D F I K	
Iron	A B E G I J	I—possible membrane fouling
Lead	A B E I J	B—requires pH adjustment
Magnesium	E G I J	
Manganese	A B E G I J	I—possible membrane fouling
Nickel	A B G I J	B—requires pH adjustment
Silica—reactive	E H I	E—hot
Sulfates	H I J	Some adsorption with lime
Sulfides	A E F H	
Suspended Solids	B C	
TOC	A F H I	
Zinc	B C E G I J	B—requires pH adjustment

A = Chemical oxidation

B = Filtration

C = Clarification

D = Physical Separation (API, DAF/IAF)

E = Lime or soda ash softening

F = Air/Steam stripping

Source: Karen S. Elbe and Jennifer Feathers, p. 83–85.

G = Cation Exchange

H = Anion Exchange

I = Reverse Osmosis

J = Electrodialysis Reversal

K = Biological/secondary treatment

Once treated, the plant can either choose to reuse the water on-site, reducing the volume of water it needs to purchase, discharge directly to surface water in accordance with its NPDES permit, or discharge to a POTW. In such cases, reuse requirements will usually not result in overall process redesign or plant modernization, but will simply raise

<sup>14</sup> Karen S. Elbe and Jennifer Feathers, "Water Reuse Optimization Requires Knowledge of Cleanup Methods", *Oil and Gas Journal*, Vol. 90, No. 40, Oct. 5, 1992, p. 83–85.

the cost of production, unless the cost savings of the recycled materials compensates for the cost of installing the pollution control device. Moreover, if the capital is not available for the upgrades, then it is possible the plant will be forced to close or relocate to a place without such stringent environmental regulations. Other plants in the industry, located outside the United States, may be able to produce the same good at a lower cost, due to lax environmental standards. However, consistent incentives (e.g. tariffs to equilibrate the environmental cost with the added economic cost) can prevent the movement of business across borders due to environmental regulations.

By requiring pretreatment at the source, EPA is helping to close a longstanding loophole in wastewater treatment practice and to minimize the level of treatment required for the POTWs to remain in compliance with federal effluent limitations. Because industrial wastewater is usually more concentrated and more toxic than domestic wastewater, it typically requires more treatment per volume. With industrial pretreatment reducing the amount of treatment required at the POTW, the POTW will benefit from improvements in the water quality of the influent. For example, if only one plant in an area is discharging a certain heavy metal to a POTW, it is usually less costly overall to remove it at the plant than to transfer the problem from the factory to the POTW. At the POTW volume of the feed stream is much larger, while the overall quantity of heavy metal to be removed remains the same. With the larger feed stream, much more extensive ion exchangers are required, than if the heavy metals had been removed at the factory. Furthermore, the energy requirements for pumping additional volumes of water through the ion exchangers are increased. However, if the POTW treats waste from many small industrial sites, economies of scale might suggest placing one large pretreatment facility on the site of the POTW for the industrial wastewater rather than at each of the small facilities.

### 2.1.2. Zero Discharge and Sludge Recycling

Congress, in 1972, enacting the Clean Water Act, had in mind a lofty ideal as to how to produce clean water. With its oft quoted "national goal that the discharge of pollutants into the navigable waters be eliminated (CWA 101[a])", the Clean Water Act and subsequent amendments never quite lived up to this premise. However, in the last two decades, water pollution control technologies have been developed and perfected to such an extent that "zero discharge" in some industries is now possible. In some cases, there is an industry-wide mandate<sup>15</sup> by the US EPA to head towards "zero discharge". Other times, local conditions—such as deteriorating ground or surface water quality—induce local environmental agencies or departments to mandate a facility become "zero discharge". The water from advanced wastewater treatment centers, if not absent of pollutants, is much closer to the ideal of zero pollutants than traditional primary and secondary treatment facilities.

The concept of "zero discharge" is a difficult to define. What exactly is "zero"? This can be interpreted in a number of ways. It can mean volume, toxicity, or pollutants. For instance, zero in terms of volume simply means that no effluent at all is being discharged from a plant. Zero in terms of toxicity means that the water being discharged is harmless, according to a predetermined notion of what harmless is, in terms of water quality indicators and concentrations of various ions, compounds and atoms. Finally, zero in terms of pollutants means that the water leaving the plant has no detectable pollutants. However, this last definition has an obvious problem: "If one puts a finger in waters of a pristine lake, contamination is introduced already (grease, bacterium, epidermis). Therefore, we are not talking about pollution 'elimination', but about lowering the levels of

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<sup>15</sup> David Bowlin and Rodi Ludlum, "Case Studies: Zero Liquid Discharge Systems at Three Gas-Fired Power Plants", 1992 ASME Cogen Turbo Power Congress, Houston, Sept. 1992, p. 1.

discharged byproducts of human activities to values comparable to existing background levels comparable to existing background levels"<sup>16</sup>. The most advanced of the wastewater reuse facilities produces water that is comparable to nearby raw water sources, narrowing in on this goal. But overall, for most POTWs and industrial facilities, is this a feasible goal? Congress in 1972 thought it was.

The feasibility of zero discharge requires that the technology exists and that the costs are reasonable. The technology now exists such that the dirtiest, most contaminated water can be made pure. Many of these technologies, however, are extremely energy dependent and require enormous inputs of electricity. Other technologies require additional chemicals to solve contamination problems. Combining the direct economic costs with the environmental costs of producing both the electricity and the chemicals might in some cases put the original goal of zero discharge in question. Benefits come from a possible decrease in cost, from both the money saved on inputs (e.g. metal recycling, reduced water bills) and reduced discharge and sludge disposal fees; and a decrease in potential liability that results from restitutive and punitive fines being accrued by violating wastewater discharge permits<sup>17</sup>.

Depending on the processes used, there will be the issue of sludge. If the contaminant is merely transferred from the water to the sludge, this is little improvement over the current situation. If, however, the sludge can be reused for beneficial purposes, or optimally sold as an input for other processes or as a product people need, then the treatment plant or industrial facility comes closer to being closed-cycle, where little is discarded and nearly everything is reused.

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<sup>16</sup> Mikhail Schiller and Matthew E. Hackman, "Water Reuse Systems for Zero Discharge", *Environmental Protection*, September 1993, p. 72.

<sup>17</sup> Mikhail Schiller and Matthew E. Hackman, *Ibid.*, p. 74.

Sludge, euphemistically known as biosolids, is the non-water end product of the municipal and industrial wastewater treatment process. The inherent composition and quantity of the sludge, both of which vary over time, are a function of the inputs to the treatment facility and the treatment processes utilized. While popularly conceived of as a solid, the sludge produced at publicly owned treatment works (POTWs) is initially in a liquid or semiliquid form, with a solids content ranging from 0.25 to 12 percent by weight<sup>18</sup>. From this state, the sludge is often treated before disposal. Treatment options include physical, chemical and biological processes and are usually designed to deal with the unique problems associated with sludge: high organic content, easily degradable, offensive smelling, pathogenic, and high water content. Due to these same characteristics, sludge is, however, inherently recyclable. Because of its high organic content and nutrient level it is easily compostable, easily applied to damaged land, and is good for daily cover at landfills. It is more from the odor and appearance of sludge rather than from a bona fide public health risk that make the general public wary of using the 8.5 million dry tons of municipal sludge<sup>19</sup> produced every year in the US for personal and municipal purposes. Industrial sludge can be more toxic, and depending on the concentrations of various components, like municipal sludge, can be classified as hazardous waste and regulated under the Resource Conservation and Recovery Act (RCRA). In cases where it is hazardous waste, the options for beneficial reuse are close to nil.

Federally, the United States Environmental Protection Agency published the Part 503 Standards for the Use and Disposal of Sludge in the *Federal Record* (58FR9248) on February 19, 1993<sup>20</sup>, which was codified in 40 CFR Section 503. The deadline for compliance was set at one year later, or February 19, 1994. This followed more than a

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<sup>18</sup> George Tchobanoglous and Franklin L. Burton, *Ibid.*, p. 765.

<sup>19</sup> Ann Hasbach, "Putting Sludge to Work", *Pollution Engineering*, December 1991, p. 63.

<sup>20</sup> Nora Goldstein, "News and Views on Part 503", *Biocycle*, Vol. 34, No. 7, July 1993, p. 50.

decade of rulemaking by the US EPA to come up with guidelines and regulations for the disposal of sewage sludge which protects human health and the environment, as mandated by the Clean Water Act (CWA), Sections 405(d) and (e)<sup>21</sup>. In promulgating this rule, EPA addressed not only possible risks to public health, but overall risks to affected ecosystems, a first for the agency. Furthermore, in Part 503, EPA strove to achieve a multi-media approach to the problem, assuring that the pollution was not simply being transferred from one media (sludge) to another (e.g. air or groundwater). For instance, there would be a sludge to air transfer if the sludge were incinerated and pollutants at a harmful level were released through the smokestack or a sludge to water transfer if nitrates from the sludge, applied to soil, were to percolate through the soil column and contaminate an aquifer. Part 503 covers only three areas of sludge use and disposal: land application, landfilling and application on dedicated sites, and incineration. Co-disposal, disposing sludge along with municipal solid waste (MSW) at a municipal solid waste landfill or similarly as daily cover at the same type of landfill or incinerating it at a regional multi-purpose incinerator, is not covered by Part 503. Such disposal options are covered under other previously promulgated regulations authorized jointly under Resource Conservation and Recovery Act (RCRA) and the CWA.

Part 503 regulates only 10 pollutants: arsenic, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium and zinc. The EPA classifies pathogen reduction requirements into two categories, depending on the end use of the sludge. There are processes to significantly reduce pathogens (PSRPs), such as aerobic digestion, air drying and lime stabilization; and processes to further reduce pathogens (PFRPs), such as composting, heat drying, heat treatment and thermophilic aerobic digestion<sup>22</sup>. For land

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<sup>21</sup> Chris Bryant, "Sludge Standards Set Numerical Limits", *Pollution Engineering*, July 1993, p. 48.

<sup>22</sup> George Tchobanoglous and Franklin L. Burton, *Ibid.*, p. 904.

applied sludge, only a PSRP is required; in cases where the sludge is sold to the public or used for crops or grazing, a PFRP becomes necessary.

Beneficial reuse of sludge falls into three main categories: land application, composting and pelletization for use as fuel or fertilizer. Land application, the most common method of sludge disposal in the United States, is the eventual end for nearly 40% of all municipal sludge, and as high as 80% in some states<sup>23</sup>. In this method, the sludge is applied either onto the surface of the soil or injected below the surface by means of specialized trucks or equipment. The quantities applied are determined by the physical properties of the soil and the underlying aquifer, the weather, the type of crop to be grown and a number of other factors. Regulations concerning maximum metal concentrations per volume, area and time were written into Part 503, as explained previously.

In under an hour, a pelletizer plant can reduce the volume of sludge by ninety percent and produce a pile of pathogen-free pellets, containing most of the sludge's original nutritional value but with only five to ten percent water content. A portion of these pellets can be fed to the pelletizer as a fuel source. Options for the remainder of the pellets include land application, resale as either fertilizer or a low-BTU fuel source, or transporting away. The great reduction in volume facilitates all of these possibilities<sup>24</sup>. Because pelletizer plants can deal with large quantities of sludge, but only require a small amount of land, they are often the disposal method of choice in large land-tight municipalities which used to depend on ocean dumping. For example, a \$34 million dollar contract was recently awarded in Baltimore for the construction of a thermal processing pelletizer plant with the capacity to transform 650,000 liquid gallons of sludge per day into 55 dry tons of fertilizer pellets<sup>25</sup>.

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<sup>23</sup> Ann Hasbach, *Ibid.*, p. 64.

<sup>24</sup> Ann Hasbach, *Ibid.*, p. 67.

<sup>25</sup> "Sludge Pelletizing Facility", *Biocycle*, Vol. 33, No. 2, February 1992, p. 87.

Composting as an option for sludge disposal has skyrocketed in the last decade. Five major designs are utilized: aerated static pile, in-vessel, windrow, aerated windrow, and static pile. Ten years ago, there were 61 operation facilities composting sludge, compared to 159 today, with nearly a hundred more in the development, design, permitting or start-up phase<sup>26</sup>.

These facilities are operated either alone or in conjunction with a municipal solid waste facility. The most common admixture is lawn or garden waste, followed by mixed paper waste, for which there is a small to non-existent market. Additionally, food waste, primarily from institutions and commercial ventures, is a common admixture. Finally, in other cases, manure and other agricultural byproducts, fish waste and other food processing byproducts, and wood ash are mixed in<sup>27</sup>.

The market for the compost varies with the location of the plant. Excluding compost that is given away, the compost is sold for between \$1.00 and \$22.00 per cubic yard. The largest three segments of end users are landscapers, nurseries and public works applications. Other smaller regional markets include use as landfill topsoil, topsoil blenders, golf courses, farms, mine reclamation projects, tree farms and schools<sup>28</sup>. Interesting enough, in some states, compost from sludge is not allowed on certifiable organic farms, even when it meets all applicable EPA regulations<sup>29</sup>. Approximately 45 companies provide composting systems<sup>30</sup>, while 30 operational composting facilities nationwide are run privately<sup>31</sup>.

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<sup>26</sup> Nora Goldstein, David Riggle and Rob Steutville, "Sludge Composting Maintains Growth", *Biocycle*, Vol. 34, No. 12, December 1992, p. 50.

<sup>27</sup> Nora Goldstein, David Riggle and Rob Steutville, *Ibid.*, p. 50-51.

<sup>28</sup> Nora Goldstein, David Riggle and Rob Steutville, *Ibid.*, p. 55.

<sup>29</sup> "Biosolids Disallowed on Certified Organic Farms," *Biocycle*, Vol. 34, No. 4, April 1993, p. 24.

<sup>30</sup> "Composting Equipment and Systems for Solid Waste and Biosolids", *Biocycle*, Vol. 34, No. 4, April 1993, p. 82-83.

<sup>31</sup> Nora Goldstein, David Riggle and Rob Steutville, *Ibid.*, p. 55.

Another small scale projects using recycled municipal sewage sludge is the production of high quality bricks, appropriate for use in sewers, walkways and signs. At the temperature of firing, approximately 2000 F, any toxic organic or pathogenic material is completely oxidized away. Although still not mainstream, a number of projects, including using 120 tons of sludge to produce half a million bricks have proved the technology viable, although at a cost greater than land application<sup>32</sup>. However, if the bricks were to be sold commercially, a portion of this cost could be recouped.

Both zero discharge and sludge recycling are ways in which inputs to facilities are recycled or reused. Zero discharge facilities recycle the water and the inputs at the facility itself, whereas in most cases the sludge is used off-site for a variety of purposes.

Wastewater recycle and reclamation is an abridged form of a zero discharge facility—the wastewater is substantially reduced in toxicity and is reused for a beneficial environmental or consumptive purpose. The more inputs, including water, are reused or recycled, the less overall pollution is released into the environment, and this brings industry, including the wastewater industry, closer to being part of the solution to water pollution, rather than simply another contributor to the problem.

### 2.1.3. Developing Countries vs. the Industrialized World

While using reclaimed wastewater is possible anywhere water budgets are being met only with difficulty, it should be recalled that, if treated improperly, reclaimed wastewater is highly dangerous. In the United States, most reclaimed wastewater is highly treated. Following biological treatment, tertiary methods are used to remove more dissolved and suspended substances, heavy metals, and the like. Following this the wastewater is disinfected, usually with chlorine, and often then partially dechlorinated, to prevent the

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<sup>32</sup> Ann Hasbach, *Ibid.*, p. 69.

formation of carcinogenic trihalomethanes. Each step of the treatment sequence requires capital to build and capital to operate. The more complicated the treatment plan, the more expensive the overall capital investment and operating and maintenance costs will be. In the developing world, basic sanitation is often non-existent. Worldwide in 1990, 29% of the urban population and slightly more than 50% of the rural population is without basic sanitation, adding up to more than 1.7 billion. As for drinking water, the situation is almost as severe. 1.2 billion people, or about 18% of all urban dwellers and 37% of all rural inhabitants are without safe and adequate water supply<sup>33</sup>. For these people, wastewater recycle is often a dangerous, inadvertent reality. Often the only source available is contaminated directly by raw sewage, leading to indirect, involuntary reuse. Wastewater treatment facilities of any kind require capital and an infrastructure to connect households with the facility. Without basic sanitation, the reuse and reclamation of wastewater is not feasible; the issues involved in these regions are quite different. Therefore, this report will focus on the developed world, and in particular on the United States, and the issues it faces when using reclaimed wastewater.

#### **2.1.4. Public Health and Ecological Risks**

In some cases, reclaimed wastewater will meet federal drinking water standards, but in most cases, it does not. However alarming this may seem, there are many uses for water for which potable water is not necessary and so the drinking water standards are excessive. In such cases, reclaimed wastewater can be use if the overall risk incurred to human health and the environment is minimal.

Even with low overall risk, certain groups of people will bear the brunt of the risk, and, as with any amount of risk, there is the issue of equity: Will certain groups of people

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<sup>33</sup> Robin Clarke, *Ibid.*, p. 5.

incur very high amounts of risk, while the general populace is only exposed to minute levels? How much risk is allowable for those groups of people? How much risk those at the highest risk will incur is a public policy issue, a decision that must be made at the regulatory level. Exposure to reclaimed wastewater can be either direct or indirect. Depending on the exposure route, various groups are potentially at higher risk from the use of reclaimed wastewater as compared to potable water. Broadly speaking, these consist of workers who come in direct or near contact with the water, consumers of food irrigated with reclaimed wastewater, and lastly, the general public, who may come into the vicinity of a reuse project on occasion. Typical routes of exposure include direct contact with the reclaimed water, indirect contact via aerosolized wastewater, and contact with products grown or produced with reclaimed water.

Historically, public health risks from agriculture irrigated with reclaimed wastewater have resulted in exposure to soil-transmitted nematodes which require no intermediate host and moderately persistent bacteria. Nematodes of particular danger include the human roundworm (*Aschasis lumbricoides*), hookworms (*Ancylostoma duodenale* and *Necator americanus*) and the human whipworm (*Trichuris trichuria*), while the bacteria include *Vibrio cholerae*, *salmonellae*, and *shigellae*<sup>34</sup>. While sewage has been responsible for many public health epidemics over the years, these are easily avoided by disinfecting the effluent stream, a fundamental element of the wastewater treatment stream. In regions of the world with insufficient or non-existent sanitation infrastructure, diseases from nematodes, moderately persistent bacteria and other waterborne vectors run rampant among the populace, causing widespread disease. Worldwide, approximately 80% of all disease is waterborne. Furthermore, it has been estimated that at any one time, half the

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<sup>34</sup> S.B. Niedrum, A. Karioun, D.D. Mara, and S.W. Mills, "Appropriate Wastewater Treatment and Reuse in Morocco—Boujad: A Case Study", *Water Science and Technology*, Vol. 24, No. 9, p. 206.

world's population suffers from infections from water-related disease<sup>35</sup>. In developing countries without the proper infrastructure existing or the capital necessary to construct such facilities, wastewater and raw sewage are not so benevolent. Raw sewage, first implicated in the spread of cholera almost 140 years ago<sup>36</sup>, was responsible for at least two overseas widespread outbreaks of typhoid and cholera as late as the past decade, illustrating the potential danger to public health that reclaimed wastewater can pose. Proper disinfection and monitoring of the effluent stream, which happens as a matter of course in industrialized nations like the United States, helps prevent transmission of these diseases. However, part of the risk of using reclaimed wastewater is that part of the system will fail and disinfection will not occur.

In fact, wastewater effluent can in fact be used as a drinking water source, either directly or, as is usually the case, indirectly. In the United States, direct potable reuse is not currently occurring. However, in the late fifties a four-year drought forced direct reuse on a small town, Chanute, Kansas. For a six month period beginning October 14, 1956, treated wastewater was mixed with stored river water and used as a source for raw drinking water. One complete cycle through the wastewater treatment center and back through the water treatment center was estimated to take 20 days; thus, over the sixth month period, the water was cycled through the system around seven times<sup>37</sup>. After a few cycles, the color of the water turned a pale yellow color and, while no adverse health effects were reported, it was unpalatable aesthetically<sup>38</sup>. In 1978, in Windhoek, Namibia a wastewater treatment plant was modified to treat effluent for direct potable reuse, the first such plant worldwide.

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<sup>35</sup> Robin Clarke, *Ibid.*, p. 126.

<sup>36</sup> Howard Hu and Nancy K. Kim, "Drinking-Water Pollution and Human Health", in Critical Condition: Human Health and the Environment, Eric Chivian, Michael McCally, Howard Hu, and Andrew Haines (eds.), MIT Press, Cambridge, MA, 1993, p. 31.

<sup>37</sup> Kenneth J. Miller, "US Water Reuse: Current Status and Future Trends", *Water Environment and Technology*, Nov. 1990.

<sup>38</sup> Carl L. Hamann and Brock McEwen, *Water Environment and Technology*, January 1992, p. 80.

The process utilized involves pretreatment equivalent to conventional secondary treatment, followed by lime treatment, air stripping (to remove VOCs), recarbonation (injected with CO<sub>2</sub> in order to neutralize the high pH), chlorination, Granular Activated Carbon (GAC) treatment (to remove microorganics such as pesticides that are not oxidized by the microorganisms in biological phase), a second chlorination, filtration, and a third chlorination. The water is then blended with treated surface water before being sent to the consumers.

In the US, two plants (Washington, DC and Denver, CO) did initial testing to begin experimenting with direct potable reuse in the early eighties<sup>39</sup>. Currently, a demonstration project in San Diego, CA, also exists. Consisting of seven post-secondary treatment unit processes—coagulation, filtration, reverse osmosis, air stripping, carbon absorption and final disinfection—the San Diego Advanced Water Treatment (AWT) plant has been the subject of a number of epidemiological studies which have compared the water quality of AWT effluent with the water quality of the intake water for one of San Diego's major drinking water facilities, the Miramar Water Treatment Plant. These studies found no difference in the number of viruses found in either supply; none were found in any sample, even those as large as 1000 gallons. Experiments that seeded an attenuated vaccine strain Poliovirus saw a removal efficiency in the AWT plant as high as 99.999999%, or eight orders of magnitude. No enteric bacteria (e.g. *Salmonella* sp., *Shigella* sp. and *Campylobacter* sp.) were detected in either source. Furthermore, the AWT water, prior to disinfection, met all microbiological requirements for raw drinking water and recreational waters and had higher microbiological quality than the Miramar water<sup>40</sup>. This suggests that it is, in fact, safe from a public health perspective to use highly treated domestic wastewater

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<sup>39</sup> Quality Criteria for Water Reuse, National Research Council Report, National Academy Press, 1982, p. 11.

<sup>40</sup> K. Thompson, R.C. Cooper, A.W. Olivieri, D. Eisenberg, L.A. Pettegrew, and R.E. Danielson, "City of San Diego Potable Reuse of Reclaimed Water: Final Results", *Desalination*, Vol. 88, 1992, p. 201-214.

as a source for raw water. However, if extreme care is not taken, it can be extremely dangerous. Furthermore, because public opinion is against the use of wastewater for this purpose, it is not suggested.

Using reclaimed wastewater can damage or change the ecology of an area in any number of ways. One of the most pressing concerns to the ecosystem is the concentration of dissolved salts which may build up over time if care is not taken. If the TDS concentration is too high, the fragile topsoil region may be damaged, preventing certain salt-sensitive crops from growing. This problem with salt in the topsoil region has plagued farmers dependent on irrigation to bring water to their fields for over five thousand years. Archeological studies have shown that between two to three millennia BC both wheat and barley yields in Mesopotamia dropped dramatically due to increases in salt in the soil matrix caused by poor drainage in irrigated fields<sup>41</sup>. Furthermore, increased nutrient levels can cause a flourishing of microbial communities, causing the flow in the aquifer to be seriously attenuated, in essence plugging the aquifer. High concentrations of carcinogens may cause cancer in certain animals in the area. An environmental or ecological risk assessment, or a complete environmental impact statement/report, may be necessary in order to prevent long-term harm to the ecosystem.

#### **2.1.5. Water Rights**

In locations where water is not plentiful enough to meet demand, it is considered a valuable natural resource, essential to economic and political growth. This is true in Mexico and the Middle East, and it is becoming true in more and more parts of the United States. Exacerbated in areas where water is scarce, even in regions where water is not of the status of natural resource, there are often disputes over who owns the water, who can

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<sup>41</sup> Robin Clarke, *Ibid.*, p. 15-16.

use the water, and who pays for the water. Disputes exist over lakes, rivers, aquifers and any other source of water that straddles a border or sits in multiple jurisdictions. Within the US, fourteen major aquifers are located under more than one state and are drawn upon by communities in two or more states. Not limited to interstate disputes, the right to water in an aquifer can also be an international issue: one major aquifer straddles the US-Canadian border and another the US-Mexican border. Rivers and lakes often present even more difficult conditions. Watersheds for rivers and lakes extend for tens to hundreds to thousands of square miles. Whereas in North America, rivers and lakes come under the jurisdiction of at most two countries, elsewhere in the world up to nine different countries can be involved in watershed management and water use controversies. Rivers polluted in the US can affect the wellbeing and livelihood of Mexicans. Who is then responsible? Who pays for the damage? Who enforces treaties between the nations? The water quality of rivers and lakes can also be an issue between cities, states and countries. This poses more than a few questions of responsibility, rights and environmental equity. Are upstream communities responsible if cities downstream receive water that is of poor quality? If aquifers are overdrawn or contaminated, who is responsible for providing potable water or the necessary technology to remedy the situation for the affected communities? Federally, the United States is dealing with water quality problems along the US-Mexican border by allocating a proposed \$200 million dollars in fiscal year 1993 for wastewater and drinking water facilities in border communities in both countries<sup>42</sup>. Along the northern US border, the US and Canada are working together to help preserve and protect the Great Lakes.

Dependence on water has only increased with modernization. As the population increases both globally and locally, the need for fresh water becomes more pressing. This

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<sup>42</sup> Securing Our Legacy: An EPA Progress Report, 1989-1991, United States Environmental Protection Agency, EPA 175 R-92-001, April 1992, p. 42.

is especially true in arid, over-populated very industrial or very agricultural regions. For instance, based on rainfall and domestic sources of water, the Los Angeles Basin is able to support naturally only about 250,000 people with their water needs. However, due to large-scale civil engineering projects which allow for the daily import of tons of water closer to 14.5 million people live, farm and do business there. Currently, states that are supporting more people and industry than their water systems can handle include California, Florida, Arizona, Texas, Colorado and Virginia.

As the population grows and water becomes more scarce, the issue of water rights will become more pronounced. This issue is exacerbated, to a certain extent, by questions of economics. Where money is available, technology can be found to remove contaminants and clean up a water supply, either at the source or at the facility level. Where money is not so readily available, uncontaminated sources of water are all the more precious. In some instances, wastewater reclamation can help alleviate water concerns, but there may be very pressing concerns. First, wastewater reclamation requires money. Upgrading or constructing a POTW to advanced treatment levels costs a lot of money. In some cases, this money is just transferred by the water utility from one expenditure to another, such as money allocated to pay from NPDES discharge permit fees being used to make permanent investments in capital. In other cases, the plant can be paid for from state or federal grants; in still other cases raising water rates is required. Second, even when the money is available, if there is a question of water budgets being tied among communities, using reclaimed wastewater can only add to the sound and the fury, because of the intrinsically recyclable nature of water. For instance, a community located along a river may be dependent upon a certain volume of river water being available to draw upon for their water needs. If this amount of water is curtailed because suddenly a large city upstream is no longer discharging effluent from its wastewater treatment center into the river, the community may feel their right to fresh water is being impinged upon. Without the river

water, the downstream community needs to search for a new water source. Or, they may decide it is in their best interests to sue the large upstream city. Whatever the outcome of such a legal battle, the situation might easily be tied up in court for years.

Lastly, in areas where there is a public perception that water is "running out", regional economic growth might be curtailed. Industrial activities typically require large amounts of water. If the risk of running out of fresh water or of the price skyrocketing is real, industry will be less likely to move into that area. By reducing dependence on freshwater supplies to the point where demand equals the supply naturally available, economic growth won't be discouraged.

#### 2.1.6. Environmental Concerns

Fresh water is a precious natural resource. Fresh water systems, while possessing some mechanisms for self-cleaning, are easily disturbed. The entirety of the Great Lakes are riddled with heavy metal as well with recalcitrant organics such as PCBs and dioxins. Aquifers are easily contaminated and restored only with great difficulty.

With improvements in monitoring technology, the evidence of disturbance becomes all the more apparent. Discharges into surface or ground water disturbs or damages ecosystems. Reducing the quantity of effluent or improving the quality of the effluent can have positive effects on the natural environment with repercussions throughout the watershed. Furthermore, preserving or restoring ecosystems can have economic repercussions as well. Strongly believing this, the Federal government has targeted the Great Lakes, the Chesapeake Bay, the Gulf of Mexico and other estuaries and fresh water systems to receive federal funds<sup>43</sup>.

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<sup>43</sup> Securing Our Legacy: An EPA Progress Report, 1989-1991, Ibid., p. 32-33.

Two to three percent of all electricity generated in the United States is used for water and wastewater treatment<sup>44</sup>. Furthermore, this demand is predicted to increase by almost 40% over the next two decades. Because POTWs use a tremendous amount of electricity, there is a concern on the part of the water utilities and the electric utilities about improving efficiency at POTWs in order to reduce both energy usage and operating costs. A second order environmental concern is the amount of emissions from electrical plants directly related to the operation of POTWs. Air emissions, odor and noise problems and sludge disposal are of additional concern to POTW management. Controlling Volatile Organic Compounds (VOC) emissions at POTWs is currently in legislative vogue; while such legislation will increase operating costs, it does reduce the likelihood of transferring the pollution from the water to the air. Depending on the feed stream, the composition of the sludge will vary. Especially of concern is heavy metal content which often may preclude the use of sludge in such commercial ventures as a component of mulch. At higher concentrations, the sludge will have to be landfilled in a hazardous waste landfill.

#### 2.1.7. Demand Side Management

In terms of water use, demand side management is usually referred to simply as water conservation. Water conservation measures can be applied to all sectors—municipal, agricultural, industrial and electrical—and can reduce substantially the amount of water a community needs. For instance, subterranean irrigation systems reduces considerably evaporation, evapotranspiration and water required as compared to traditional spray irrigation systems. While cost considerations will prevent these from being used in some cases, in others cost savings from water bills will pay for the capital expenses many times over. If human resistance or lack of financial capital doesn't prevail, these types of devices

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<sup>44</sup> John Douglas, "Electrotechnologies for Water Treatment", *EPRI Journal*, Volume 18, Number 2, March 1993, p. 6.

provide win-win economic-environmental situations. In the home, water saving devices such as aspirators on the shower and taps are widely accepted in many areas of the country.

#### **2.1.8. Uses for Reclaimed Wastewater**

In the United States, the possible uses for reclaimed wastewater are almost as diverse as fresh water. They range from preventing oranges from freezing during cold snaps in Florida, to providing a source of water for snow making machines in California, to recharging an aquifer in Arizona, to controlling dust at a roadside construction site in Texas. However many variations exist, it is quite simple to classify the plethora of possibilities into a few large categories. These categories are extremely important because the end use of the water determines the level of treatment necessary to ensure protection of human health and the environment; and while it is impossible to have a guideline for each and every use of wastewater, broad classifications reduce the chore to a manageable level. The following are the most common uses for reclaimed wastewater.

- Urban reuse,
- Irrigation,
- Agricultural reuse,
- Recreational and landscape impoundments,
- Industrial reuse,
- Construction use,
- Environmental reuse,
- Groundwater recharge,
- Indirect potable reuse,
- Direct potable reuse.

### **2.1.9. General Considerations**

A community's decision to meet burgeoning water needs by using reclaimed wastewater is not a simple one. Economic, legal, regulatory, environmental, political and public opinion aspects must play into the decision. The following factors should be considered by any community<sup>45,46</sup>:

- The daily and seasonal fluctuations in demand,
- The daily and seasonal fluctuations in supply,
- The pricing of water according to end use and quality;
- The end uses for the reclaimed water;
- The water quality required for each use;
- The amount of treatment required to bring the water to this level of quality;
- The overall economics of the situation;
- The environmental harm or benefits from using reclaimed water;
- Other additional infrastructure that using reclaimed water will require;
- Any possible risks to public health or the environment;
- The degree of public acceptance, enthusiasm and/or endorsement;
- Legal aspects concerning responsibilities, risks, liabilities, ownership and "water rights";
- Political nature of the water, especially in the case when reclaimed water from one area is being proposed for use elsewhere.

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<sup>45</sup> Steven X. McHaney, "Satellite Wastewater Reclamation Plants: How to Get What You Bargain For," *Desalination*, Volume 88, 1992, p. 219.

<sup>46</sup> Gedaliah Shelef, "Wastewater Reclamation and Water Resources Management", *Water Science and Technology*, Vol. 24, No. 9, p. 252.

### **2.1.10. Public Resistance**

People have an innate resistance to change. Often, even when the change will bring about benefits, there is a tendency to distrust new and innovative approaches to old problems and situation and, concomitantly, a tendency to be comfortable with the status quo. If public opinion is swayed too far against a project, members of a community working together can effectively halt large projects like these. Examples abound in the area of siting hazardous waste facilities to prove this point. For this reason, it is important to keep the public educated, informed and involved, including members of the community in the decision-making process. In areas where there is public resistance to accepting or adopting the concept, practice and products of reclaimed wastewater, it is even more important to keep the channels open between citizens and the more traditional decision makers. Meeting and discussing problems with the public, involving them directly in the decision-making process and making sure their concerns are addressed will help ensure that they accept the decision to use reclaimed wastewater in the community.

## **2.2. Technology Descriptions**

The technologies covered in this sections fall broadly into three groups: aquifer storage recovery (ASR), natural systems, and membrane separation methods. The membrane separation technologies that will be discussed are reverse osmosis, electrodialysis, ultrafiltration, microfiltration, and nanofiltration.

### **2.2.1. Aquifer Storage Recovery (ASR)**

**2.2.1.1. General Background.** Aquifer storage recovery is a storage method for potable water. It provides a method for a local water utility to upgrade the total capacity of a drinking water facility at approximately fifty percent of the cost of a traditional upgrade. In particular, it helps a utility to meet peak demand. Currently, 11 ASR facilities are

operational within the United States (see Figure 2.3), 7 of which were designed by CH2M Hill, Inc. It is a non-patented technology. Installation of an ASR facility requires typical design, testing, and construction techniques.

**Table 2.3 Aquifer Storage Recovery Facilities in the United States<sup>47</sup>**

Location	Year Operation Began	Storage Zone	ASR Well Capacity (MGD)	Maximum Demand (MGD)
Wildwood, NJ	1968	sand	3.5	12
Gordon Corner, NJ	1971	clayey sand	2.4	10.5
Goleta, CA	1978	silty, clayey sand	6.0	21
Manatee County, FL	1983	limestone	3.5	40
Peace River, FL	1985	limestone	4.9	10
Cocoa, FL	1987	limestone	8.0	37
Las Vegas, NV	1988	sand	20/50	196
Port Malabar, TX	1989	limestone	1.0	6
Oxnard, TX	1989	sand	8.6	--
Chesapeake, VA	1990	--	3.0/10	15
Kerrville, TX	1991	dolomitic sandstone	1.0	7

Source: Andrea R. Aiken and R. David G. Pyne, 1993.

**2.2.1.2 ASR for Subsurface Water Storage.** ASR is a subsurface water storage method which allows a water utility to meet increasing water demands without immediate expansion of supply, treatment or transmission capacity. Furthermore, it enables a water utility to operate a water treatment facility at close to peak year-round. During periods of excess supply, such as in the late spring, treated drinking water is injected into the aquifer by means of a dual-purpose recharge well. Later, when the demand for water exceeds the supply, such as during the hot, dry summer months, the water is pumped back out of the well. Following retrieval, the water is disinfected and distributed to the customers.

**2.2.1.3. Requirements for an ASR System.** For ASR to be feasible, there are certain requirements that must be met. These are:

<sup>47</sup> Andrea R. Aiken and R. David G. Pyne, "Aquifer Storage Recovery: Recent Developments", DEN/200B/047.51, 1993, p. 8.

- Seasonal water variation in water supply and water demand;
- Maximum-annual-day to average-annual-day demand ratio of at least 1.3;
- Minimum of 1 MGD additional water required;
- Reasonable scale of water facilities already available, usually 1 MGD or greater.
- Suitable storage zone available.

2.2.1.4. Objectives for an ASR System. Water utilities have a number of objectives they are trying to meet. Selecting ASR as a method in which to meet increasing demands allows for both consumptive and environmental benefits. Table 2.4 summarizes these.

**Table 2.4 Typical Objectives of Aquifer Storage Recovery<sup>48</sup>**

• Seasonal storage	• Nutrient reduction in agricultural runoff
• Long-term storage or water banking	• Enhance wellfield production
• Emergency or strategic water reserve	• Defer expansion of water facilities
• Diurnal storage	• Reclaimed water storage for reuse
• Restore groundwater levels	• Soil aquifer treatment
• Reduce subsidence	• Stabilize aggressive water
• Maintain distribution system pressure	• Improve water quality
• Maintain distribution system flow	• Maintain water temperature for fisheries
• Hydraulic control of containment plumes	• Reduce environmental effects of streamflow diversions
• Prevent salt water intrusions into an aquifer	• Compensate for surface salinity barrier leakage losses
• Agricultural water supply	

Source: Andrea R. Aiken and R. David G. Pyne, 1993.

2.2.1.5. Aquifer Recharge. ASR differs from other aquifer recharge systems in two distinct ways. First, potable water is injected into the aquifer, rather than wastewater. Second, the same well is used for injection and retrieval. Groundwater injection methods of aquifer recharge usually involve distinct injection and retrieval wells, separated physically by enough distance to ensure that the injected water remains underground for a minimal amount of time. In many cases involving wastewater, this leads to clogging of

<sup>48</sup> Andrea R. Aiken and R. David G. Pyne, *Ibid.*, p. 8.

some of the wells over the course of a couple of years, due to both bacterial growth in the vicinity of the wells and physical blockage. Because potable water is used, bacterial growth is minimized; furthermore, the biennial cycling prevents physical blockage in the environs of the well.

2.2.1.6. Environmental Issues. ASR can be helpful environmentally. Like other aquifer recharge methods, ASR can help prevent saltwater intrusion, as well as mitigate localized contamination (nitrates, solutes, and organics) of the aquifer. However, depending on the level of contamination, some other form of treatment in addition to disinfection may be necessary, prior to distribution of the water to the customers.

2.2.1.7. Permitting. Because ASR uses potable water, permitting tends to be easier than for other aquifer recharge systems. Requirements vary from state to state. Federally, they are regulated under the Safe Drinking Water Act of 1974, Underground Injection Control (UIC) program.

2.2.1.8. Economics. ASR is a method that allows a water utility to expand its production during one part of the year, without having to construct large storage and treatment facilities which are unnecessary most of year. Because of this, the utility is able to save a considerable amount of money while still providing expanded capacity. Table 2.5 compares the cost of expanding with ASR versus the cost of expanding capacity in a more traditional means. In all cases, the savings is considerable.

**Table 2.5 ASR Economics<sup>49</sup>**

<b>Location</b>	<b>Expansion Costs with ASR (Million \$)</b>	<b>Expansion Costs without ASR (Million \$)</b>
Wyoming, MI	9	31
Peace River, Fl	46	108
Manatee County, Fl	2	38
Florida Keys, FL	5	35
Kerrville, TX	3	30

Source: R. David G. Pyne, 1993.

Capital costs for an ASR system included feasibility assessment and testing, engineering and modeling, permitting, water quality monitoring, hydraulic testing, piping, and well and wellhead construction costs. Excluding piping and construction costs, these are borne primarily by the first well and run from \$200,000 to \$500,000 per MGD recovered<sup>50</sup>.

Costs for additional wells are considerably less and include the cost of piping and construction.

**2.2.2. Natural Systems**—Natural systems for wastewater treatment can be broadly defined as any method or system that treats wastewater in a manner that mimics nature with a minimal reliance on additional inputs such as electricity. There is, of course, nothing revolutionary in the basic concept of using natural processes to treat wastewater.

Traditionally, the field of sanitary engineering has sought merely to improve on the physical, chemical and biological processes that already exist in nature. For instance, primary treatment is based upon the natural tendency of particles to settle; secondary or biological treatment utilizes the microorganisms to break down large organic molecules in the treatment stream as exist on farms, in rivers, and in swamps. However, the backdrop and mindset of these projects is completely technological and extremely dependent on electricity. Because traditional POTWs are dependent on external power sources, utilizing

<sup>49</sup> R. David G. Pyne, "Well Injection with Reclaimed Water: Regulatory Issues and Current Experience", 6th Biennial Symposium on Artificial Recharge on Groundwater, Phoenix, AZ, May 19-21, 1993.

<sup>50</sup> Andrea R. Aiken and R. David G. Pyne, *Ibid.*, p. 4.

2% of all electricity produced in the US, they are large, if indirect, contributors to other environmental problems, such as air pollution. The success of a plant can be measured by how efficiently in terms of time and space and how effectively in terms of water quality indicators the water is cleaned. A second drawback is traditional facilities tend towards unappealing aesthetics and have always been quite successful at keeping members of the general public at bay.

Natural systems have an entirely different philosophy to their design. Instead of being highly dependent on technology, they mimic natural processes in natural settings. This usually means that their land requirements are significantly higher, but the overall capital, operation and maintenance costs tend to be lower. Highly toxic chemicals, necessary to remove pathogens and viruses in traditional systems, are not necessary in natural systems, because the reduction is accomplished within the system, rather than at the end-of-the-pipe<sup>51</sup>. Furthermore, they can be integrated positively into a community and used for purposes other than merely treating wastewater. For instance, some are used as parks or recreational area, complete with running, walking and biking trails; others remain as nature reserves. Ecologically, natural systems—especially constructed wetlands—can provide seasonal refuge for migrating and breeding waterfowl, which depend on wetlands for survival. Additionally, wetlands are the permanent homes for a wide variety of plants, freshwater fish, birds, and other animals. This includes over 20% of the plants and animals on the United States endangered or threatened species lists which depend on marshes and other wetlands for survival<sup>52</sup>.

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<sup>51</sup> Susan Peterson and Bruce Strong, "Ecological Engineering for Wastewater Treatment", *US Water News*, April 1993, p. 7.

<sup>52</sup> James M. Riley and Harry A. Wojnar, "Treating and Reusing Industrial Wastewater", *Water Environment and Technology*, November 1992, p. 53.

Natural systems for wastewater treatment can be subcategorized into three main groups. These consist of constructed wetlands, aquaculture facilities and greenhouse-type facilities. Constructed wetlands and aquaculture facilities operate at the ecosystem level, thereby using an entire ecosystem to help solve an environmental problem. Greenhouse-type facilities operate on a much smaller level, but mimic the resources of an ecosystem.

**2.2.2.1 Constructed Wetlands.** The most common form of natural treatment in the United States is constructed wetlands. Mostly used to "polish", or further treat, the wastewater following some form of pretreatment, there are over 150 wetlands in use today that were constructed to polish wastewater<sup>53</sup>. Facultative and aerated lagoons, secondary treatment, and septic tanks provide pretreatment for 90% of these wetlands; the remaining wetlands had various other pretreatment methods, including advanced treatment<sup>54</sup>. Depending on their location, size and design, constructed wetlands can be used to treat agricultural and urban runoff, and industrial and municipal wastewater from both point and non-point sources. Furthermore, they all can help a community, state or facility to meet the "no net loss" wetlands provision, as well as provide a low-cost method for primarily smaller, rural communities, towns and cities with more land than money, to meet the effluent limitations of the Federal Water Pollution Control Act Amendments of 1991. Other common uses for constructed wetlands include controlling acid mine drainage; textile, agricultural, and photo lab waste; pulp mills and refinery effluent; agricultural and urban runoff; and landfill leachate<sup>55</sup>. There are, within many of these categories, large potential for growth. For example, if passive methods were used for acid mine drainage instead of conventional

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<sup>53</sup> Sherwood C. Reed and Donald S. Brown, "Constructed Wetlands—the First Generation", *Water Environment Research*, Vol. 64, No. 6, Sept./Oct. 1992, p. 776.

<sup>54</sup> Sherwood C. Reed and Donald S. Brown, *Ibid.*, p. 779.

<sup>55</sup> James T. Watson, Sherwood C. Reed, Robert H. Kadlec, Robert L. Wright, and Alfred E. Whitehouse, "Performance Expectations and Loading Rates for Constructed Wetlands", in Constructed Wetlands for Wastewater Treatment, Donald A. Hammer (ed.), Lewis Publishers, 1989, p. 319.

chemical treatment methods, the American mining industry would save over \$1,000,000 daily<sup>56</sup>.

There are two basic designs for wetlands constructed to treat wastewater—free water surface (FWS) wetlands and subsurface flow (SF) wetlands. Construction of a FWS wetland usually involves a transformation of a parcel of dry land into one with standing water, or, in other words, into a marsh. In order to accomplish this, a drainage system is installed; following this, the land is flooded and subsequently planted with the appropriate variety of floating and rooted plants, mimicking the speciation of a natural occurring wetland<sup>57</sup>. With the flow occurring below the topsoil, subsurface flow systems have a tendency to malfunction by clogging up or by overgrowth. However, when running properly, these types of wetlands contain the sight and smell of sewage much better than FWS systems. They are constructed from a series of semi-submerged rocks to which the bacteria and flora that break down the sewage cling.

According to a 1991 survey of constructed wetlands for wastewater treatment carried out by the United States Environmental Protection Agency Risk Reduction Laboratory, these wetlands are predominately small. 70% of the FWS and 90% of the FS wetlands have flow rates of less than 1 MGD<sup>58</sup>, which is similar to the 80% overall figure for low flow facilities in the US<sup>59</sup>. Average construction costs are summarized in Table 2.6.

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<sup>56</sup> Robert L.P. Kleinmann and Robert S. Hedin, "Treat Mine Water Using Passive Methods", *Pollution Engineering*, Vol. 25, No. 13, August 1993, p. 20.

<sup>57</sup> Shawna Moos, "More Than Just Sewage Treatment", *Technology Review*, August/September 1991, p. 16.

<sup>58</sup> Sherwood C. Reed and Donald S. Brown, *Ibid.*, p. 777.

<sup>59</sup> George Tchobanoglous and Franklin L. Burton, *Ibid.*, p. 3.

**Table 2.6 Average Construction Costs for Two Types of Wetlands Designed to Treat Wastewater<sup>60</sup>**

	Number of Wetlands Surveyed	Average Construction Costs (\$/Acre)	Average Cost/Gallon Treated (\$/1000 gal.)
Free Water Surface	19	\$22,000	0.62
Subsurface Flow	18	\$87,000	0.78

Source: Constructed Wetlands—The First Generation

The higher price tag on the subsurface flow wetlands is largely attributable to the cost of buying, transporting and arranging the rocks in the system. Maintenance costs for these types of wetlands is minimal<sup>61</sup>. Another comparison is to look at the costs of treating one million gallons a day, the capacity needed to meet the needs of a small rural community of 10,000 people. Loading rates indicated that 20 acres at \$1.74 million dollars in capital would be required for a SF system. 50 acres would be needed for a FWS, leading to a capital cost of \$1.1 million dollars<sup>62</sup>. The average cost of the water would then be \$780/day for the FWS and \$620/day for the SF system. Because the cost of land is not included in this figure, it is impossible to determine which method would be more cost effective from the point of view of capital. However, when the price of land is substantial, as is the case near urban areas, this method becomes economically prohibitive.

**2.2.2.2 Aquaculture Facilities.** This type of facility uses principles of aquaculture to treat wastes. In these systems, the waste flows into large ponds; and free-floating plants, as well as fish, help to digest the waste. These plants have to be harvested periodically in order to allow for a constant uptake of organics and other nutrients. Until recently, the fast growing water hyacinth was used to uptake the organics and nutrients; however, without much commercial value, the hyacinth adds no value to the project following its harvest and

<sup>60</sup> Sherwood C. Reed and Donald S. Brown, *Ibid.*, p. 778.

<sup>61</sup> Shawna Moos, *Ibid.*, p. 16.

<sup>62</sup> Kevin L. Griffith, *Constructed Wetlands: A Growing Opportunity for the Construction Industry*, MIT Master's Thesis, February 1992, p. 21–22.

has to be composted or landfilled. Recently, advances in design and harvesting technology have been made that allow fast-growing free-floating duckweed (*Lemna* sp.) to be farmable. With the protein equivalence of soybean meal, duckweed can be pelletized and sold commercially for animal feed, the only presale requirements being harvesting and drying. In the southern US, one acre of duckweed grown in nutrient enriched wastewater will result in 15,000 lbs of high quality protein and will remove over 2,351 lbs of nitrogen, 588 lbs of phosphorus, 784 lbs of potassium, 784 lbs of calcium, 235 lbs of sulfur, 313 lbs of magnesium and 392 lbs of chloride<sup>63</sup>. This allows the facility to recoup some of the money spent on the treatment process. Landscaping is designed to enhance public awareness and enjoyment of the facility.

Applications for these types of systems range from polishing primary treated waste to secondary treatment, and secondary treatment to tertiary standards. Systems also exist with which to remove eutrophication causing nutrients from the wastewater stream.

A typical example is the Lemna<sup>®</sup> Corporation's systems.

**2.2.2.3 Greenhouse-Type Facilities.** Greenhouse facilities are solar-powered, or semi-solar-powered, systems comprised of a series of tanks through which the wastewater flows. In each of these, various plants, animals, bacteria and fungi use the organics and nutrients to carry out their life processes. Mimicking life in the wild and natural food chains, the tanks are arranged to allow the water to become cleaner and cleaner as it flows through each one. Tanks receiving raw wastewater contain organisms typically found in highly eutrophic fresh water bodies such as bacteria, zooplankton, algae and snails. The bacteria break down organic matter, similar in concept and action to their role in biological treatment in standard secondary treatment, and convert ammonium to nitrite and nitrate.

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<sup>63</sup> Becky Gillette, "The Green Revolution in Wastewater Treatment", *Biocycle*, December 1992, p. 48.

Proliferating on the sides of the tank, algae help consume nutrients in the water, and in turn are consumed by both the zooplankton and the snails. In later tanks, the zooplankton and the algae are eaten by such fish as striped bass, tilapia, and minnows. Hydroponic water plants such as water hyacinths and microorganisms existing in symbiotic relationships with them help consume remaining nutrients and organics. Further downstream, simulated tidal marshes consisting of bullrushes, cattails and other species cycle through denitrification and nitrification phases, mimicking life at the edge of the ocean and providing anaerobic and aerobic treatment, as well as a buffer against toxic shocks to the system. An example of a toxic shock might be an elevated level of trichloroethylene in the wastewater, due to an illegal industrial dumping into the system.

A typical example is the Solar Aquatics® system operating at the Sugarbush Ski Resort in Stratton, Vt. Designed as a small pilot-scale facility to help the resort meet nitrogen effluent limits, it has an average daily flow of only 330 gallons, taken from the original treatment facility. Three tanks accepted the incoming wastewater and discharged it to an open water raceway before it was finally discharged to six more tanks, designed for polishing the water. Plants in the raceways included the black willow, pussy willow, water willow, duckweed, umbrella plant, purple loose strife and *Eucalyptus camaldulensis*, while in the wetland portions cattails, bulrushes and reeds were used. Bacteria, micronutrients and trace elements were added periodically to the system, and baking soda utilized to ensure nitrification. As can be seen from Table 2.7, this system was quite successful at reducing BOD, suspended solids and all forms of nitrogen, except ammonia, and unsuccessful at removing phosphorus.

**Table 2.7 Average Performance Data, January 1988 to March 1989<sup>64</sup>**

	<b>Influent (mg/l)</b>	<b>Effluent (mg/l)</b>	<b>Removal (%)</b>
5-day biochemical oxygen demand	220	10	95
Total suspended solids	162	6	96
Total Kjeldahl nitrogen	51	12	77
Organic nitrogen	29	4	86
Ammonia	22	8	64
Nitrate	0.6	9	-
Total nitrogen	52	21	60
Total dissolved phosphorus	5	5	0
Fecal coliform (no./100 ml)	$6 \times 10^6$	1500	99+

Source: Sherwood C. Reed, p. 64.

Construction costs for the indoor greenhouse-type facility were \$26,000, including tank and greenhouse construction, pumps and other mechanical equipment. A 14-month pilot run, from January, 1988 to March, 1989 resulted in operating costs of \$5000 and labor costs of \$11,000. If this were amortized over a ten-year period, the cost per gallon treated would only be \$0.04<sup>65</sup>.

**2.2.3. Membrane Separation Technologies:** There are four basic membrane separation technologies used extensively in drinking water treatment, municipal wastewater reclamation, and industrial water reuse: electrodialysis, reverse osmosis, microfiltration and ultrafiltration. Other variants include electrodialysis reversal and nanofiltration. The principle common to all of these processes is that it is possible to force water hydrostatically or electrically through certain types of semipermeable membranes. In doing this, molecules are trapped on the membrane, stripping the water of all compounds larger than the pore size.

<sup>64</sup> Sherwood C. Reed, "Solar Aquatics Treat Resort Wastewater", *Water Environment and Technology*, July 1992, p. 64.

<sup>65</sup> Sherwood C. Reed, *Ibid.*, p. 66.

Seven factors make membrane separation processes attractive:

- Continuous process design, allowing for round-the-clock operation of the facility;
- No phase nor temperature changes of either the solute or the process water, reducing energy costs;
- No chemical or biological transformation of the solute or the process water;
- Modular design, allowing for wide variations in the size of plant or project;
- Few moving parts, resulting in low maintenance costs;
- Ensured physical separation of contaminants and process water by the membrane;
- No additional of chemicals are used, with the exception of antifoulants<sup>66</sup>.

While similar, each of the membrane separation technologies is differs in terms of certain design parameters, as outlined in Table 2.8. Additional factors that add to the relative cost of the system—such as energy inputs and membrane replacement requirements—are also shown. Pretreatment and post-treatment requirements, although not outlined in Table 2.8, also differ, and can add substantially to the overall cost of a project.

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<sup>66</sup> Peter S. Cartwright, "Zero discharge/water reuse—the opportunities for membrane technologies in pollution control", *Desalination and Water Reuse*, Vol. 3, Proceedings of the 12th International Symposium, Institute of Chemical Engineers, 1991, p. 225.

**Table 2.8 A Comparison of Membrane Separation Technologies<sup>67</sup>**

Feature	Micro-filtration	Ultra-filtration	Reverse osmosis	Electro-dialysis
Suspended solids removal	yes	yes	yes	no
Dissolved organic removal	no	yes	yes	no
Dissolved inorganic removal	no	no	yes	yes
Osmotic pressure effect	none	slight	high	none
Concentration capabilities	high	high	moderate	high
Permeate purity	high	high	high	moderate
Energy usage	low	low	moderate	moderate
Membrane stability	high	high	moderate	high
Operating cost (outside estimates) (other sources) (\$/1000 gal)			0.50-1.00 (low pressure) <sup>B</sup> 1.50-2.00 (brackish water) <sup>A, B</sup> 2.00-3.50 (sea water) <sup>A, B</sup>	
Operating cost (\$/1000 gal.)	0.50-1.00	0.50-1.00	1.00	1.00
Average total cost (\$/1000 gal)			0.75-1.25 (low pressure) 1.00-1.50 (brackish water) 4.00 - 6.00 (sea water) <sup>B</sup>	

A: John Douglas, p. 13.

B: Bipin S. Parekh, p. 83.

Adopted from: Peter C. Cartwright, p. 231.

The cost of a membrane separation system is a function of the initial capital cost and the operation and maintenance cost. First, the capital cost will be partially determined by the water quality of the influent and the water quality desired of the effluent. These two factors will help delineate the pretreatment and post-treatment measures. For many processes, the pretreatment technology of choice is another membrane process. For example, prior to an RO unit, ultrafiltration is usually required to prevent particles clogging the pores of the RO membranes. Following RO, depending on the ultimate use of the water, a disinfectant might be required. Each individual unit process added will push the

<sup>67</sup> Peter S. Cartwright, Ibid., p. 231.

total price of the system higher. Second, the lower the consistency of the wastewater in terms of flow, temperature, pH, heavy metal content and other such factors, the higher the price tag. This is both because inconsistent quality is much more likely to inflict harm upon the membrane and certain devices are required to smooth out the systems. Third, the price of membrane separation technology itself will add to overall cost.

Operational and maintenance are largely a function of the price of electricity and the price of the membranes. By working with the power utility it may be possible to reduce electrical consumption and costs somewhat. However, if electrical rates increase significantly—for instance, in order to offset increases from the installation of environmental control devices—the cost of treating water will increase proportionally. Membranes, on the other hand, can have their working life lengthened significantly with the proper care and pretreatment measures.

Qualities of interest in a membrane include selectivity, or the capacity to separate solutes from water; capacity, in terms of specific output; chemical and thermal resistance; long-term consistent performance; and strength, in order to allow for the transport, installation and storage of the membrane<sup>68</sup>. The higher each of these factors is the better the quality of the membrane.

Three major problems with membrane separation technologies are membrane scaling, membrane fouling, and membrane attack. Membrane scaling refers to the formation of a hard precipitate on the membrane and can result in loss of system productivity, removal capacity, membrane permeability, and can lead to irreversible membrane damage<sup>69</sup>. Membrane fouling, on the other hand, is any organic, inorganic or

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<sup>68</sup> Rational Use of Water and Its Treatment in the Chemical Industry, United Nations Economic Commission for Europe, ECE/CHEM/78, 1991, p. 68.

<sup>69</sup> Bipin S. Parekh, "Get Your Process Water To Come Clean", *Chemical Engineering*, January 1991, p. 74.

biological attack on the membranes and can lead to deterioration of the membrane. Inorganic foulants include carbonate, sulfate, fluoride and phosphate salts of divalent cations ( $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{CaF}_2$ ,  $\text{BaSO}_4$ ,  $\text{SiSO}_4$ , and  $\text{SiO}_2$ ); metal hydroxides and sulfides; silica; chlorine; and acids and bases. Methods for dealing with inorganic foulants include the removal of the ion prior to separation, the addition of a precipitant-inhibiting chemical to the feed water, and pH adjustment of the water prior to entry into the unit. Ion removal can be achieved in some cases by additional pH control; other cases require an ion-exchange pretreatment process. If fouling does occur, the membrane cartridge usually has to be removed from the plant and cleaned, a time and chemical intensive process. The growth of microorganisms on the cartridge, or biofouling, can be prevented by disinfecting the water prior to RO or treated by occasionally cleaning the membrane with detergents and acid or caustic solutions<sup>70</sup>.

In general, membrane separation processes are well equipped to deal with typical water problems, such as the desalination of brackish groundwater for drinking water purposes and the removal of such contaminants as salts, gypsum, nitrates, sodium, hardness, chlorides, sulfates and fluorides, as long as the proper pretreatment measures are taken. However, it is the industrial uses—internal water reuse and recycle—that are pushing the edges of the technology. Through improvements in the membranes and the systems themselves, possibilities for use continue to grow.

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<sup>70</sup> B.J. Marinas, "Reverse Osmosis Technology for Wastewater Reuse", *Water Science and Technology*, Volume 24, No. 9, p. 225–226.

### 2.2.3.1. Electrodialysis Reversal (EDR)

Electrodialysis reversal is an electrically-driven membrane separation technology that was developed as an offshoot of electrodialysis. In an EDR cell or unit, a direct-current (dc) is applied to electrodes, separated by water-filled compartments defined by alternating cation-permeable and anion-permeable membranes. This current induces the ions in the water to move, as determined by their charge and the laws of physics. Anions travel toward the anode and cations toward the cathode. Due to the composition of the membranes, permeable only to ions of a given charge, progress of the ions toward the electrodes is impeded. Thus, anions are inhibited from passing through cation-selective membranes and cations from anion-selective semipermeable membranes. Because the two types of membranes alternate within the cell, alternating compartments of demineralized water and concentrated brine solutions arise. Both the water and the brine solutions are removed from the system<sup>71</sup>. In the compartments adjacent to the electrodes, other chemical reactions may occur. At the cathode, hydrogen gas and hydroxide ion are produced, due to the reductive dissociation of water:  $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2(\text{OH}) + \text{H}_2(\text{g})$ . At the anode, water is oxidized:  $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2(\text{g}) + 4\text{e}^-$ . Furthermore, the chloride ion may form chlorine gas:  $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ <sup>72</sup>.

Differentiating EDR from electrodialysis, the polarity of the electrodes is changed a few times an hour, allowing for electronic cleansing of the membrane surface. For approximately one minute the current flows in the opposite direction, and the fresh water and brine solutions are not collected. Because a single-stage unit will only return 50% demineralized water and 50% concentrate, a fraction of the concentrate will often be

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<sup>71</sup> "How Electrodialysis Works", Bulletin #140, Ionics Inc, Watertown MA, 1991, p. 3.

<sup>72</sup> Floyd H. Miller (ed.), Electrodialysis and Electrodialysis Reversal, Ionics Inc., Watertown MA, 1984, p. 11-12.

recycled or processed through another EDR unit. Typically, between two and six units are arranged in series, achieving higher recovery volumes and more concentrated brines<sup>73</sup>. EDR units can be used to treat water of up to 10,000 ppm Total Dissolved Solids (TDS). With an influent stream of 1,000 ppm TDS, a product water of 3-5 ppm is produced<sup>74</sup>.

The 0.1 to 0.7 mm EDR membranes are stacked sheets, each comprised of 100 to 1,000 smaller cells. While neither convection nor diffusion of any ions or molecules can occur across these membranes, neither are bacteria, viruses, and neutral organics removed from the effluent stream. Because of this, disinfection is required before discharge of the effluent.

In recent years, nearly all the EDR systems sold in the United States have come from one company, Ionics, Inc. (Waltham, MA)<sup>75</sup>, and over 1000 Ionics EDR systems are in operation worldwide<sup>76</sup>. Models include the Aquamite® I, III, V, X, XV, XX, 50, and 100. With an operating capacity of 500-2000 gal/day, the Aquamite® 1 is the smallest of these units. On the other end of the spectrum, the Aquamite® 100 provides 0.5 - 1.2 MGD of process water<sup>77</sup>. Membranes include the Mark-III membrane stacks (with model 204 Anion and AZL Cation membranes). These membranes have pores that are 10 µm in diameter and a scale inhibitor is not necessary<sup>78</sup>.

The brine produced by an EDR treatment facility must be disposed of. If the direction of the current is reversed regularly, chemical additions are not necessary. When

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<sup>73</sup> Karen S. Elbe and Jennifer Feathers, "Water Reuse Optimization Requires Knowledge of Cleanup Methods", *Oil and Gas Journal*, Vol. 90, No. 40, October 5, 1992, p. 85.

<sup>74</sup> Karen S. Elbe and Jennifer Feathers, *Ibid.*, p. 85.

<sup>75</sup> James C. Lozier, Gary Smith, Jerry W. Chapman, and David E. Gattis, "Selection, design, and procurement of a demineralization system for a surface water treatment plant", *Desalination*, Vol. 88, 1992, p. 10.

<sup>76</sup> The Aquamite® Spectrum, Bulletin #120-E, Ionics Inc., Watertown MA, 1992, p. 4.

<sup>77</sup> The Aquamite® Spectrum, *Ibid.*, p. 2.

<sup>78</sup> James C. Lozier, Gary Smith, Jerry W. Chapman, and David E. Gattis, *Ibid.*, p. 12.

reversal does not occur, chemical antifoulants are needed and may contaminate the brine, limiting disposal options. Depending on location and the pertinent state and local regulations, disposal options include ocean outfalls, deep well disposal (on the order of 600 m), and landfilling. Other contaminants in the brine, such as heavy metals or organic micropollutants, might limit disposal options further.

EDR is used for such diverse projects as the removal of solutes from brackish groundwater in order to provide drinking water treatment for remote prairie communities, to the removal of salts from the effluent stream from a wastewater treatment or industrial facility, to pretreatment for RO systems.

The economics of a typical EDR facility are difficult to determine because they are a function of many variables including the nature of the waste stream; the location of the facility; the pretreatment processes necessary; the type of membrane utilized and the module selected, the recovery rates and regenerant system; and the local costs of labor, disposal, and electricity. The following table, Table 2.9, gives the economics of an EDR system for the removal of metals from a waste stream.

**Table 2.9 Costs for a 90% Recovery Electrodialysis System for Metals<sup>79</sup>**

Metal Recovered	Capital Cost (\$)	Annualized Capital Cost <sup>A</sup> (\$)	Annual Operation and Maintenance Cost <sup>B</sup> (\$)	Cost of Metals (\$/lb)	Amount of Metals in Liquid Waste (lb/year)	Annual Metal Saving (\$)	Total Annual Cost <sup>C</sup> (\$)	Annual Disposal Cost <sup>D</sup> without Recovery (\$)
Cadmium	101,500	17,235	13,311	1.2	33,254	35,915	-5,369	3,118
Copper	101,500	17,235	12,181	0.675	12,324	7,487	+21,929	1,156
Chromium	101,500	17,235	12,346	1.25	15,380	17,303	+12,278	1,442
Nickel	101,500	17,235	12,727	3.45	22,447	69,697	-39,735	2,105
Zinc	101,500	17,235	19,147	0.44	141,331	55,892	19,510	13,250

Assumptions: All metals are soluble and at concentrations of 0.5 oz/gal (2800 ppm); flow rate is 4 to 7 gal/min (5760 to 10,080 gal/day).

A: Amortized at 11% for 10 years.

B: Electricity costs are \$06/kW/hr; includes allowance for insurance at 1% of capital.

C: Total annual costs equals annualized capital costs + annual O and M costs minus annual metal savings.

D: Cost for secure landfill disposal, including collection and transportation, is \$75/cubic yard.

Adapted from: J.C. MacNeil, "Membrane Separation Technologies for Treatment of Hazardous Wastes", *CRC Critical Reviews in Environmental Control*, Vol. 18, No. 2, 1988, p. 91-132.

### 2.2.3.2. Reverse Osmosis (RO)

Reverse Osmosis is a hydrostatically-driven membrane separation technology that separates all salts and molecules larger than 0.001 micron in size<sup>80</sup>. The three main uses for reverse osmosis are reclamation of wastewater, traditional desalination, and water purification; the latter can be either for municipal, agricultural, or industrial purposes. Reverse osmosis is one of two commercially available technologies available for desalination, the other being the multi-stage flash process. The multi-stage flash process is too expensive to ever be economically viable as a technique for reclaiming wastewater, as well as for most industrial and municipal purposes. For reverse osmosis the key cost factors are electricity, pretreatment, membrane replacement, and discharge costs<sup>81</sup>.

Osmotic pressure, the resistance of the solvent portion of the solution to pass through the membrane, will be a limiting factor in reverse osmosis; solute concentrations

<sup>79</sup> Yi-Chu Huang and S. Sefa Koseoglu, *Ibid.*

<sup>80</sup> Peter S. Cartwright, *Ibid.*, p. 226.

<sup>81</sup> Bipin S. Parekh, "Get Your Process Water To Come Clean", *Chemical Engineering*, January 1991, p. 85.

are limited to less than 31,000 mg/l<sup>82</sup>. Economics will further limit solute concentrations. As the solute concentration increases, the hydrostatic pressure and hence the electricity required to force the water through the membranes increases accordingly. Concentrations of less than 5000 mg/L require a hydrostatic pressure of up to 1 MPa over osmotic pressure. At 20,000 mg/L to 30,000 mg/L, 5 to 10 MPa over osmotic pressure is needed<sup>83</sup>. The increased pressure requirements require additional electricity. Because the cost of electricity is roughly half the total operating cost, this will increase the O and M costs significantly.

Two factors make RO increasingly attractive for water reclamation purposes. First, high removal rates are possible for most organic, inorganic and microbiological contaminants. For example, heavy metal removal rates, of interest both to industries and municipalities, are shown in Table 2.10. Second, improvements in the technology have led to decreasing capital and operation-and-maintenance costs.

**Table 2.10 Heavy Metal Removal Rates by Reverse Osmosis<sup>84</sup>**

Metal	Removal Rate (%)	Metal	Removal Rate (%)
Arsenic (V)	< 90	Copper	< 95
Barium	> 95	Lead	> 95
Cadmium	> 90	Mercury	< 85
Chromium (III)	< 90	Selenium (IV)	75 - 99
Chromium (IV)	< 90		

Adopted from: *Chemical Engineering*, 1988, Vol. 95, No. 16, p. 76.

An RO system requires four major components: general pretreatment, membrane treatment, permeate post-treatment, and concentrate (brine) treatment/disposal. General pretreatment will be a function of the influent water quality; usually ultrafiltration is required beyond standard secondary treatment processes.

<sup>82</sup> Peter S. Cartwright, *Ibid.*, p. 232.

<sup>83</sup> *Rational Use of Water and Its Treatment in the Chemical Industry*, United Nations Economic Commission for Europe, ECE/CHEM/78, 1991, p. 71.

<sup>84</sup> *Rational Use of Water and Its Treatment in the Chemical Industry*, *Ibid.*, p. 64.

An RO treatment unit consists of two compartments separated by an RO membrane. The feed water is introduced into one side of the unit at a pressure of 30-40 psi. Due to innovative designs, the actual pressure against the membrane itself is much higher, achieving pressures as high as 1000 psi. Pressures of this level allow for extremely high flow through rates, a factor helps make RO systems more economical. This pressure forces some of the water to permeate the membrane, traveling from the high-concentration feed water side to the low-concentration effluent side<sup>85</sup>. A solute rich concentrate is left on the feed water side. As this concentrate flows out of the unit, it is depressurized and then either treated, disposed, or recycled through the system. The clean water is forced out of the unit and into the next unit process<sup>86</sup>.

There are two basic configurations for RO membranes: spiral-wound membrane cartridges and hollow fiber membrane cartridges. Both configurations have great advantages over the typical flat membrane in that they allow for greater pressures against the membrane and higher flow rates, both of which make the system more economical. Spiral-wound RO modules are designed to have a layer of fresh water squeezed between two semi-permeable membranes. Separated by spacer layers from other trilayers, they are spirally wound around a hollow tube, through which the feed water is fed. Holes in this tube allow for the feed water to enter the system at pressures of up to 1000 psi. Hollow fiber membranes, on the other hand, can withstand pressures of up to fifty percent more. The feed water is forced into the fibers where pores allow for the separation of process water and solutes. Commercially available membranes are typically synthetic cellulose acetate, polyamide polymers or are of a proprietary composition. Typically, low pressure

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<sup>85</sup> In traditional osmosis a semi-permeable membrane separates regions of high and low concentration; water from the low concentration side will permeate the membrane, effectively lowering the concentration of the high concentration side.

<sup>86</sup> B.J. Marinas, "Reverse Osmosis Technology for Wastewater Reuse", *Water Science and Technology*, Volume 24, No. 9, p. 219-220.

composite membranes are more energy efficient than comparable cellulose membranes.

Dupont (Permassep® model B-15 elements) is a representative low pressure composite RO membrane.

With identical feed streams, reverse osmosis systems generally have a lower process recovery than electrodialysis recovery systems. A function of the feed stream, recoveries of 90-95% can be achieved. However, recovery rates of 75% are more typical. In the concentrate, salt rejection of 98% can be expected.

75 municipal water systems use RO as part of the municipal water treatment process. 30 more are in the planning<sup>87</sup>. Around fifteen wastewater reclamation facilities use RO as the primary separation process, but this number is increasing. Industrial use of RO systems is much higher. RO is especially useful in small-scale water treatment; for plants with productions of 16 MGD and less, capital costs for RO plants are less than for conventional lime-softening plants<sup>88</sup>. Table 2.11 examines the capital, operating and capital costs of low- and high- pressure RO unit processes for small (0.10 MGD) and very small (0.010 MGD) systems. Pretreatment of the water— usually ultrafiltration—is required in order to preserve the membrane.

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<sup>87</sup> "Reverse Osmosis Treatment Saves the Day in Small Town", *Filtration News*, January/February 1993, Volume 3, Number 1, p. 42.

<sup>88</sup> Gary S. Logsdon, Thomas J. Sorg, and Robert M. Clark, "Capability and Cost of Treatment Technologies for Small Systems", *Journal AWWA*, June 1990, p. 65

**Table 2.11 Estimated Capital and Operating Costs for Small-Scale RO Unit Processes for Drinking Water Treatment<sup>89</sup>**

Process	Capital Cost <sup>A</sup> (\$)	Energy <sup>B</sup> , Maintenance, Materials, and Labor <sup>C</sup> Costs (\$/year)	Cost for Chemicals <sup>D</sup> (\$/year)	Total Operating Costs (\$/year) (\$/1000 gal)
0.10-MGD High- pressure	275,000 (TDS ≤5,000 mg/l)	36,500	4,800	8,500 0.23
0.10-MGD Low- pressure	275,000 (TDS ≤2,000 mg/l)	29,800	4,800	10,300 0.28
0.01-MGD High- pressure	84,000 (TDS ≤5,000 mg/l)	8,200	600	14,600 0.4
0.01-MGD Low- pressure	84,000 (TDS ≤2,000 mg/l)	7,200	600	49,000 0.134

A: Amortization of capital at 10% interest over 20 years; all figures are in 1989 dollars.

B: Based on a cost of \$0.07/kW for electricity.

C: Based on a cost of \$11.00/hour for labor.

D: Includes sodium hexametaphosphate, sulfuric acid, and sodium hydroxide.

Adopted from: Gary S. Logsdon et al, p. 62.

For metal removal, the situation and the economics are slightly different. First of all the flow rates are much lower, usually less than 0.01 MGD. Second, the recovered material, the metals, are quite valuable; and the cost of disposal high, often requiring hazardous waste treatment. Therefore, recycling—that is, either reusing the metal in an upstream process or selling the recovered metal—is attractive economically, and either helps considerably to reduce the total cost of the system or saves more money than it costs. Economics like these make such types of recycling economically attractive to the company, thereby reducing the need for regulatory control. Table 2.12 compares the capital, and operation and maintenance costs for reverse osmosis metal recovery systems for four metals; resale values and disposal costs for the metals and total annual costs are also shown.

<sup>89</sup> Gary S. Logsdon, Thomas J. Sorg, and Robert M. Clark, *Ibid.*, p. 62.

**Table 2.12 Costs for a 95% Recovery Reverse Osmosis System<sup>90</sup>**

Metal Recovered	Capital Cost (\$)	Annualized Capital Cost <sup>A</sup> (\$)	Annual Operation and Maintenance Cost <sup>B</sup> (\$)	Cost of Metals (\$/lb)	Amount of Metals in Liquid Wastes (lb/year)	Annual Metal Saving (\$)	Total Annual Cost <sup>C</sup> (\$)	Annual Disposal Cost <sup>D</sup> without Recovery (\$)
Cadmium	26,000	4,415	12,938	1.20	33,254	37,909	-20,556	3,118
Copper	26,000	4,415	10,228	0.675	12,324	7,903	+6,740	1,156
Chromium	26,000	4,415	10,963	1.25	15,380	18,264	-2,886	1,442
Nickel	26,000	4,415	8,327	3.45	22,447	73,571	-60,829	2,105

Assumptions: All metals are soluble and at concentrations of 0.5 oz/gal (2800 ppm); flow rate is 4 to 7 gal/min (5760 to 10,080 gal/day).

A: Amortized at 11% for 10 years.

B: Electricity costs are \$06/kW/hr; includes allowance for insurance at 1% of capital.

C: Total annual costs equals annualized capital costs + annual O and M costs minus annual metal savings.

D: Cost for secure landfill disposal, including collection and transportation, is \$75/cubic yard.

Adapted from: J.C. MacNeil, "Membrane Separation Technologies for Treatment of Hazardous Wastes", *CRC Critical Reviews in Environmental Control*, Vol. 18, No. 2, 1988, p. 91-132.

In 1992, Envitec, the world's largest exhibition of environmental technologies occurred in Dusseldorf, Germany. At that time, 31 companies exhibited reverse osmosis systems<sup>91</sup>. Major North American manufacturers include:

- ARI Technologies, Inc. (Palantine, IL),
- Bio-Recovery Systems, Inc. (Las Cruces, NM),
- Davis Water & Waste Industry, Inc. (Thomasville, GA),
- Desalination, Inc. (San Diego, CA),
- Infilco, Inc. (Richmond, VA),
- Ionics, Inc. (Watertown, MA),
- Kinetico Engineered Systems, Inc. (Newbury, OH),
- Osmonics (Minneapolis, MN),
- Ozone Research & Equipment Corporation (Phoenix, AZ),
- PURA, Inc. (Provo, UT),
- Serck Baker, Inc. (Huntington Beach, CA),

<sup>90</sup> Yi-Chu Huang and S. Sefa Koseoglu, *Ibid.*

<sup>91</sup> "Envitec is #1", *Clear Solutions*, July 1992, No. 1, p. 3.

- **Smith & Loveless, Inc. (Lenexa, KS),**
- **Sverdrup Corp. (St. Louis, MO),**
- **US Filter / IWT (Rockford, IL),**
- **Universal Process Equipment, Inc. (Roosevelt, NJ),**
- **UV Waterguard Systems, Inc. (Port Moody, British Columbia, CANADA),**
- **Zenon Environment Systems, Inc. (Burlington, Ontario, CANADA).**

**Manufacturers of membrane cartridges include:**

- **Basic Technologies, (West Palm Beach, FL)**
- **Dupont (Wilmington, DE),**
- **Fluid Systems (San Diego, CA),**
- **Hydranautics (San Diego, CA),**
- **Universal Oil Products (UOP), (San Diego, FL).**

**As with EDR systems, the concentrated brine solution must be dealt with.**

**Depending on the makeup of the concentrate and location of the plant, it might be possible to dispose of the brine directly in the ocean. In other situations, deep-well injection, landfilling or further treatment is required.**

#### **2.2.3.3. Ultrafiltration (UF)**

**Ultrafiltration is a pressure-driven membrane separation technology often used as a pretreatment process for EDR or RO in order to protect the pores in those membranes from clogging. The soluble material not removed by UF is then removed by EDR or RO. Furthermore, UF is able to operate under higher flow conditions than either EDR or RO, making it more feasible for certain applications, and requires a hydrostatic pressure of between 0.3 and 1 MPa . One important industrial application is the separation of oil-water**

emulsions<sup>92</sup>. Ultrafiltration itself does not remove salts or heavy metals well, but does remove insoluble material in the 0.001 to 0.1 micron range as well as colloids, bacteria, pyrogens, and high-molecular organics<sup>93</sup> with molecular weights of 300 to 300,000<sup>94</sup>. The removal of molecules on the lower end of this range can be enhanced by the addition of surfactants to the effluent as well as by a modification of the membrane surface<sup>95</sup>. Additionally, it is possible to remove certain heavy metals—aluminum, arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc—by the addition of a chemical precipitant to the wastewater stream. If properly operated, up to 99% of the heavy metals can be removed by a combination precipitation/filtration system<sup>96</sup>.

The two main classes of ultrafiltration membranes are polymers and inorganic materials. Comprising a much wider variety of polymers than are available for reverse osmosis membranes, the polymeric materials include cellulose acetate, polyacetal, polyacrylate, polyamides, polycarbonate, polysulfones, polyvinylidene fluoride; copolymers of acrylonitrile and vinyl chloride; crosslinked polyvinyl alcohol; and polyelectrolyte complexes. The inorganic materials include alumina, borosilicate glass, pyrolyzed carbon, zirconia/carbon and zirconia/steel<sup>97</sup>.

Generally, companies that manufacture reverse osmosis systems also manufacture UF systems.

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<sup>92</sup> *Rational Use of Water and Its Treatment in the Chemical Industry*, Ibid., p. 69.

<sup>93</sup> Bipin S. Parekh, Ibid., p. 83.

<sup>94</sup> Yi-Chu Huang and S. Sefa Koseoglu, Ibid..

<sup>95</sup> Yi-Chu Huang and S. Sefa Koseoglu, Ibid..

<sup>96</sup> E. Rodha Krishan, Ronald J. Turner, et al., "Overview of Metals Recovery Technologies for Hazardous Wastes", Proceedings of the National Research & Development Conference on the Control of Hazardous Materials, Feb. 20–22, 1991, Anaheim, CA in *The Hazardous Waste Consultant*, Vol. 9, No. 3, May/June 1991, p. 1.22–1.28.

<sup>97</sup> Yi-Chu Huang and S. Sefa Koseoglu, Ibid..

#### 2.2.3.4. Microfiltration (MF)

Microfiltration is a pressure-driven membrane separation technology similar to ultrafiltration, but with different size pores in the membrane. Typically, MF is the first stage in a treatment chain, preceding ultrafiltration. MF removes insoluble material in the range of 0.1 to 10.0 microns and is basically a method to remove suspended solids and captures little else. However, as with ultrafiltration, it is possible to combine microfiltration with chemical precipitation and remove the solid precipitates from the wastewater. Hydrostatic pressures of between 0.01 and 0.1 MPa are required.

Memcor Ltd. (Wirksworth, UK) has a microfiltration process that removes bacteria, oil and grease, suspended solids, BOD and COD from sewage. Operating commercially at a 1.35 megaliter/day plant (Blackworth Sewage Treatment Works) near Sydney, Australia, 480 modules of hollow-fiber polypropylene membranes remove all SS greater than 0.2 mm in diameter, 87% of the BOD (which means that the plant will meet secondary treatment standards), 78% of the COD, 99.5% of the SS, 99.96% of the turbidity, 73% of the total Kjeldahl nitrogen and 99% of the oils and grease. The membranes are cleaned periodically by a patented pulsed-gas treatment. Pretreatment consists of straining with rotating disks. Post-treatment disinfection is not required. A similar system is priced at \$960,000 with O and M costs of \$67,000/year.<sup>98</sup>

#### 2.2.3.5. Nanofiltration (NF)

NF is another variation on pressure-driven membrane separation technologies. It can remove all macromolecules with a molecular weight of greater than 200-300. However, because it operates at much lower pressure than RO or EDR, it has much lower

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<sup>98</sup> "Microfiltration can disinfect sewage without chemicals", *Chemical Engineering*, August 1992, p. 19.

operating costs. Commercially available since 1986, nanofiltration thin film membranes achieve hat same flow rates at 100 psi that more traditional cellulose acetate membranes achieve at 200 psi<sup>99</sup>.

One application of nanofiltration has been to treat reclaimed wastewater that has been discharged to an aquifer. This has led to a current use in conjunction with on-site slow sand filtration at a water reclamation center, designed to mimic aquifer recharge. This method would allow higher levels of treatment at lower costs. A patent on this process was to be granted in 1992<sup>100</sup>.

NF is useful for use treating drinking water. By using NF, it is possible to meet very stringent disinfection byproducts (DB) limits, which were developed in response to the passage of the 1986 Safe Drinking Water Act Amendments. Especially in areas like South Florida, where drinking water is drawn from an aquifer with high organic content (which tends to oxidize with the addition of chlorine to levels of 72-hour trihalomethane (THM), a common DBP, formation precursor that is above the 400 µg/l. NF allows for a product water that has high organic precursor removal with ultimately low DBP levels. A plant in Ft. Meyers, Florida estimated that for a 12 MGD NF reclaimed wastewater plant, overall costs range from \$0.50-0.60/1000 gallons<sup>101</sup>. In comparison, a 12 MGD advanced treatment system in California had capital costs of \$0.67/1000 gallons, operation and maintenance costs of \$0.70/1000 gallons, and total costs of \$1.37/1000 gallons for the NF unit process, with 80–85% recovery<sup>102</sup>.

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<sup>99</sup> C. Brent Cluff, "Slow sand/nanofiltration for secondary treated wastewater", *Desalination*, Vol. 88, 1992, p. 53–67.

<sup>100</sup> C. Brent Cluff, *Ibid.*, p. 53–67.

<sup>101</sup> C. Brent Cluff, *Ibid.*, p. 53–67.

<sup>102</sup> Todd Fuqua, Paul T. Bowen, and Robert S. Ortiz, "Using Reclaimed Water for Shallow Aquifer Recharge" *Desalination*, Vol. 88, 1992, p. 249.

## **2.3. Regulatory and Social Acceptability**

### **2.3.1. Regulatory Acceptability**

The Federal Water Pollution Control Act (FWPCA) mandates that all sewage must be treated to at least secondary treatment levels. The "do nothing" and "do little" alternatives, long preferred by communities across the country, are no longer viable options for dealing with sewage and wastewater. Communities of all sizes around the country are upgrading currently existing facilities and constructing additional ones to meet the national standards.

In some parts of the country, POTWs are required to upgrade facilities to advanced water treatment. In these cases, usually nutrient removal is necessary to preserve or restore the ecosystem surrounding the receiving water. However, for municipalities effluent limitations are mandated, not technologies. For industrial discharges it is a different story. Industry-wide effluent limitations have been written for 51 separate industries. While effluent limitations in theory, they were all based on the Best Available Technology (BAT) commercially available for that industry. For some industries, zero discharge is required.

Besides discharging to surface water, it is possible to discharge effluent to deep-wells or to aquifers. Deep-well disposal is possible only in some areas of the country and is legislated by federal, state and local deep-well disposal regulations. Discharges to aquifers are regulated under the Safe Drinking Water Act of 1974, and must meet the minimum standards of the Underground Injection Control (UIC) program. More stringent effluent limitations apply if the discharge is in the vicinity of an uptake well. Depending on the location, quantity and quality of the effluent, an environmental impact statement might be required. Permits will be required in both of these cases.

Permits for discharge are granted by the state in accordance to, or stricter than, federal standards. Furthermore, a plant must be in compliance with any additional state and local regulations, including those pertinent to air, water, solid waste, noise, and hazardous waste pollution. Typically, the information required for permits include:

- Detailed engineering report,
- Environmental documentation,
- Easements,
- Construction permits,
- Filing of applications,
- Bargainment of fees<sup>103</sup>.

Other permit provisions that may be included are requirements for monitoring the effluent quality of the plant and water quality of the use areas once the plant becomes operational, and monitoring and testing to ensure there is no cross connection between potable water and reclaimed water lines<sup>104</sup>.

### 2.3.2. Social Acceptability

The public acceptance of a wastewater recycle and reclamation project is key to its success. Over the past decade, the public has become more and more distrustful of large projects that theoretically benefit the larger whole by incurring some amount of risk to those who live, work, or play nearby. Furthermore, the general public is more aware than ever of the collective power they hold to halt or stall indefinitely the construction of such facilities by taking legal action. The current difficulty in siting incinerators, hazardous waste landfills and low-level nuclear waste facilities exemplifies this. Therefore, it is

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<sup>103</sup> Steven X. McHaney, "Satellite Wastewater Reclamation Plants: How to Get What You Bargain For," *Desalination*, Volume 88, 1992, p. 219.

<sup>104</sup> Steven X. McHaney, *Ibid.*, p. 219.

necessary to have the public goodwill behind such projects. The public must accept the project on two levels.

First, the public in general must be willing to use reclaimed wastewater once it becomes available. Therefore, the idea must be accepted that using reclaimed wastewater for specific purposes is beneficial—either economically, environmentally, or as a way to meet water budgets. If the public does not, the facility itself could be forced to close, becoming a giant red herring in a community, like the abandoned nuclear power plants that remain around as eyesores of the landscape. A series of surveys (see Table 2.13) conducted in the states of California and Colorado shows that the public is not adverse in general to the use of reclaimed wastewater, but their opinions vary widely with the proposed end use of the water.

**Table 2.13 Percentage of Respondents Opposed to 27 Uses of Reclaimed Water in the General Opinion Surveys<sup>105</sup>**

	Bruvold	Stone and Kable	Kasperson et al.	Olson et al.	Bruvold	Milliken and Lohman	Lohman and Milliken
Food preparation in restaurants	56			57			
Drinking water	56	46	44	54	58	63	67
Cooking in the home	55	38	42	52		55	55
Preparation of canned vegetables	54	37		52			
Bathing in the home	37	22		37		40	38
Pumping down special wells	23			40			
Home laundry	23		15	19		24	30
Swimming	24	20	15	25			
Commercial laundry	22	16		18			
Spreading on sandy areas	13			27			
Irrigation of dairy pastures	14			15			
Irrigation of vegetable crops	14		16	15	21	7	9
Vineyard irrigation	13			15			
Orchard irrigation	10			10			
Pleasure boating	7	14	13	5			
Hay or alfalfa irrigation	8	9		8			
Commercial air conditioning	7			9			
Golf course hazard lakes	3	8		5	8		
Electronic plant process water	5	5	3	12			
Home toilet flushing	4	5		7		3	4
Residential lawn irrigation	3	6		6	5	1	3
Irrigation of recreational parks	3			5	4		
Golf course irrigation	2	5	2	3	4		
Irrigation of freeway greenbelts	1			5			
Road construction	1			4			

Source: William H. Bruvold, p. 46.

As these results show, the general public is not adverse to most common uses of reclaimed wastewater: agricultural and urban reuse. However, such uses as direct potable reuse and using reclaimed wastewater for cooking are quite unfavorable to the general

<sup>105</sup> William H. Bruvold, "Public Opinion on Water Reuse Options", *Journal WPCF*, Volume 60, Number 1, p. 46.

public across all the surveys. Forcing the public to use reclaimed water for purposes with which they are not comfortable is inadvisable, because of the nature of the repercussions that could occur.

Second, lessons from other areas of environmental remediation strongly urge that the people who live near the proposed plant not be adverse to its existence. Even if the reclamation facility is an upgrade of an existing POTW, the public must be kept informed and, to the greatest extent possible, happy. Suggestions of how to maintain good and positive relations with nearby residents include<sup>106</sup>:

- Establish a good footing early on,
- Keep the community informed of all facts and developments,
- Encourage and respond to input from the community,
- Respond to criticisms and complaints in a positive, meaningful manner,
- Design and construct facilities that are as unobtrusive and inoffensive as possible,
- Be a "good neighbor",
- Respond to the specific needs of the community, be it a request for local hiring, specific architecture, increased grooming of the grounds, or any other need.

As with all projects that subjugate small numbers of people to increased risk for the benefit of the larger good, it is necessary to establish good relations early on and maintain them through the life of the project. Once a negative connotation is associated with a project like these, it is extremely difficult to cultivate positive feelings.

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<sup>106</sup> Steven X. McHaney, *Ibid.*, p. 223.

## 2.4. Market Characteristics

Pollution control is an enormous market in the United States. By 1986, 1.67% of the GNP was being spent on pollution control devices, and by 1990 it is estimated that 2.1% of Gross National Product (GNP) was being spent on pollution control activities. If the market continues to grow at its current 7% a year, by the year 2000 between 2.6 and 2.8 percent of GNP will be spent satisfying environmental regulations<sup>107</sup>. The pollution control market is characterized by five sectors: air and radiation, water, land, chemical control, and multi-media. Satisfying three federal pieces of legislation and their subsequent amendments—the Marine Protection, Sanctuaries and Research Act of 1972, Clean Water Act as amended in 1991, and the Safe Drinking Water Act as amended in 1986—helped establish the water pollution control market, which currently is the largest segment of the pollution control market, accounting for 42.9% of all pollution control dollars spent in 1987<sup>108</sup>. While estimates suggest that by the year 2000 other segments—in particular, land and air—will be gaining percentage points, the largest segment will still be the water sector, making it a promising area to be involved in. An estimated 42.4 billion dollars were spent in 1990, and an estimated 49 billion dollars will be spent in 1993 (all in 1986 dollars)<sup>109</sup>.

As early as 1972, water pollution control resulted in the greatest amount of spending of any environmental sector. Originally driven by public opinion, it has continued to grow. Part of the steady growth in water pollution control can be attributable to municipalities and industries slowly revamping rundown POTWs and water treatment facilities in order to come into compliance with the recent amendments to the Federal Water

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<sup>107</sup> Environmental Investments: The Cost of a Clean Environment. A Summary, US EPA, EPA 230/12-90-084, p. 2-1.

<sup>108</sup> Environmental Investments: The Cost of a Clean Environment. A Summary, Ibid., p. 2-2.

<sup>109</sup> Environmental Investments: The Cost of a Clean Environment. A Summary, Ibid., p. vi.

Pollution Control Act (Clean Water Act) and the Safe Drinking Water Act . Part can be attributed to water and wastewater technology manufacturing, both for domestic and international sales. Part can be attributed to select industries, such as power producers, heading toward "zero discharge", and requiring high tech water pollution control devices to enable this. Lastly, some of the steady increase can be attributed to burgeoning population bases in areas with limited water resources, requiring increasingly technological solutions to meet water needs.

In 1992, the federal government alone allocated more one billion dollars for environmental restoration programs, or approximately 1.5% of the Gross Domestic Product (GDP)<sup>110</sup>. State and local needs, and manufacturing, research and development and industrial projects accounted for the rest. This money will be partially spent in the traditional specters of environmental remediation— the design, construction and general upgrades of wastewater, drinking water, and solid waste facilities; and the manufacture and installation of control devices. It will also be spent in the emerging areas of site investigation and remediation, environmental audits and preventative services<sup>111</sup>. As can be seen in Table 2.14, the money required to complete POTW construction, upgrades and install the necessary infrastructure to support such facilities in the community reaches into the tens of billions of dollar range. Billions more will be spent on advanced treatment facilities.

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<sup>110</sup> Thomas Kvan, "Environmental Market Is Growing Here and Abroad", *American Consulting Engineering*, p. 17-20.

<sup>111</sup> Thomas Kvan, *Ibid.*, p. 17-20.

**Table 2.14 Needs For Publicly Owned Wastewater Treatment Facilities, In Billions of 1990 Dollars<sup>112</sup>**

Needs Category	Estimated Cost		State Contributions
	Current	Design Year	
Secondary Treatment	18.5	24.9	12.4
Advanced Treatment	3.6	4.7	6.6
Infiltration/Inflow Correction	2.8	2.8	0.8
Replacement/Rehabilitation	3.6	3.6	0.7
New Collector Sewers	10.9	13.8	3.2
New Interceptor Sewers	9.1	14.1	3.3
Combined Sewer Overflows	16.5	16.5	3.2
<b>TOTALS</b>	<b>65.0</b>	<b>80.4</b>	<b>30.2</b>

Source: *1990 Needs Survey, Report to Congress*, United States Environmental Protection Agency, October 1991, EPA 430/09-91-024.

This money translates into the construction and upgrades of many individual treatment centers across the US. The division of treatment centers by levels of treatment provided is shown in Table 2.15.

**Table 2.15 Treatment Facilities by Level of Treatment, in Number of Facilities<sup>113</sup>**

Level of Treatment	1988	When Needs Met	Net Change
Less than secondary	1,789	48	-1,741
Secondary	8,536	9,659	1,123
Greater than secondary	3,412	5,293	1,881
No discharge	1,854	2,363	509
Other	117	11	-106
<b>TOTAL</b>	<b>15,708</b>	<b>17,374</b>	<b>1,666</b>

Source: *Assessment of Needed Publicly Owned Treatment Facilities in the United States, 1988 Needs Survey Report to Congress*, United States Environmental Protection Agency, October 1991, EPA 430/09-89-001, February 1989.

The tremendous amount of money being spent in this area has given rise to the development of many new technologies and products and the birth and growth of

<sup>112</sup> Thomas Kvan, *Ibid.*, p. 17-20.

<sup>113</sup> George Tchobanoglous and Franklin L. Burton, *Ibid.*, p. 4.

companies. As the technologies improve both technically and economically, they become more accessible to communities and industries for incorporation into water treatment facilities. This has happened with many of the membrane separation processes and consequently they are being utilized at more and more municipal and industrial sites. Furthermore, as public acceptance grows, as with both reclaimed wastewater and natural systems to treat or polish wastewater, the use of the technology also increases. Among the many possible uses of constructed wetlands, the market with the most potential is for wastewater treatment, especially in small and rural communities which lack the economic resources to construct high tech wastewater treatment systems. Already 150 of these systems have been constructed, and there are still many smaller communities not yet in compliance with the Clean Water Act. In these communities, where land is more abundant than money, the potential for natural system is high.

The 1992 market for separation technologies (including pervaporation, or permeate vapor separation) in hazardous waste remediation, a large part of land pollution control, has been estimated to be approximately \$139 million with an annual growth rate of 5 to 6%<sup>114</sup>. At this rate, the market will be approximately \$227 million to \$263 million in size just for hazardous waste remediation. The market size for other purposes in the water sector—municipal and industrial water and wastewater—is much larger. The Environmental Protection Agency estimated that over 11 billion dollars—4.7 billion dollars of federal funds and 6.6 of supplemental state funds—are needed to upgrade facilities to meet advanced treatment needs<sup>115</sup>. Part of this money will go toward the installation of membrane separation technologies.

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<sup>114</sup> Business Communications Company, Inc., "Advanced Hazardous Waste Technologies Making Gains", *The Hazardous Waste Consultant*, Vol. 10, No. 6, November/December 1992, p. 1.28-1.29.

<sup>115</sup> 1990 Needs Survey. Report to Congress. US EPA, EPA 430/09-91-024, October 1991.

Lastly, the noose is tightening around industrial dischargers. Whereas once the United States Environmental Protection Agency was lax in their monitoring and control of industrial dischargers, it is in this area that "zero discharge" is becoming reality. As each factory comes into compliance with such requirements, the market for tertiary and higher treatment will only increase. Because no one company in the United States has a complete monopoly on all the equipment, patents and knowledge, there is currently room to enter this market. The only barriers to entry are in the acquisition or possession of the technologies. Furthermore, because it is for these applications that are pushing the technological innovation, research and development in this area could prove quite profitable.

In summary, the market is characterized in terms of a steady rate of growth. There are many vendors of the technologies, without monopoly players in most areas, allowing for increased competition. The technology for membrane separation technologies tends to be patented and proprietary. Constructed wetlands are not patented, whereas some of the other natural methods are. Aquifer storage recovery is increasing in popularity, although it is not a patented process. Geographically, the market for reclaimed wastewater is generally in arid, populated regions of the country. Industrial recycle of water is not centered in any particular location geographically, but is an issue nationwide.

## **2.5. Market Attractiveness to the Construction Industry**

**2.5.1. Strategic Attractiveness.** For natural systems, greenhouse-type facilities are still in the pilot-plant phase of design. For an analysis of the market of constructed wetlands refer to Kevin Griffith's Constructed Wetlands: A Growing Opportunity for the Construction Industry.

The overall market for ASR facilities is still quite small, with less than 20 existing nationwide. The original leader in this market was CH2M Hill, which designed the original facilities and can claim more than half of the facilities as theirs. As the technology becomes better accepted, other companies have moved in. The threat of entrant is, however, low, as this type of work is within the ken of many construction firms and doesn't require much specialized skills or equipment. The threat of alternatives is expansion of existing drinking water facilities or the construction of above-ground storage tanks, both expensive propositions. The threat from the suppliers is low, as many suppliers can fulfill the requirements. The threat from the buyer is medium. Overall, this market is of only medium strategic attractiveness to a construction company.

The next market can be defined as the design and construction of membrane separation technology units at municipal and industrial facilities. In this market, the threat of entry is large, because many medium to large construction companies are capable of designing and constructing these facilities. The threat of alternatives is variable and is a function of the effluent stream, the location of the facility, the regulatory pressures and a host of other factors. In some areas, there are no alternatives and in others many. For instance, for rural facilities, achieving a very high quality effluent by the construction of a wetlands is possible. In industrial parks, there might not be any alternatives. The threat from suppliers of the components of the membrane units is medium to low. While in EDR there is an industry leader, for the remainder of the membrane separation market, the top 16 companies only occupy 40% of the market. The buyers for this market are the municipal and industrial facilities. Because the need for these technologies is often driven by regulations, the threat from the buyer is low. Overall, this market has a medium strategic attractiveness for a construction company.

**2.5.2. Cost Effectiveness for Customers.** The customers for water and wastewater conservation, recycle and reclamation projects are water utilities representing the general public and the industrial dischargers. Customers for natural systems and constructed wetlands will be water utilities in regions where the price of land is low and the need for compliance high. In particular, these will be small towns, although larger systems are available. For these utilities, natural systems and constructed wetlands are extremely cost effective, especially in terms of operation and maintenance costs; employees of small utilities hired to run an outdated plant may prove unnecessary, which could present a community relations problem. For the customers, they are also extremely cost effective and have the added environmental and social benefit of adding a wetland to a community.

ASR systems are economically attractive to communities with the correct combination of demand needs and geological formations. Besides potential environmental benefits, it is attractive to both the customers and the water utility because of cost savings.

Membrane systems are expensive, high-tech options for removing contaminants from aqueous streams. The costs of the systems can be prohibitive, and so are feasible for select purposes in municipal and industrial water and wastewater treatment. In such cases, the costs, including disposal, will have to be balanced against the benefits of having the contaminants removed. In all cases, the specifics of the system will dictate feasibility.

### **2.5.3. Suitability**

Opportunities for the construction industry in the area of wastewater reuse and reclamation exist in three broad areas. The first area is the design and construction of the treatment center, constructed wetland, or ASR wellfield. This involves carrying the project through the planning stage, helping to coordinate permitting, and working as an intermediary between city, customers and site throughout the entire procedure. Along with

traditional construction related activities, this involves either acquiring the necessary technologies or working with a vendor or distributor of the technology. Second, opportunities exist in constructing the distribution system that will connect the reclaimed water facility with the user or users; these distribution networks include constructing pumping stations, laying out the piping, building any necessary storage areas, and designing and maintaining any monitoring systems. Typically, general local contractors can do this work. The third is in the area of industrial discharges. It is for this market that the push to develop technology is the strongest. Industrial dischargers, forced by regulations and economics, to reduce the quantity and toxicity of its discharges to surface water and POTWs will require high tech solutions to keep in compliance. Some will be able to use constructed wetlands to achieve this same goal. This market has only just begun to develop, and membrane separation technologies will play an active role.

A survey conducted by Florida's five water management districts shows the average and median construction costs incurred by users in order to be able to use reclaimed wastewater. For instance, to use reclaimed water in an orange grove requires an extension of a service main from the actual reclamation center to the grove. Not included in the survey (see Table 2.16) were any costs that would be incurred regardless of the source of water, such as making lake improvements, installing or reconfiguring irrigation distribution systems, or upgrading a pumping system.

**Table 2.16 Construction Costs of Reclaimed Water Improvements in Florida<sup>116</sup>**

Use category	Average cost (\$)	Median Cost (\$)	Average cost (\$)/ac
Golf course	144,533	74,829	1,338
Agriculture/horticulture	249,766	47,965	558
Commercial (office/retail)	271,394	237,290	1,798
Commercial (manufacturing)	41,908	41,231	9,621
Commercial (other)	14,597	11,376	9,465
Residential (multifamily)	92,929	1,560	1,785
Residential (single family)	469,648	329,955	4,487
Recreation (parks and others)	40,960	40,960	8,192
Education	279,961	870	2,145
Other public service	269,644	3,378	26,967
Other	513,242	1,611	311
Average (all categories)	192,763	58,059	2,938

Source: Melvin Paret and Mark Elsner, p. 48.

The overall costs for reclaimed, or Title 22 water, is given in Table 2.17. As can be seen, both capital and operation and maintenance costs vary considerably. While capital costs differ by a factor of two or three, O and M costs vary by almost an order of magnitude. These differences are a function of the unit processes necessary to bring the effluent to the desired quality.

**Table 2.17 Treatment Costs for California Title 22 Water<sup>117,118</sup>**

Agency	Capital Cost (\$/MG)	O and M Cost (\$/AF)
South Coast Water District	650	95
Fallbrook Sanitary District	590	95
L.A. County Sanitation District	300	10
Los Alisos Water District	730	40
Moulton Niguel Water District	600	95

Source: James G. Ashcroft and Michael G. Hoover, p. 345-354.

<sup>116</sup> Melvin Paret and Mark Elsner, "Reclaimed Water Perspectives", *Water Environment & Technology*, February 1993, p. 48.

<sup>117</sup> Title 22 of the California Administrative Code defines levels of treatment for reclaimed water depending on its intended use, probability of human contact, and place of discharge. Water from these districts was disinfected, oxidated, coagulated, clarified, and filtered.

<sup>118</sup> James G. Ashcroft and Michael G. Hoover, "Water Reuse—Implementation and Costs in Southern California", In *Water Supply and Water Reuse, 1991 and Beyond*, American Water Resources Association Conference, June 1991, p. 345-354.

The distribution costs for three water districts in Southern California are shown in Table 2.18. In this case, while the distribution costs vary considerably, the cost to the user remains similar, around \$330 per acre-ft.

**Table 2.18 Distribution/User Costs (Pumps, Piping, Storage, Control and Monitoring, Manuals, and Training)<sup>119</sup>**

Agency	Distribution Cost (\$/MG)	User Cost (\$/AF)
South Coast Water District	800,000	366
Fallbrook Sanitary District	1,400,000	335
Walnut Valley Water District	4,000,000	315

Source: James G. Ashcroft and Michael G. Hoover, p. 345-354.

## 2.6. Investment Requirements

Investment requirements will vary with the type of project. Within this report, costs have been reported for various types of projects. Construction costs for constructed wetlands, ASR facilities, RO and EDR facilities were reported in the various technology reports. Construction costs for different end uses of reclaimed water were noted in the market attractiveness section. Lastly, costs for specific projects are delineated in the case studies.

All membrane separation processes will require either working jointly with a manufacturer or distributor or acquiring the technology itself. Some of the technologies are available from a number of vendors across the United States; others are less available. With the exception of very specialized natural processes, the other segments of the wastewater reclamation market do not involve proprietary technologies. Most of the construction work will require equipment typical of a large contractor.

<sup>119</sup> James G. Ashcroft and Michael G. Hoover, *Ibid.*, p. 345-354.

## 2.7 Case Studies

Three case studies are included to illustrate actual uses of ASR, natural systems, membrane separation processes. A fourth case study was added to illustrate to show some of the issues involved in implementing wastewater recovery into a community.

### 2.7.1. Aquifer Storage Recovery Case Study<sup>120,121</sup>

The City of Kerrville, Texas has been experiencing yearly increases in water usage which is predicted to grow from a current demand of 3.2 MGD to about 5.0 MGD by 2015, more than a 50% increase, and to more than 130% within 40 years. Relying on a combination of surface and ground water, the city receives its water from two main sources: the Guadalupe River that runs through Kerrville and the Hosston-Sligo formation of the Trinity Group Aquifer. This aquifer is located approximately 500 feet below ground and is dolomitic sandstone; the Guadalupe River fluctuates in flow and volume.

The Upper Guadalupe River Authority predicted that peak capacity of its 5 MGD Kerrville surface water drinking water plant would be reached by the end of 1992. While the city operates a wellfield of 11 wells with a capacity of 8MGD for peaking purposes, normal uptake is limited to 0.5 MGD to avoid overdrawing the aquifer. Options for meeting increased demand included expanding the current drinking water plant to 20 MGD or constructing an above-ground reservoir, both expensive propositions. Because of downstream water quality and volume requirements, reclaimed wastewater was not an option. However, because of large seasonal variations in water supply and demand, the possibility of aquifer storage recovery was investigated. These variations ranged from a

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<sup>120</sup> Larry C. Amans and John McLeod, "Kerrville, Texas—A Case Study for Aquifer Storage Recovery", Water Supply and Water Reuse: 1991 and Beyond, American Water Resources Association Conference, June 1991, p. 249–257.

<sup>121</sup> Andrea R. Aiken and R. David G. Pyne, *Ibid.*, p. 6.

yearly low in December of 72% of annual average to a yearly high in August when demand runs 153% of annual average. With ASR, the existing treatment plant would be upgraded and some small storage areas built for some interim storage.

When drinking water is injected into the ground, as is the case with ASR, the possibility for contaminating an aquifer is considered low. For these reasons, the permitting process in Texas for ASR is relatively easy. Furthermore, controversies over water rights could arise. With recharge, more water can be pulled from the aquifer without the danger of drawdown. Because of this combined with low costs, this may be tempting for some residents or companies. However, because all new wells require a city permits, this issue can probably be resolved through the city if it arises.

The feasibility study consisted of the construction of a test ASR well. ASR feasibility studies typically require a few complete cycles consisting of an injection phase, in the water abundant season, followed by a withdrawal phase, during the hot dry summer months. The contract was awarded to the low bidder of \$420,717 for a 16-inch-diameter steel-cased well. The water will be injected and recovered in the Hosston-Sligo formation of the artesian aquifer, which is located at 500-600 feet and has a naturally yields 500-900 gal/min. Recharge for this system is by direct infiltration across rock outcrops located 20 miles away, with yearly recharge of approximately 900 acre-ft. The volume available for storage is between 3,600 acre-ft and 36,000 acre-ft.

Because the test was successful, the city decided to go ahead and build a 1 MGD ASR facility. Total costs were estimated to be \$7.8 million, which can be broken down into two major components. First, the test program and the well construction were \$1.0 million; next, the treatment plant was upgraded and equalization storage added at \$4.8 million. Finally, additional wells were required for carryover storage at a cost of \$2 million. In contrast, a conventional full-scale expansion of the existing facilities, along with the

construction of an above-ground reservoir, would have cost \$31.6 million dollars, \$28.6 million of which would have been for the 15,000 acre-ft reservoir. ASR allowed for a cost savings of \$24 million. The plant went on line in 1991.

### 2.7.2. Natural System Case Study<sup>122,123,124</sup>

The town of Union, Mississippi is a town of 2,000 people, a small, rural community with more land than money. Faced with recent amendments to the Clean Water Act, requiring a minimum of secondary treatment for all wastewater discharges, they considered building a new treatment center. However, the town still had more than \$334,000 to pay off on loans borrowed to construct a conventional wastewater treatment center, now obsolete. Options for traditional systems included a new mechanical system with an initial capital investment of \$1,250,000, annual maintenance fees of \$55,000, and energy costs of \$60,000; or an upgrade on their existing system, for \$660,000 up front and annual energy costs of \$64,000 and similar maintenance requirements.

On the suggestion of Dr. Bill C. Wolverton, an environmental scientist with Wolverton Environmental Services, a less traditional option was proposed: a 14-acre constructed wetland to treat about 500,000 gal/day. Constructed wetlands for treating wastewater are quite popular in Mississippi, being one of two states with 15 or more municipal wetlands in operation, the other being neighboring Louisiana. Furthermore, the Mississippi Department of Environmental Quality (DEQ) is supportive of using wetlands for that purpose due to their low cost and high rate of success, making the permitting process easier despite sometimes stringent NPDES limits. Additionally, the size of the wetland generally fit in with the DEQ quotient of 30 to 40 acres per million gallons of

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<sup>122</sup> Shawna Moos, *Ibid.*, p. 16.

<sup>123</sup> Becky Gillette, *Ibid.*, p. 44–48.

<sup>124</sup> Sherwood C. Reed and Donald S. Brown, *Ibid.*, p. 776–781.

wastewater treated per day. The wetland Bill Wolverton suggested was moderately priced at around \$450,000, with the real savings coming in reduced maintenance and energy costs. All weekly maintenance and monitoring can be accomplished in a couple of hours by the wastewater superintendent and one other worker, for around \$2000 per year. Energy savings are equally impressive, falling to a mere \$300. For a town with only 2000 people, a constructed wetland is well within economic reach.

While most constructed wetlands in Mississippi have been subsurface flow, Bill Wolverton is moving away from these for a number of reasons. First, the rocks necessary for building such a system are scarce in Mississippi, leading to increased prices. Second, the rock/reed filters tend to clog. The system designed for Union, Mississippi is an artificial marsh system. This type, with aerators in its primary lagoons accounting for the three hundred dollar annual energy costs, consists of a lagoons and shallow channels and utilizes aquatic plants to accomplish the treatment.

### 2.7.3. Membrane Separation Process Case Study<sup>125</sup>

Facing the need to expand water supply capabilities, the city of Suffolk, Virginia and surrounding communities evaluated 12 options ranging from extending a pipeline from Lake Gaston to provide an additional 60 MGD to expanding surface water storage to desalination of groundwater. The latter was selected as a near term option because legal and environmental issues promised to tie up the more popular plans for five to ten years.

Once desalination was selected as the short term plan, it was necessary to decide between RO and EDR for the 3 MGD desalination plant for well water with 563 mg/l TDS, 4.77 mg/l fluoride, and 185 mg/l sodium. A feasibility study was conducted in order to

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<sup>125</sup> Mark A. Thompson, and Millard P. Robinson, Jr., "Suffolk Introduces EDR to Virginia", presented at the American Water Works Membrane Conference, Orlando, Florida, March 1992. Reprinted as Bulletin TP 353, Ionics, Inc, 1991, p. 1-5.

verify cost and performance results, extrapolate performance data to full scale, choose between RO and EDR, and to demonstrate the technology.

Results from the feasibility study concluded that both RO and EDR were feasible. However, EDR will operate at a higher recovery rate (95% vs. 85%), producing 2.85 MGD from the 3 MGD pumped out of the ground. RO would only provide 2.63 MGD. In neither case is brine disposal an issue, since an NPDES permit should be easy to acquire because surface water of a compatible quality exists less than half a mile away. Costs estimates, including the city's \$0.86/1000 gallon charge for treatment, were a bit more expensive for EDR: \$1.62 per 1000 gallon versus \$1.53 for RO. However, operating costs proved lower for EDR: \$0.23 versus \$0.30 per thousand gallon. Both were considerably less than the option of expanding the surface water reservoir (\$2.11 per 1000 gallons). Both facilities could be constructed within one year.

Following a pilot scale comparison of RO and EDR units from Ionics, Inc., Fluid Systems and UOP, EDR was selected for the full scale plant. This was primarily due to the lower operational costs, higher recovery rates and lower nutrient loading in the effluent. The design selected called for three Aquamite 120 systems operating in parallel. A total of 72 Mark III spiral wound polypropylene membrane cartridges, each consisting of 500 cell pairs, were installed.

The system went on line in 1992, following a thirteen month construction period. At \$0.20 per 1000 gallons, operating costs were lower than expected. These do not include routine maintenance, including membrane replacement, which will add to the overall cost to the city. Odor and taste improvements in the city drinking water supply were noted by members of the community, due to removal of organics, TDS and other compounds.

#### 2.7.4. Wastewater Recycle Case Study<sup>126,127,128</sup>

El Paso, Texas, a city of 480,000 people, sits in the middle of the desert, where rainfall averages less than eight inches per year. While the city is near the Rio Grande River, the city's water supply comes primarily (>65%) from the deep lying Hueco Bolson aquifer, which is slowly but surely being depleted. Estimates by the El Paso Water Utilities General Manager John Hickerson predicted the aquifer would be 97% depleted by 2040 if current withdrawal rates are not supplemented by additional aquifer recharge. In response to concerns about maintaining an adequate water supply for the city, a committee of 17 people, representing all the various interests in the community, met over the course of a year to determine how to respond to the water supply problem. At the conclusion of the study, the committee voted unanimously to recommend that El Paso begin to reclaim its wastewater in order to begin to recharge the aquifer. At that time the city was also evaluating other proposals to help meet its water needs. These included tapping water resources within a fifty mile radius of the city but in the State of New Mexico, implementing conservation measures, and negotiating for use of Rio Grande water.

The New Mexico aquifer, much of it under federal land, has five times the amount of water as is available anywhere in Texas within a one hundred mile radius. Until recently, the State of New Mexico had a groundwater embargo for out-of-state usage; however, the federal courts recently overturned this law, allowing El Paso to drill on federal land and transport the water to the city. Furthermore, the city led a water conservation program, combined with a five-tiered water rate schedule. The city has been replacing traditional water-intensive green grass in its parks with native vegetation and has encouraged residents to do the same. These types of programs encourage water

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<sup>126</sup> "Recycling Wastewater: El Paso reclaims potable water from municipal sewage", *ENR*, May 9, 1985, p. 11.

<sup>127</sup> Jonathan W. Rogers, "Putting Wastewater to Work", *EPA Journal*, April 1985, p. 5-6.

<sup>128</sup> Carl L. Hamann and Brock McEwen, *Ibid.*, p. 79.

conservation: per capita water consumption dropped from 216 gallons per day in 1977 to 185 gallons per day by 1984. The last measure, negotiations to exchange sewage effluent for water from the Rio Grande, ultimately failed.

The design of the 10 MGD Fred Hervey Water Reclamation Plant combines biological and activated carbon to remove all nitrogen and organic compounds. Wastewater is then treated with lime to remove heavy metals and raise the pH. Wet-air generation with reclaim the powered carbon and oxidize the sludge. An ozone disinfection scheme is used, followed by GAC polishing. The effluent is then injected into the aquifer in ten wells at depths of 350 to 600 feet. It is estimated that it will take the reclaimed effluent two years to reach the water table, where it in effect becomes part of El Paso's potable water supply.

At a total cost of \$32 million dollars, El Paso received a grant from EPA for approximately two thirds of it, or \$20.3 million dollars. Operating costs were estimated at \$0.85 per 1000 gallons, well within El Paso's water pricing scheme, but turned out closer to \$1.90 per 1000 gallons, \$1.30 higher than prior costs. The Fred Hervey Water Reclamation Plant has been helping to provide for El Paso's water needs since it went on-line in 1985.

## **2.8. Conclusions**

Wastewater recycle and reclamation provides a way for communities across the United States to meet their water budgets, leading to many opportunities for the construction industry. Overall, the market includes water treatment facilities, advanced wastewater reclamation facilities, industrial wastewater treatment, and providing the infrastructure necessary to integrate these facilities and systems into the community. Aquifer storage recovery provides a lower cost method for communities to meet their peak demand for water, but their use is restricted to communities with large seasonal demands in water use and the

proper underlying geological formations. Natural systems, including constructed wetlands, have applications in domestic and industrial wastewater, and are especially promising for small-scale systems, such as small communities and companies, which lack the capital necessary to build large high-tech projects. Furthermore, these systems can help a region meet "no net loss" of wetlands requirements. Membrane separation technologies are promising for water treatment in small communities, advanced wastewater treatment and industrial wastewater treatment.

Currently, water pollution control is the largest segment of the pollution control industry, with a total annual market size of over \$40 billion dollar. Coming into compliance with recent amendments of the Clean Water Act and Safe Drinking Water Act is helping to drive all segments of the market, including those aspects involved with municipal and industrial wastewater reuse and recycle and municipal water supply. Opportunities for the construction industry range from the construction of the facilities to integrating them into the community and factory. Such opportunities will last into the next century, giving companies with expertise in this area a sound investment in the future.

Lastly, the noose is tightening around industrial dischargers. Whereas once the United States Environmental Protection Agency was lax in their monitoring and control of industrial dischargers, it is in this area that "zero discharge" is becoming reality. As each factory comes into compliance with such requirements, the market for tertiary and higher treatment will only increase. Because no one company in the United States has a complete monopoly on all the equipment, patents and knowledge, there is currently room to enter this market. The only barriers to entry are in the acquisition or possession of the technologies. Furthermore, because it is for these applications that are pushing the technological innovation, research and development in this area could prove quite profitable.

In summary, the market is characterized in terms of a steady rate of growth. There are many vendors of the technologies, without monopoly players in most areas, allowing for increased competition. The technology for membrane separation technologies tends to be patented and proprietary. Constructed wetlands are not patented, whereas some of the other natural methods are. Aquifer storage recovery is increasing in popularity, although it is not a patented process. Geographically, the market for reclaimed wastewater is generally in arid, populated regions of the country. Industrial recycle of water is not centered in any particular location geographically, but is an issue nationwide.

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## **Chapter 3 Chemical Oxidation**

### **3.1. Introduction**

Chemical oxidation is the process by which organic compounds are oxidized and an oxidant is concomitantly reduced. Thus, organic compounds, undergoing a complete oxidation, are transformed from the organic state to carbon dioxide, water, inorganic salts, and metals. This naturally-occurring process is employed by many industries for a variety of purposes, including the disinfection of wastewater, reduction of toxicity, elimination of carcinogens and other priority pollutants, and treatment of contaminated groundwater and landfill leachate. Industries that utilize chemical oxidation processes range from municipal drinking water and wastewater facilities to the chemical processing and petrochemical business to federal, state, and local governments which oversee the cleanup of contaminated sites. Table 3.1 lists a number of industries which employ chemical oxidation techniques, along with characterization of the wastewater. Not included in this table are municipal wastewater facilities, drinking water facilities, and environmental restoration projects.

**Table 3.1 Wastewater Amenable to Chemical Oxidation, Characteristics by Industry<sup>1</sup>**

INDUSTRY	CHARACTERISTICS
Organic chemicals	Dissolved organics, including acids, aldehydes, phenolics, and free and emulsified oils.
Petroleum refining	Phenolics, free and emulsified oils, and other dissolved organics.
Pulp and paper	Dissolved and suspended organics and inorganics.
Plastics and resins	Dissolved organics, including acids, aldehydes, phenolics, cellulose, alcohols, surfactants and oils.
Rubber Textiles	Dissolved and suspended organics, fats and oils.
Coke and Gas	High in phenolics, ammonia and dissolved organics

Adopted from: *Chemical Engineering*, June 1992, p. 80.

Chemical oxidation processes have advantages over many other physico-chemical processes because the toxicity of the organics is partially or completely eliminated. In this manner, a chlorinated solvent such as tetrachloroethylene which has leaked out of an underground storage tank is completely transformed to carbon dioxide, water, and chloride ion. Other clean-up methods, such as air-stripping, Granulated Activated Carbon (GAC) and Powdered Activated Carbon (PAC) adsorption, and in situ vitrification, merely shift the pollutant from one media to another, rather than actually reducing the overall quantity and toxicity of the pollution itself. Furthermore, chemical oxidation processes also have advantage over thermal oxidation, or incineration, which generally achieves the same end result. First, public opinion is not aligned against chemical oxidation processes as it is

<sup>1</sup> Mervyn C. Goronszy, W. Wesley Eckenfelder, and Emery Froelich, "Wastewater: A Guide to Industrial Pretreatment", *Chemical Engineering*, June 1992, p. 82.

against thermal oxidation. This lends itself to a great reduction in controversy over the siting and operation of facilities, both mobile and permanent. Second, destruction tends to be more complete in chemical oxidation. Therefore, dangerous carcinogenic byproducts such as dioxins are not produced, thereby reducing the overall pollution problem. Third, chemical processes tend to be more economical than thermal processes, although this may change by the time they reach widespread commercial use due to additional monitoring, safety and pollution control requirements of the regulatory agencies.

This report will discuss conventional chemical oxidation processes as well as emerging ones. In particular, it will focus on high temperature and pressure oxidation technologies, wet oxidation (WO) and supercritical water oxidation (SCWO) and advanced oxidation processes (AOPs). Along with technology descriptions, the current market as well as future prospects will be discussed. Furthermore, the current social and regulatory environment and status will be touched upon. Lastly, opportunities for the construction industry, along with any investment requirements and the overall market attractiveness of the industry will be discussed.

### **3.2. Technology Descriptions**

Strong oxidants such as ozone have been used in Europe for almost one hundred years as disinfectants in the drinking water and wastewater industries. However, because ozone does not have any residual effect---that is, it does not continue to disinfect, like chlorine does, past the point of contact---in the water supply system, it never caught on in terms of popularity here in the United States. However, due to much concern over the effects of chlorinated disinfection byproducts (DBP), interest in strong oxidants such as ozone and hydrogen peroxide is increasing.

Conventional chemical oxidants that are used to oxidize organic contaminants found in municipal and industrial wastewater include chlorine, chlorine dioxide, potassium

permanganate, ozone, and hydrogen peroxide. Short living radicals such as the hydroxyl (OH•) ion, easily produced when hydrogen peroxide comes into contact with ultraviolet light, are the strongest oxidants of all. Table 3.2 qualitatively compares the most commonly used oxidizers in terms of their ability to oxidize common wastewater pollutants.

**Table 3.2 Reactivity of Various Oxidants with Common Pollutants<sup>2</sup>**

	Cl <sub>2</sub>	ClO <sub>2</sub>	KMnO <sub>4</sub>	O <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	OH•
Sulfide	C	C	C	C	C	C
Phenol	P	C	C	C	P	C
Ammonia	C	N	P	N	N	N
Bacteria	C	C	C	C	P	C
Amines	C	P	P	P	P	C
Carbohydrates	P	P	P	P	N	C
BTEX	P	P	P	P	N	C
Chlorinated Solvents	P	P	P	P	N	C

C = Contaminant reacts completely with the oxidant

P = partial reaction occurs between the contaminant and the oxidant

N = no reaction

Source: Chemical Engineering, June 1992, p. 82.

As can be seen, the hydroxyl radical is the strongest oxidant and for this reason advanced oxidation processes utilize its ability to completely oxidize toxic organics. Advanced oxidation processes exploit the oxidation strength of the hydroxyl free radical in combination with an energy source: irradiation, ultrasound and electron beam. However, due to limitations in reaction and contact time, not all organics are completely destroyed by these oxidation processes, thus limiting their efficacy for highly toxic, highly concentrated wastes. For cases when destruction is required by the US Environmental Protection Agency (EPA) to be greater than 99.99 or 99.9999%, more complete oxidation is required. The two processes most capable of near-complete destruction are high temperature and pressure oxidation systems, such as supercritical water oxidation, and thermal incineration. The next two sections discuss SCWO and wet oxidation, a process capable of near if not

<sup>2</sup> Meryvn C. Goronszy, et al., Ibid., p. 80.

complete oxidation of organics and suitable for similar types and concentrations of wastes as SCWO. Following those descriptions, advanced oxidation processes will be discussed.

### **3.2.1. Supercritical Water Oxidation (SCWO)**

Supercritical water oxidation is a branch of technologies that harness properties of supercritical fluids in order to completely oxidize hazardous organics in order to detoxify and destroy them. The other branch of this field is supercritical fluid extraction which is employed to remove organics from soil matrices. Supercritical fluid extraction falls beyond the scope of this paper and will not be further discussed

Supercritical fluids are formed under high-temperature, high pressure conditions. In this state, the supercritical fluids exhibit properties of both gases and liquids that are excellent for the oxidation of noxious organics. In particular, supercritical fluids have an extraordinary ability to dissolve organics. Furthermore, with the exception of two acids, hydrochloric acid (HCl) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), inorganics are only sparingly soluble under SCWO conditions and therefore are quite easy to neutralize and precipitate out. Because supercritical fluids mix well with O<sub>2</sub>, CO<sub>2</sub>, as well as CH<sub>4</sub> and other alkanes, they are able to sustain combustion extremely well, allowing for complete oxidation. The combustion itself is self-sustaining in oxygen as long as the solids concentration is approximately five percent or higher. Oxidants can be pure oxygen, hydrogen peroxide, or other compounds containing oxygen.

Figure 3.1 shows the phase drawing for a pure substance, including the supercritical region.

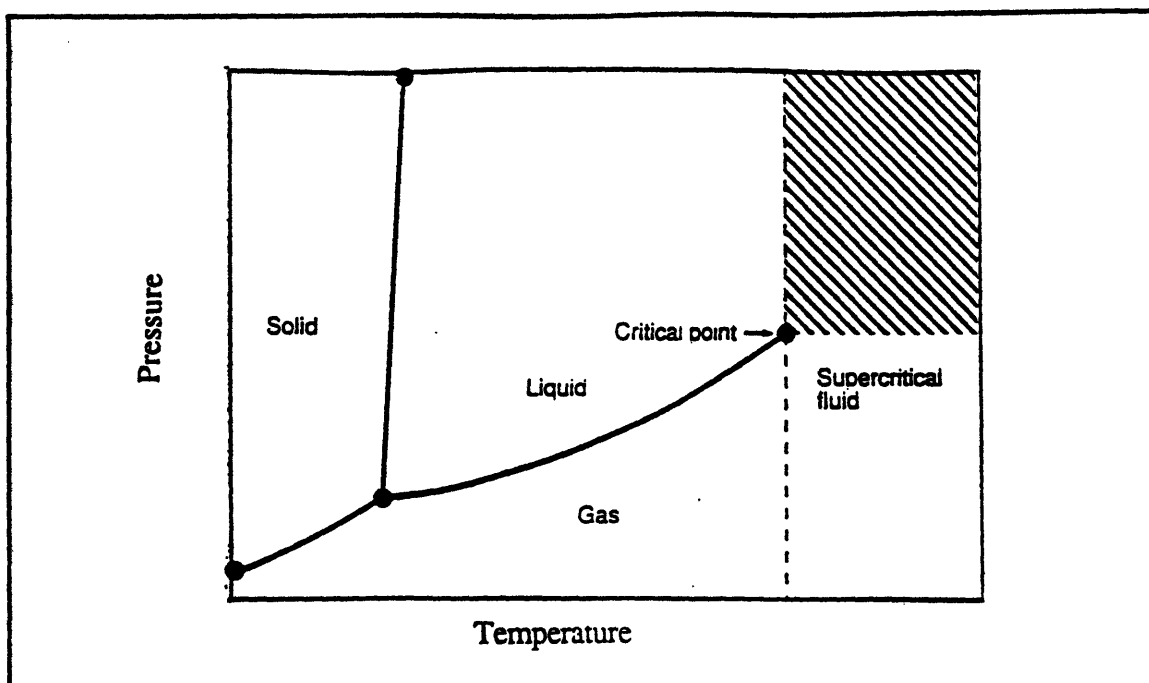


Figure 3.1. Phase Diagram for a Pure Substance<sup>3</sup>

Water becomes supercritical at 374° C and 221 bar (23 MPa). In comparison, carbon dioxide, used in supercritical fluid extraction, has a critical point at 31° C and 74 bar. In the supercritical state, all reactions occur homogeneously with products and reactants in the same phase, thereby negating all phase transfer hindrances. In the supercritical state water is completely miscible with oxygen, benzene and most other organic compounds. Because the surface tension of water in the supercritical phase is approximately zero, the oxidant is able to penetrate all pores, regardless of size, allowing for more complete oxidation and all organic heteroatoms are transformed to inorganics. All carbon becomes CO<sub>2</sub>, hydrogen becomes water, sulfurs are transformed to sulfates, phospho-organics to phosphates, halogens to haloacids, and compounds that contain nitrogen to either nitrogen gas or nitrous oxides. NO<sub>x</sub> is not formed during supercritical oxidation because the temperature is too low.<sup>4</sup> Due to low solubility, inorganics form salts

<sup>3</sup> *Chemical & Engineering News*, Dec. 23, 1991, p. 28 in Vinod K. Jain "Supercritical Fluids Tackle Hazardous Wastes", *Environmental Science and Technology*, Vol 27, No. 5, 1993.

<sup>4</sup> H. E. Barnes et al., *Journal of Hazardous Materials*, Vol. 31, 1992, p. 1-17.

and can easily be precipitated out. Carbon monoxide is very limited, with final reactor concentrations of 0.05 mg/l. SO<sub>2</sub> and NO<sub>x</sub> production is orders of magnitude less, with final concentrations seen at 0.001 mg/l.<sup>5</sup>

The only other treatment technology to realize such complete destruction of organics is incineration. Problems with incineration range from the political to the regulatory to the economic to the environmental, in terms of additional byproducts formed. Table 3.3 provides a simple comparison of the two technologies.

**Table 3.3 Operating Parameters of SCWO and Incineration<sup>6</sup>**

	<b>Supercritical Water</b>	<b>Incineration</b>
<b>Operating Temperature</b>	500-600° C	2000-3000° C
<b>Fuel</b>	Less—can be self-sustaining	More—self-sustaining only when the COD of the waste stream is between 300,000–500,000 mg/l
<b>Byproducts System</b>	CO <sub>2</sub> , H <sub>2</sub> O, inorganic salts Closed	Includes SO <sub>2</sub> , NO <sub>x</sub> , dioxins Open
<b>Public Opinion</b>	Unknown	Extremely negative
<b>Regulatory Climate</b>	Not Established	Moderate

As stated above, the SCWO system, to be described, is completely enclosed. Therefore, it meets the requirements of the United States Environmental Protection Agency's "Totally Enclosed Treatment Facility" (TETF) program, designed to minimize secondary pollution. The ash that is produced passes EPA's Toxicity Characteristics Leaching Program (TCLP) tests. Because of this, ash from an SCWO facility is not regarded as a hazardous waste and can be landfilled in a sanitary landfill.

SCWO has been used on many toxins and carcinogens at the bench scale and pilot scale. Efficiency of destruction is a function of the temperature of reaction (which varies widely depending on the project and design), time of reaction, pressure, oxidant chosen,

<sup>5</sup> H. E. Barnes et al., *Ibid.*, p. 1–17.

<sup>6</sup> Vinod K. Jain, "Supercritical Fluids Tackle Hazardous Wastes", *Environmental Science and Technology*, Vol. 27, No. 5, 1993.

and chemical. It has been proven to successfully degrade a wide number of toxic organics including phenols, PCBs, other chlorinated hydrocarbons, medical and pharmaceutical wastes, munitions, propellants, and ammonia containing wastes. The destruction efficiency is, however, temperature related. Between 374° C and 500° C, destruction is not as complete as it is above 500° C. Above 500° C, the temperature at which most organics are completely insoluble, destruction is nearly complete. Table 3.4 shows various commonly encountered organic toxins and the destruction efficiency of these chemicals by SCWO, and Table 3.5 shows the destruction efficiency by SCWO for various industrial and municipal wastewaters and sludges.

**Table 3.4 SCWO Destruction Efficiency: Organic Compounds<sup>7</sup>**

Compound	Temp(°C)	Time(min.)	Concentration		Destr. Eff. (%)
			in(mg/l)	out(mg/l)	
2-Butanone	400	5	6210	251	95.96
	450	5	5140	136	97.35
	500	5	6210	71	98.86
	400	10	6210	197	96.83
	450	10	6224	2	99.96
p-Chlorophenol	450*	3	1000.0	<0.1	>99.99
o-Cresol	400	3	10043	71.9	99.28
	450	10	10043	20.9	99.79
2,4-Dichlorophenol	400	10	300.0	1.2	99.6
	450	5	300.0	0.9	99.7
	500	5	500.0	1.6	99.7
	450*	4	1000.0	<0.01	>99.999
2,4,6-Trichlorophenol	500*	2	200.0	<0.01	>99.995
Pentachlorophenol	400	2	500.0	<0.04	>99.99
	450	2	500.0	<0.04	>99.99
	500	2	500.0	<0.04	>99.99
Pyridine	400	5	500.0	352.6	29.5
	450	10	500.0	4.1	99.2
	500	5	1000.0	24.3	97.6
	500	20	500.0	1.8	99.6
Trichloroethylene	450	1	1827	32	98.2
	450	5	1827	13	99.3
2,4-Dinitrotoluene	410	3	84.0	14.0	83.0
	528	3	180.0	<1.0	>99.0
	450*	1	200.0	<1.0	>99.5
Ethylene glycol	450*	2	1000.0	<1.0	>99.9
Diethyl ether	450*	2	1000.0	<1.0	>99.9

1. All SCWO data were obtained from batch tests.
2. Pressure for all SCWO tests was about 275 bar (4000 psi).
3. \* Hydrogen peroxide was used; and oxygen was used for all other tests.

Source: Gloyna, Earnest F. and Lixiong Li, "Supercritical Water Oxidation, An Engineering Update", *Proceeding of the Fifth Annual Conference on Emerging Technologies: Metals, Oxidation, and Separation*, Gulf Coast Hazardous Substance Research Center, 1993.

<sup>7</sup> Earnest F. Gloyna and Lixiong Li, "Supercritical Water Oxidation, An Engineering Update", *Proceeding of the Fifth Annual Conference on Emerging Technologies: Metals, Oxidation, and Separation*, Gulf Coast Hazardous Substance Research Center, Beaumont TX, Feb. 1993.

**Table 3.5 SCWO Destruction Efficiency: Wastewaters and Sludges<sup>8</sup>**

Compound	Temp(°C)	Time(min.)	Concentration		Destr. Eff. (%)
			in(mg/l)	out(mg/l)	
Industrial Wastewater <sup>1</sup>	400	1	1840	27	98.5
	450	1	1840	15	99.2
	500	1	1840	4	99.7
Industrial Sludge <sup>2</sup>	400	30	30,300	120	99.6
	450	10	30,300	50	99.8
	450	5	30,300	400	98.7
Mixture of Industrial Wastewater & Sludge	400	4	39,000	4520	88.4
	450	4	39,000	831	97.9
	500	4	39,000	429	98.9
Municipal Sludge	400	8	14,020	687	95.1
	450	4	14,202	84	99.4

1. Total organic carbon.

2. Total chemical oxygen demand.

Source: Gloyna, Earnest F. and Lixiong Li, "Supercritical Water Oxidation, An Engineering Update", *Proceeding of the Fifth Annual Conference on Emerging Technologies: Metals, Oxidation, and Separation*, Gulf Coast Hazardous Substance Research Center, 1993.

Two reasons make the SCWO technology more appropriate for concentrated organics rather than dilute wastes. First, the system is quite severe. Second, the system becomes self-sustaining, thus requiring less input, at approximately five percent solids. For these reasons, SCWO is quite appropriate for the treatment of municipal and industrial sludges, as well as any other organic wastes that have been concentrated to between two percent and five percent. Above five percent, the heat produced by the system may exceed the design characteristics of the system. Below two percent, the temperature cannot be maintained. An SCWO process is essentially a compilation of various unit processes. Figures 3.2 and 3.3 show two flow charts of SCWO systems, one designed by Eco-Waste Technologies, and one by Modar Inc.

<sup>8</sup> Earnest F Gloyna, *Ibid.*, 1993.

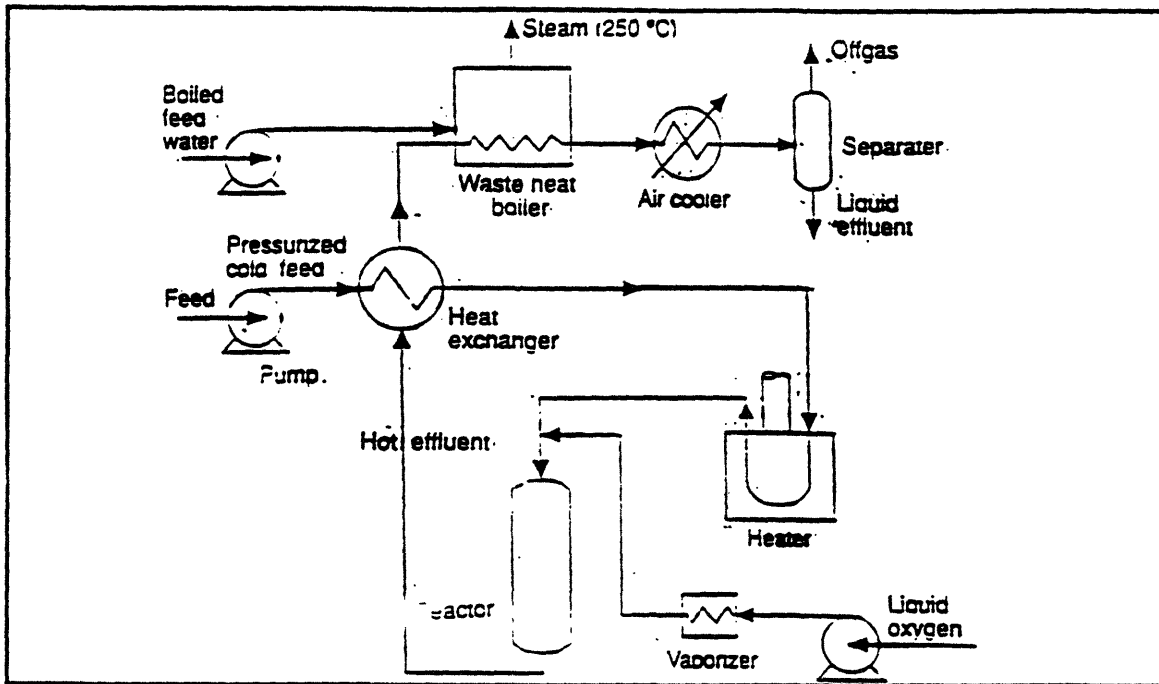


Figure 3.1 Eco-Waste Technologies SCWO System

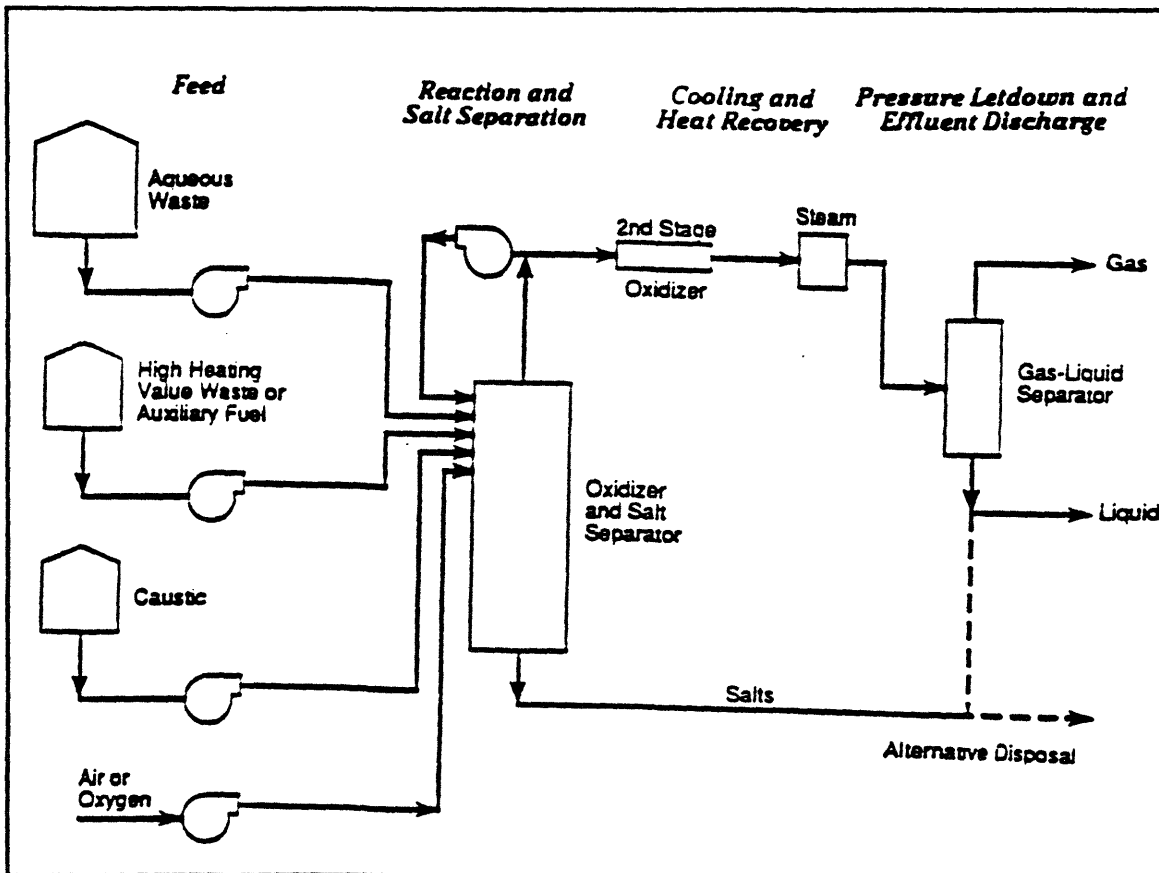


Figure 3.3 Modar, Inc SCWO System

Central to both systems is an SCWO reactor capable of withstanding the effects of extreme pressure and temperature. Also seen are feed systems, heat exchangers and methods for dealing with the solids or brines produced (solid/liquid separators and/or vapor/liquid separators). Key to successful operation is knowledge and consideration of the following<sup>9</sup>:

- Reactor residence times and temperatures,
- Reactor pressures and temperatures,
- Adequate materials for the construction of each part of the system,
- Solids separation/removal and control from the supercritical fluid and/or reactor effluent,
- Careful operations and maintenance of facility,
- Compliance with any regulatory requirements including safety, monitoring, and disposal of the remains.

Preliminary cost estimates for SCWO systems vary depending on the manufacturer of the system, the size of the system and the nature of the waste stream. The MODAR system has an estimated cost of \$500/ton for a 500 gal/day system, treating a waste stream with 1,750 BTU/lb. With a 50 times larger system (25,000 gal/day), the cost is reduced to \$40/day<sup>10</sup>. The Oxydyne deep-well reactor has initial cost estimates of \$100 to \$150 per 1000 gallons of waste<sup>11</sup>.

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<sup>9</sup> Earnest F Gloyna, *Ibid.*, 1993.

<sup>10</sup> "Supercritical Water Oxidation", *The Hazardous Waste Consultant*, May/June 1988, p. 4.37.

<sup>11</sup> "Oxydyne Supercritical Wet Oxidation Process", *The Hazardous Waste Consultant*, May/June 1988, p. 4.42.

### 3.2.2. Wet Oxidation

Operating under condition less severe than supercritical water oxidation, wet oxidation (WO) offers an attractive alternative for high-flow wastes with Chemical Oxygen Demand (COD) on the order of 20,000 mg/l to 200,000 mg/l; wastes with CODs as low as 4000 mg/l can be treated, with some loss of efficiency. In the ten thousand to hundred thousand mg/l range, the wastes are too dilute to be incinerated and too concentrated to be treated via biological treatment methods.<sup>12</sup> For wastes with CODs of 70,000 mg/l or above, enough excess energy is generated to produce steam, which can then be sold. Expected COD reduction is on the order of seventy-five percent to ninety percent.<sup>13</sup>

Oxidation occurs in the liquid phase at subcritical temperatures and pressures, or 150–325° C (302–617°F) and 1-20 MPa, respectively. Either air or pure oxygen can be used as the oxygen source for the oxidation of the wastes. Traditionally, air was used, and as such the entire process was referred to as wet air oxidation. However, both air and oxygen based systems fit under the rubric of wet oxidation and are identical except for the air/oxygen feed system.

In wet oxidation, heated aqueous wastes are pumped into a wet oxidation reactor via a high-pressure pumping system. Additionally, an oxygen source is needed to provide the oxidant within the reactor. This can be accomplished in one of two ways, by pumping it into the pump discharge, or directly, by pumping it into the reactor itself. For wet air oxidation, an air compressor is used to feed the air into the system; while in the oxygen based system, liquid oxygen is converted into a gas by a vaporizer, before it is fed into the system (see Fig. 3.4 and 3.5).

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<sup>12</sup> H.G. Joglehar, S.D. Samant, J.B. Joshi, "Kinetics of Wet Air Oxidation of Phenol and Substituted Phenols", *Water Resources*, Vol. 25, No. 2, p. 135.

<sup>13</sup> H.G. Joglehar, et al., p. 136.

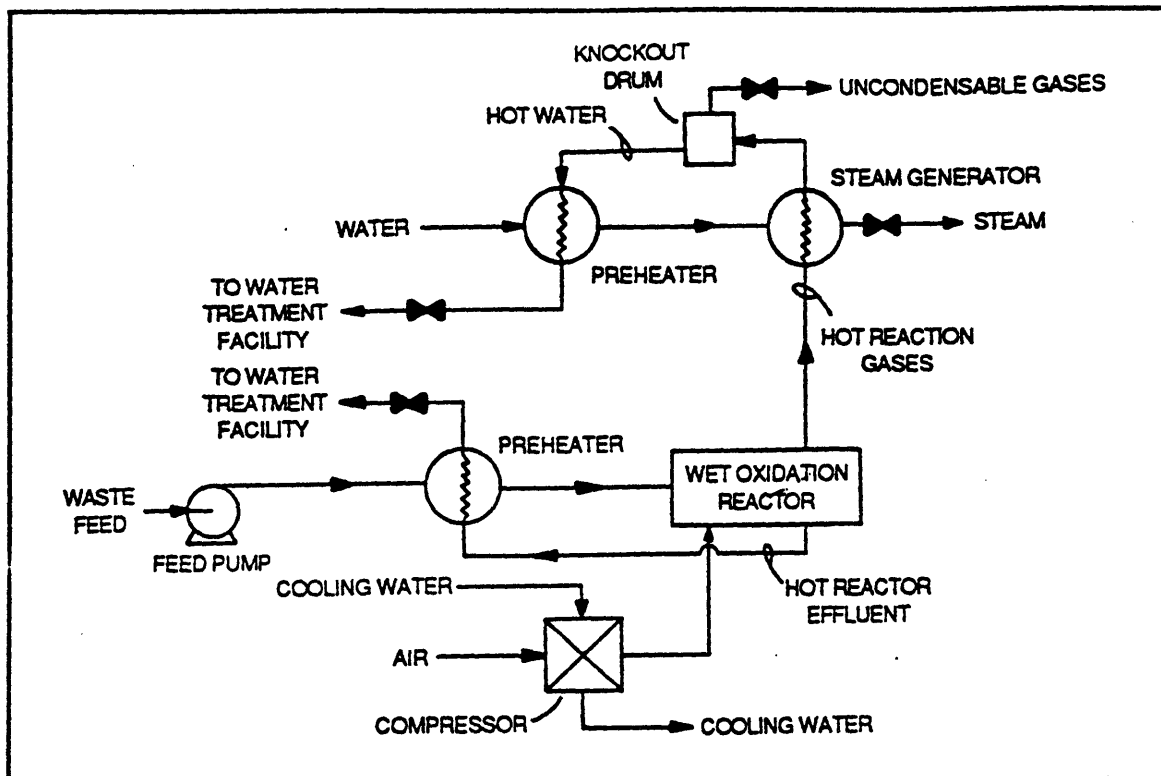


Figure 3.4 Air-Based Wet Oxidation System with Steam Generation

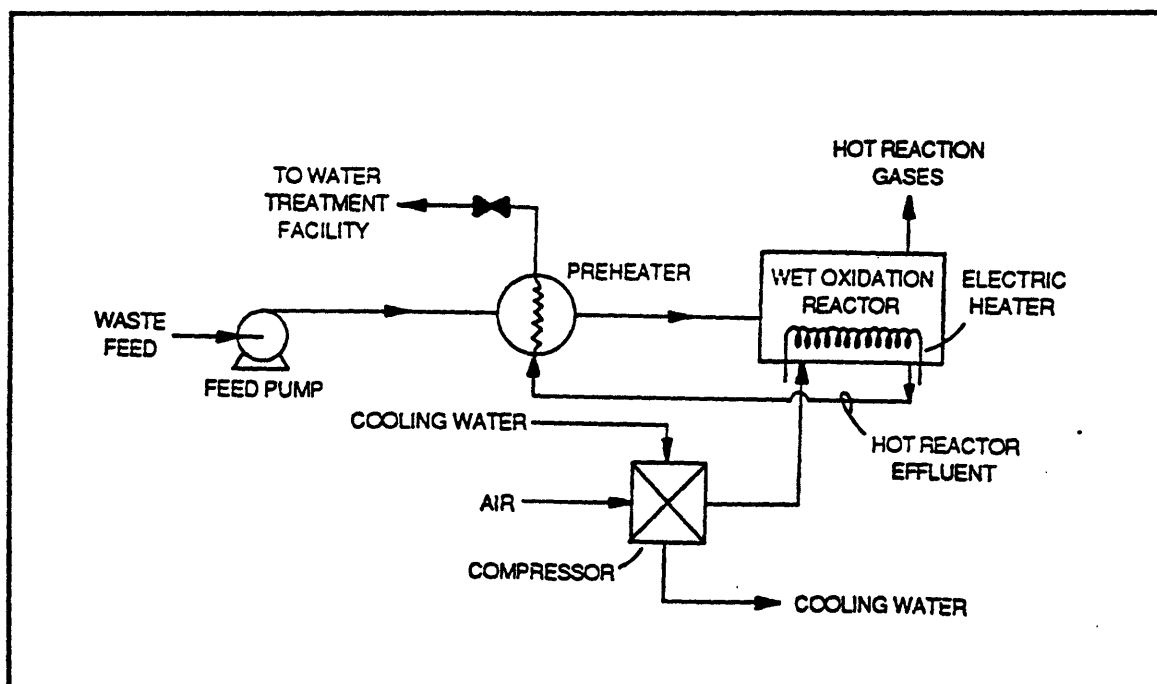


Figure 3.5 Air-Based Wet Oxidation without Steam Generation<sup>14</sup>

<sup>14</sup> Jawaharlal Prasad, "Comparative Study of Air- and Oxygen-Based Wet Oxidation Systems", *Proceedings of the 7th National Conference on Hazardous Wastes and Hazardous Materials in The Hazardous Waste Consultant*, Vol. 8, No. 6, November/December 1990, p. 1.16-1.19.

Once in the reactor, the usual residence time varies between 20 minutes and one hour. With some WO systems, enough heat is produced in the reactor to generate steam, which can then be sold to offset the price of the system. Following oxidation of the waste stream, heat is exchanged with the incoming feed stream and the temperature reduced to below the flash point. At this point, the pressure is reduced to atmospheric pressure via a pressure control valve.

The following tables (Table 3.6 and Table 3.7) outline the economics of wet oxidation for both air and oxygen based systems, with and without steam generation. All systems treat 20,000 gallon per day of wastewater, and operate 24 hours per day, 260 days a year. A COD reduction of 90% and an oxygen transfer efficiency of 90% were assumed. Two types of wastewater were investigated, high-TOC (70,000 mg/l) and low-TOC (4,000 mg/l). The equipment included preheaters for the waste feed and the steam water, the feed pumps, the wet oxidation reactor, the air compressor, steam generator, knockout drum and electric heater; however, not all equipment is used in each system<sup>15</sup>.

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<sup>15</sup> Jawaharlal Prasad, *Ibid.*, p. 1.16–1.19.

**Table 3.6 Capital Costs of Air- and Oxygen- Based Wet Oxidation Systems With and Without Steam Generation<sup>16</sup>**

	Treatment of high-TOC wastewater with steam generation		Treatment of low-TOC wastewater without steam generation	
	Air-based system	Oxygen-based system	Air-based system	Oxygen-based system
	(\$)	(\$)	(\$)	(\$)
<b>Total equipment cost</b>	<b>755,390</b>	<b>413,005</b>	<b>464,866</b>	<b>417,375</b>
Direct cost				
Installation	158,632	86,731	97,622	87,649
Instrumentation	45,323	24,780	27,892	25,042
Piping	226,617	123,901	139,460	125,212
Electricity, services, etc.	75,539	41,300	46,487	41,737
<b>Total direct cost</b>	<b>506,111</b>	<b>276,713</b>	<b>311,460</b>	<b>279,641</b>
Indirect cost				
Engineering and supervision	45,323	24,780	27,892	25,042
Construction	113,308	61,951	69,730	62,606
Contractor	63,453	34,692	39,049	35,059
<b>Total indirect cost</b>	<b>222,085</b>	<b>121,423</b>	<b>136,671</b>	<b>122,708</b>
Contingency	101,222	55,343	62,292	55,928
<b>Total capital investment</b>	<b>1,584,808</b>	<b>866,484</b>	<b>975,289</b>	<b>875,652</b>

The following table shows the operating costs for the same systems, and includes both direct and indirect costs, as well as contingency fees.

<sup>16</sup> Jawaharlal Prasad, *Ibid.*, p. 1.16-1.19.

**Table 3.7 Operating and Total Costs of Air- and Oxygen- Based Wet Oxidation Systems With and Without Steam Generation<sup>17</sup>**

		Treatment of high-TOC wastewater with steam generation		Treatment of low-TOC wastewater without steam generation	
		Air-based system	O <sub>2</sub> -based system	Air-based system	O <sub>2</sub> -based system
Annual operating cost	Basis for cost	(\$)	(\$)	(\$)	(\$)
Process water	\$3.00/1,000 gal	38,306	4,520	1,919	NA
Electricity	\$0.055/kwh	58,556	6,557	14,844	13,959
Labor	\$15/man-hr	124,800	124,800	124,800	124,800
Maintenance	7% total capital investment	110,397	60,654	68,270	61,296
Oxygen	\$0.40/100 scf	NA	146,406	NA	8,366
Oxygen equipment rental	\$310/month	NA	3,720	NA	3,720
<b>Total</b>		<b>332,599</b>	<b>346,657</b>	<b>209,833</b>	<b>212,141</b>
Steam Sales	\$4.50/1000 lb	(59,128)	(56,644)	NA	NA
<b>Net annual operating cost</b>		<b>273,471</b>	<b>290,013</b>	<b>209,833</b>	<b>212,141</b>

With a five-year plant life, the net present cost, in constant dollars with 15% interest, is \$2,501,526 for the high-TOC, air-based system ; \$1,838,649 for the high-TOC, oxygen-based system ; \$1,678,684 for the low-TOC, air-based system; and \$1,586,779 for the low-TOC, oxygen-based system<sup>18</sup>.

Depending on the nature of the influent stream, either partial or complete oxidation will occur, with byproducts of simple organic compounds, carbon dioxide, water, and inorganic salts. Compounds which can be oxidized include aliphatics, including multiply halogenated ones; this may result in the formation of lower molecular weight alcohols, aldehydes, ketones, and carboxylic acids. Complete oxidation occurs for aromatic hydrocarbons, as well as for halogenated aromatics as long as at least one functional group

<sup>17</sup> Jawaharlal Prasad, Ibid., p. 1.16-1.19.

<sup>18</sup> Jawaharlal Prasad, Ibid., p. 1.16-1.19.

such as hydroxyl, amino and methyl groups with the ability to donate electrons exists on the ring. Other halogenated aromatics such as 1,2-dibenzene and PCBs prove quite recalcitrant, except in the presence of certain catalysts.<sup>19</sup> Zimpro/Passavant has found that the use of a proprietary co-catalyst system increases the oxidation of chlorinated hydrocarbons<sup>20</sup>.

### 3.2.3. Advanced Oxidation Processes

An Advanced Oxidation Process (AOP), broadly defined, is an "oxidation process which produces hydroxyl radicals in sufficient quantity to affect water treatment."<sup>21</sup> Excluding elemental fluorine (F<sub>2</sub>), which tends to produce halogenated compounds during oxidation, hydroxyl radical (OH<sup>•</sup>) is the strongest known oxidant, with an oxidation-reduction potential of 2.33 volts at 25° C. Furthermore, it is short-lived and will react with almost all organics as well as some inorganics. Reacting with organics, three mechanisms predominate: hydroxyl addition, hydrogen abstraction, and electron transfer. Hydroxyl radical can be produced in aqueous solutions by a number of different ways including irradiation by either UV or ultrasound, or electron beam transfer. Catalysts such as metal ions or semiconductor or other photocatalysts are often employed to increase the production of hydroxyl radicals. Additional oxidants, usually hydrogen peroxide or ozone are also added to enhance reactivity.

AOPs can be divided into two large categories: homogeneous systems and heterogeneous systems. Within these divisions, they can be further divided into those that employ irradiation and those that do not. Table 3.8 delineates the major AOP systems.

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<sup>19</sup> C.P. Huang, Chang Dong and Zhonghung Tang, "Advanced Chemical Oxidation: Its Present Role and Potential Future in Hazardous Waste Treatment", *Proceedings of the Fifth Annual symposium on Emerging Technologies: Metals, Oxidation, and Separation*, Beaumont TX, Feb. 1993.

<sup>20</sup> "Zimpro<sup>®</sup> Wet Oxidation Process", *The Hazardous Waste Consultant*, May/June 1988, p. 4.38-4.39.

<sup>21</sup> C.P Huang, et al., *Ibid.*, 1993.

**Table 3.8 Typical AOP Systems<sup>22</sup>**

	<b>Homogeneous</b>	<b>Heterogeneous</b>
<b>With Irradiation</b>	O <sub>3</sub> /Ultraviolet H <sub>2</sub> O <sub>2</sub> /Ultraviolet Electron Beam Ultrasound (US) H <sub>2</sub> O <sub>2</sub> /Ultrasound Ultraviolet/Ultrasound	TiO <sub>2</sub> /O <sub>2</sub> /Ultraviolet TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub> /Ultraviolet
<b>Without Irradiation</b>	O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> O <sub>3</sub> /OH• H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> (Fenton's)	electro-Fenton

Adapted from: C.P. Huang (1993).

The following sections further explain these technologies.

### 3.2.3.1. Ozone/Ultraviolet Systems<sup>23,24</sup>

Commercially available since the early 1970s, ozone/UV systems were the first photo-oxidation technologies to hit the market for the treatment of aqueous hazardous waste.<sup>25</sup> In these systems, ozone is bubbled through the system and photolyzed by ultraviolet light, forming H<sub>2</sub>O<sub>2</sub>. Hydrogen peroxide ion (HO<sub>2</sub><sup>-</sup>) reacts further with ozone, producing ozone which is transformed rapidly into hydroxyl radical. The OH• then oxidizes any organics present. Designated the Best Practicable Control Technology by the United States Environmental Protection Agency for treating PCBs, this technology is widely used for groundwater pump-and-treat remediation programs at both the pilot scale and the commercial scale. The original design for the system is from Houston Research, Inc. Solarchem Environmental Systems, located in Richmond Hill, Ontario, has recently developed an UV-oxidation system that operates at 1/5 to 1/3 the cost of a standard UV-oxidation system. It relies on the addition of a special additive to help catalyze the reaction.

<sup>22</sup> C.P Huang, et al., *Ibid.*, 1993.

<sup>23</sup> C.P Huang, et al., *Ibid.*, 1993.

<sup>24</sup> Laurence P. Smith, "Chemical Oxidation for Groundwater Remediation", *Water Env and Technology*.

<sup>25</sup> Shimoda, Steven, William Prengle Jr., and James M. Symons, "Hazardous Waterborne Waste Treatment by Photo-oxidation Using Hydrogen Peroxide and Vis-UV Radiation", *Proceedings of the Fifth Annual symposium on Emerging Technologies: Metals, Oxidation, and Separation*, Beaumont TX, Feb. 1993.

With this proprietary additive, a strong oxidant such as ozone, or hydrogen peroxide is no longer necessary. This system has the ability to oxidize even single carbon bonds and so can be used to oxidize even the most stubborn chloroalkanes such as chloroethane and carbon tetrachloride. Operating efficiency for organic chlorine ran at ninety percent and another test detoxified completely 300 ppm chloroalkane.<sup>26</sup>

### 3.2.3.2. Hydrogen peroxide/Ultraviolet systems

Developed initially as an offshoot of the ozone/UV system, this system has been developed and is currently available at the commercial scale.<sup>27</sup> In this technology, hydrogen peroxide is usually added to the aqueous solution prior to entry into the reactor. Exposed to the UV light, the peroxide dissociates into two hydroxyl radicals which oxidize the aqueous organics. The number and power of the ultraviolet lights will vary with the concentration and the flow of the influent. It can be difficult to correctly match this, if the flow changes. This system has proven successful with various groundwater remediation schemes. However, elevated turbidity or color in the influent can reduce the effectiveness of the system.<sup>28</sup>

Recently the French National Institute of Applied Science in Toulouse, France, and IDE Environment, also located in Toulouse, have developed a wet peroxide process that has a removal rate of ninety-five percent for COD up to 20 mg/l—comparable or even exceeding the performance of wet-air oxidation. This is a particularly good method for chlorinated aromatics, pesticides, and long-chain aromatics. This catalyzed peroxide system operates at considerably lower temperature (60-150° C) and pressure (5 atm), allowing for fuel savings. Additionally, the less severe operating environment allows for

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<sup>26</sup> "UV-oxidation breaks chlorocarbon contaminants", *The Chementator, Chemical Engineering*, May 1993, p. 19.

<sup>27</sup> Steven Shimoda, et al., *Ibid.*, 1993.

<sup>28</sup> C.P. Huang, et al., *Ibid.*, 1993.

lower cost and less specialized materials to be used in construction. Currently, this system is in operation at three different sites in Spain, with 28,300 gal/day being treated at each site in 600 gallon reactors.

Another commercial system, applied at over 60 sites in the US, Canada, and Europe, is the perox-pure™ chemical oxidation system, developed and marketed by Peroxidation Systems, Inc. It can be applied to dilute and partially concentrated waste streams with initial organic concentrations on the order of  $\mu\text{g/L}$  to  $\text{gm/L}$ .<sup>29</sup>

### 3.2.3.3. High-energy Electron Beam Systems

When water, aqueous solution, or sludges are irradiated by an electron beam with electrons accelerated to ninety-five percent the speed of light by the high voltage of 1.5 MeV, the aqueous electron ( $e_{\text{aq}}$ ), the hydrogen radical ( $\text{H}\cdot$ ), and the hydroxyl free radical are formed in copious quantities. These species react quickly (less than 0.1 seconds) with any organics in the solution and degrade them to non-toxic byproducts. These are either  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and salts, or low molecular weight species such as aldehydes and carboxylic acids, water and salts. Mechanisms include electron transfer additions and hydrogen addition reactions, often with an organic free radical produced as an intermediate.

This method is able to treat trihalomethanes, a wide variety of chlorinated solvents; aromatics commonly found in gasoline; chlorobenzenes and dichlorobenzenes; phenol; and dieldrin, a pesticide also known as Octalox. It is appropriate for domestic and certain industrial sludges (up to eight percent solids) and aqueous waste streams. The technology was developed by the Electron Beam Research Facility in Miami, Florida in conjunction with Florida International University and the University of Miami. It is currently operating at a 170,000 gal/day commercial-scale facility in Miami, Florida, and was accepted into the

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<sup>29</sup> Superfund Innovative Technology Evaluation (SITE) program: Technology Profiles, Fifth Edition, EPA/540/R-92/077, November 1992, p. 124.

US EPA Superfund Innovative Technology Evaluation (SITE) Emerging Technology Program for further studies in 1990.<sup>30</sup>

This method has not been used extensively on industrial sites to treat hazardous wastes because of the high cost of capital and specialized equipment needed to accelerate the electrons. This acceleration can be accomplished in two ways, either by using an electron accelerator or by utilizing a gamma ray source such as Co<sup>60</sup> to produce high energy electrons<sup>31</sup>. Despite the fact that it has not been used extensively for hazardous waste, it is not an unproven technology, having been used commercially for sterilization, disinfection, and other industrial applications.

#### 3.2.3.4. Ultrasound Systems

Three ultrasound systems for the treatment of wastewater exist today: ultrasound, ultrasound with hydrogen peroxide, and ultrasound with ultraviolet irradiation. Other ultrasonic systems are available for the treatment of other forms of wastes, including sludges, soils, plastics, papers, and rags. Ultrasonic energy waves allows oxidation to proceed via three mechanisms—cavitation, nucleation, and growth, of which cavitation is the most important. Cavitation occurs when a gas vapor bubble—formed during the rarefaction portion of the adiabatic compression/rarefaction cycle produced by the energy waves—collapses. The instantaneous pressure and temperature inside a gas vapor bubble as it collapses are incredibly high; estimations of between 75,000 psi (5100 atm)<sup>32</sup> and 294,000 psi (20,000 atm)<sup>33</sup> and 7,200°C<sup>34</sup> and 9,800°C<sup>35</sup> have been proffered. During

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<sup>30</sup> EPA/540/R-92/077, Ibid., p. 240.

<sup>31</sup> "Electron Beam Treatment Destroys Toxic Organics", *The Hazardous Waste Consultant*, Vol. 8, No. 5, September/October 1990, p. 1.11–1.13.

<sup>32</sup> C.P. Huang, et al., Ibid., 1993.

<sup>33</sup> Duane P. Koszalka, "Ultrasonic Detoxification of Hazardous Wastes: PCB Solids, Soils and Sludges" presented at the AIChE 1990 National Meeting, *The Hazardous Waste Consultant*, Vol. \*, No. 6, November/December 1990, p. 1.1–1.2.

<sup>34</sup> C.P. Huang, et al., Ibid., 1993.

<sup>35</sup> Duane P. Koszalka, Ibid., p. 1.1–1.2.

cavitation, it has been speculated that the halide atoms are physically wrenched off the halogenated compounds<sup>36</sup>. Reductions of greater than ninety percent have been noted for chlorobenzene and dichlorobenzene<sup>37</sup>.

The major reaction products of water during sonolysis are  $H_2O_2$ ,  $H_2$ ,  $OH^\bullet$ , and  $H^\bullet$ . However, the quantities produced of these reaction products are not high enough to ensure rapid, complete oxidation. Residence times required are on the order of magnitude of an hour or two. Hydrogen peroxide can be added to the system to increase the reaction rate. Limitations do exist in the extreme quantities of hydrogen peroxide required, with a fifty to one molar ratio of hydrogen peroxide to trichloromethane required for a destruction efficiency of ninety-four percent. Ratios of this magnitude are too high for commercial viability. Combining sonolysis with photolysis, as in ultrasound/ultraviolet systems, allows for faster oxidation than either provides alone. (Sonolysis oxidizes miscible samples of trichloroethane faster than photolysis and slower when the sample is immiscible. Combining the two processes provides the fastest degradation in both cases).<sup>38</sup>

Trinity Environmental Technologies, Inc. (Mound Valley, Kansas) has completed bench scale experiments on a sonolytic system to detoxify contaminated sludges.

#### 3.2.3.5. Photocatalytic Oxidation Systems

Water treatment combining ultraviolet light (UV-A) and a semi-conductor catalyst have proven successful in generating hydroxyl radicals which are then able to oxidize hazardous organic compounds. The semi-conductors which have proven well suited for the destruction of organics in aqueous solutions include  $TiO_2$ ,  $WO_2$ ,  $Fe_2O_3$ ,  $MoS_2$ ,  $CdFe$ ,  $CdSe$ ,  $Si$ ,  $CdS$  and  $SrTiO_3$ . Trace amounts of Platinum (Pt) increases the reduction of

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<sup>36</sup> C.P. Huang, et al., Ibid., 1993.

<sup>37</sup> Duane P. Koszalka, Ibid., p. 1.1-1.2.

<sup>38</sup> C.P. Huang, et al., Ibid., 1993.

water for semi-conductors such as  $\text{TiO}_2$ ,  $\text{CdS}$  and  $\text{SiTiO}_3$ . Organics can also increase the rate of reaction.

One example of a  $\text{TiO}_2$  photocatalytic oxidation system is the Nulite™ photocatalytic oxidation system, a product of Nutech Environmental. Accepted into the SITE emerging technology in 1990, the Nulite™ system is effective on PCBs, phenols, benzene, toluene, ethylbenzene, xylenes, oxidizing these compounds to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and halide slats in thirty seconds to two minutes. Other compounds have less complete oxidation, resulting in lower weight organics as well. Examples of end-products are shown in Table 3.9.

**Table 3.9 Photocatalytic Dissociation of Organic Mixture by  $\text{TiO}_2$ -Pt<sup>39</sup>**

Organic Matter	End Product
glucose	$\text{CH}_3\text{CHO}$ ; $\text{C}_2\text{H}_5\text{OH}$ ; $(\text{CH}_3)_2\text{CO}$ ; $\text{H}_2$
ethanol	$\text{C}_2\text{H}_6$ ; $\text{CH}_3\text{CHO}$ ; $\text{CH}_3\text{COOH}$ ; $\text{H}_2$
cellulose	$\text{C}_2\text{H}_6$ ; $\text{C}_2\text{H}_5\text{OH}$ ; $(\text{CH}_3)_2\text{CO}$ ; $\text{H}_2$
pyruvic acid	$2\text{OH}$ ; $\text{H}_2$
glycine	$\text{NH}_3$ ; $\text{H}_2$
polyethylene	$\text{CO}_2$ ; $\text{H}_2$
polyvinyl alcohol	$\text{CO}_2$ ; $\text{H}_2$
polyvinyl chloride (PVC)	$\text{CO}_2$ ; $\text{HCl}$ ; $\text{H}_2$
proline	$\text{CO}_2$ ; $\text{NH}_3$ ; $\text{H}_2$
stearic acid	$\text{CO}_2$ ; $\text{H}_2$
potato	$\text{CH}_3\text{OH}$ ; $(\text{CH}_3)_2\text{CO}$ ; $\text{H}_2$
fatty oil	$\text{C}_2\text{H}_6$ ; $\text{H}_2$
cherry wood	$\text{C}_2\text{H}_6$ ; $\text{CH}_3\text{OH}$ ; $(\text{CH}_3)_2\text{CO}$ ; $\text{H}_2$
white dutch clover	$\text{CH}_4$ ; $\text{CH}_3\text{OH}$ ; $\text{C}_2\text{H}_5\text{OH}$ ; $\text{NH}_3$ ; $\text{H}_2$
goldenrod	$\text{CH}_3\text{OH}$ ; $\text{NH}_3$ ; $\text{H}_2$
water hyacinth	$\text{NH}_3$ ; $\text{H}_2$
dead cockroach	$\text{NH}_3$ ; $\text{H}_2$
human excrement	$\text{NH}_3$ ; $\text{CH}_3\text{OH}$
teflon	$\text{HF}$ ; $\text{CO}_2$ ; $\text{H}_2$
trichlorbenzene	$\text{HCl}$ ; $\text{CO}_2$ ; $\text{H}_2$
trichloroethylene	$\text{HCl}$ ; $\text{CO}_2$ ; $\text{H}_2$

Source: C.P. Huang (1993).

However, reducing total organic carbon can take a bit longer if larger molecular weight molecules are present in significant quantities. When the concentrations become

<sup>39</sup> C.P. Huang, et al., Ibid., 1993.

elevated, certain additives, such as hydrogen peroxide, oxygen, ammonium phosphate, potassium peroxymonosulfate and potassium bromate, can be added at about 0.0003 mole/L to accelerate the degradation by "inhibiting the hole-electron recombination process."<sup>40</sup> Eight mini-projects have been completed for this system. Costs are one to two dollars per thousand gallons, not including the costs of chemical additives.

Potential markets for photocatalytic oxidation systems include large scale projects/systems such as drinking water facilities, the treatment of industrial wastewater and industrial process water.<sup>41</sup>

#### 3.2.3.6. Remaining Systems

The remaining systems operate without irradiation and include ozone/hydrogen peroxide systems, peroxide/Fenton's reagent systems, and the electro-Fenton heterogeneous system. These systems do not seem as promising as those systems that combine chemical oxidants with photolysis or sonolysis and so won't be discussed in detail here.

### 3.3. **Regulatory and Social Acceptability**

This section examines the social, political and legal issues surrounding the development and use of supercritical water oxidation, wet oxidation and advanced oxidation processes. Potential liabilities and related public health and environmental problems are also discussed.

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<sup>40</sup> EPA/540/R-92/077, Ibid., p. 280-281.

<sup>41</sup> EPA/540/R-92/077, Ibid.. 280-281.

### **3.3.1. Legal and Regulatory Acceptability**

These technologies are mostly in the research and development stage. Some of them are in the early commercial stage; none, however, have been designated mandatory control technologies.

Permitting is an issue for the whole range of chemical oxidation technologies. Any discharge to surface or ground water, following oxidation, must be permitted and monitored under the National Pollutant Discharge Elimination System (NPDES). Furthermore, any facility dealing with hazardous wastes must be permitted as per the Resource Conservation and Recovery Act (RCRA). Due to the severe operating environments of both wet air oxidation systems and supercritical water oxidation, worker health and safety must be closely monitored. In all projects, recordkeeping must conform to all local state and federal requirements. A 1991 study showed that in some cases, dioxins and furans are produced by SCWO. If this proves true, then air pollution control devices will be required and SCWO reactors will be subject to regulation under the Clean Air Act. Previous experiments had revealed complete oxidation, thus excluding SCWO reactors from the need for air pollution control devices.

### **3.3.2. Associated Liabilities**

Potential liabilities associated with chemical oxidation devices can be separated into four categories: siting, hazardous waste, sludge and accidental release. Due to the large capital expense of oxidation facilities combined with potential conflicts with the public, problems with siting could lead to facilities that cannot be operated, leading to large loss of profits to all companies involved. Second, as with any technology that treats hazardous waste, there are all the liabilities, present and future, that come from being involved with hazardous waste. These liabilities include potentially being held responsible for any environmental damages at the site or due to the transportation and final disposal of the

waste or sludges following treatment. Liabilities associated with the sludges following treatment are possible if the sludges are still hazardous—for instance, due to elevated concentrations of heavy metals—or radioactive, as in the case of mixed waste. The last class of liabilities is concerned with accidental release of a toxin from the facility. Depending on the nature of the release, this can result in merely poor community relations or can have more severe consequences, such as lawsuits or the court-ordered closure of the facility.

### 3.3.3. Public Opinion

As with most emerging technologies, the public does not have much knowledge about any of these technologies: SCWO, WO, and AOPs. Because of this, no strong opinions have been formed. However, other concerns that the public already has, concerning facilities for the treatment and disposal of hazardous and radioactive waste, may be translated, in certain cases, to problems with similar chemical oxidation treatment processes. In particular, the construction of a high-temperature, high-pressure SCWO or WO facility may set off a string of community relations problems commonly referred to as Not In My Backyard, or the NIMBY Syndrome. In such cases, the norm when siting incineration facilities, no one community wants a facility that will, purportedly, benefit the public at the slight expense of the people in the community in which is it located. Furthermore, if dioxins and furans were being produced as a byproduct of the SCWO process (current research is inconclusive), public opinion would be quick to turn against them, as in the case of both mobile and stationary thermal oxidation devices.

The other chemical oxidation devices—the AOPs—are highly likely to be accepted without comment by the community. This is because they are operated at lower temperature and pressures, and if large-scale, tend to be used as part of the wastewater treatment process, which the public generally accepts as a necessary component of modern sanitation.

### 3.3.4. Political Acceptability

Eleven different federal agencies and national labs are actively involved directly and indirectly in research and development of chemical oxidation technologies, as elaborated upon in Section 4. The US Environmental Protection Agency's "Totally Enclosed Treatment Facility (TETF)" pollution control program stipulates that in the future systems must be completely self-contained as are SCWO and WO. Next, the wastes must be destroyed to levels stipulated by the US EPA, which may be as high as 99.99 to 99.9999 percent. While WO systems typically achieve COD reduction of up to 90%, in most cases this will allow the wastewater to be discharged to a POTW. SCWO, on the other hand, is capable of achieving the destruction efficiencies stated above, and provides a method of both toxicity and volume reduction for sludges, leachates, and wastewaters<sup>42</sup>.

In particular, the development of more benign methods to deal with the 470 million tons of municipal and industrial sludge produced each year in the US is becoming more pressing. This is due to tighter regulatory controls being placed both on POTWS and industrial facilities; the closing and increased tipping fees at many landfills; and the continual difficulties with incineration, in terms of cost, regulatory, and technical requirements, high concentrations of wastes (CODs between 300,000 and 500,000 mg/l) needed for thermal self-sufficiency, and adverse public opinion.

Furthermore, SCWO is one potential solution to the problem that mixed hazardous/radioactive waste generators—as well as commercial, industrial and military facilities currently storing mixed-waste—face in this country. As it now stands, there is no place to commercially dispose of mixed waste and few commercially available technologies to help treat the waste. The disposal conundrum stems from the fact that hazardous waste

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<sup>42</sup> Abdullah Shanableh and Earnest F. Gloyna, "Supercritical Water Oxidation—Wastewaters and Sludges", *Water Science Technology*, Vol. 23, p. 389–390.

facilities won't accept radioactive waste and low-level radioactive waste disposal facilities will not accept hazardous waste. The short-term solution to the problem is to remove the characteristic of the waste that defines it as a hazardous waste under RCRA [40 CFR 261.3(d)(1)] and then to store the waste in a radioactive disposal facility; or to remove the radioactive portion of the waste and store it as a hazardous waste. (Ion exchange provides one example of a method for removing radioactivity from mixed waste and is discussed in Chapter 4. The real solution to the problem is to curtail production of mixed wastes.) One of the proposed ways of removing the hazardous characteristic of mixed waste is SCWO. Research being conducted at the Sandia National Laboratories in Livermore, California in this regard is encouraging; but additional work is needed to mitigate the highly corrosive nature of the reactor and to improve metals separation—in order for the waste not to be classified as hazardous on the basis of elevated metal concentration<sup>43</sup>.

The military is extremely interested in the possibility of chemical oxidation for the destruction of stockpiles of chemical warfare arsenals, remnants of the Cold War Era. Furthermore, the development of more environmentally benign groundwater cleanup technologies is being pursued vigorously by both the public sector (US EPA) and the commercial sector.

### **3.3.5. Related Public Health and Environmental Issues**

Associated public health and environmental issues will be of concern if there is a malfunction of these technologies. Moreover, the byproducts of certain chemical oxidation technologies are still toxic, because the oxidation is often incomplete, such as in the case of WO. Furthermore, if there were any metals within the wastestream, these will only become more concentrated in the sludges, because the overall volume of the wastestream is

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<sup>43</sup> T.T. Bramlette et al., "Destruction of DOE/DP Surrogate Wastes with Supercritical Water Oxidation Technology", Sandia National Laboratories, SAND90-8229, November 1990.

reduced. If SCWO is utilized for dealing with mixed waste, the entire facility will be working with radioactive waste, which is a legitimate public health concern to worker's exposed to the waste and puts them at risk of a variety of leukemias and other cancers.

### **3.4. Market Characteristics**

#### **3.4.1. General Market Characteristics**

The total hazardous waste market, estimated at \$20 billion in 1992, includes a number of smaller segments, one of which is advanced hazardous waste treatment technologies, accounting for \$770 million dollars. Included in this segment are both high temperature/high pressure oxidation systems and Advanced Oxidation Processes, which account for 14% or nearly \$110 million per year<sup>44</sup>. Furthermore, it is predicted that this market segment will grow at a healthy rate of 5 to 6 percent a year<sup>45</sup>, resulting in a market size of \$175 to \$204 million within a decade. Lastly, if SCWO proves feasible for dealing with mixed waste, this opens up another large, virtually untapped market, to deal with the millions of gallons of mixed waste currently in storage at both civilian and military installations around the country.

The market for chemical oxidation systems is in the destruction, elimination, and volume reduction of industrial and municipal sludges and concentrated hazardous organics, including military, pharmaceutical, and petrochemical wastes. In particular, there are currently 470 million tons of municipal and industrial sludges produced annually that must be disposed of. Increasingly stringent environmental regulations promulgated by the EPA require 99.99 to 99.9999 percent destruction of certain toxins, which can be achieved by SCWO and thermal oxidation but no other methods. As these regulations go on-line and

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<sup>44</sup> Business Communications Company, Inc., "Advanced Hazardous Waste Technologies Making Gains", *The Hazardous Waste Consultant*, Vol. 10, No. 6, November/December 1992, p. 1.28-1.29.

<sup>45</sup> Business Communications Company, Inc., *Ibid.*, p. 1.28-1.29.

the technology of SCWO is perfected, this technology will compete with incineration for large and small projects across the country. The market for AOPs is slightly different. Most AOPs treat dilute wastes, making them competitors in the production of drinking water and ultra-pure water, groundwater remediation, and in the treatment of industrial wastewater and process water.

The current market size is small because the technologies, for the most part, are still in the pilot and demonstration phases. As the technologies are perfected and proven, they will fill existing niches within the market. The time to commercialization is two to five years. Most SCWO systems are in the last stages of pilot testing to the early stages of commercial use. Large-scale commercial projects will be feasible if the final design bugs can be worked out. Economic cost comparisons have not yet been completed.<sup>46</sup>

While traditional chemical oxidation systems have been in the market for decades, many of the advanced oxidation processes are still in the early stage of commercialization or the later stages of pilot projects. One wet-air oxidation technology (the Zimpro Process) has been around for 30 years. Certain AOPs are now on the markets and are being used in small scale projects to prove their efficiency. AOPs will be a more competitive market than for the high temperature and pressure oxidation systems, because the technology and engineering are not as complex nor are the research and development costs so high. The SCWO and WO systems are more likely to be not so competitive with each other because there are so few products likely to make it to market. They will compete with the thermal oxidation systems, however, increasing the competitiveness of the business. The next section lists all private, public and non-profit agencies involved in SCWO and WO systems.

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<sup>46</sup> Earnest F Gloyna, *Ibid.*, 1993.

### **3.4.2. Development of SCWO and WO**

In terms of supercritical oxidation processes and subcritical oxidation processes, there are a wide variety of universities, federal and non-profit agencies and private companies all involved in the various stages of research and development, product development, testing, basic research and other necessary projects required to bring these products to a viable commercial level. Eight private companies are involved extensively in product engineering and development of above and below ground super and sub-critical water oxidation. The five SCWO companies are<sup>47</sup>:

1. Eco Waste Technologies Inc. (EWT) (Austin, TX). Funded by the Defense Advanced Research Project Agency (DARPA) and the US Air Force, and a sub-contractor for General Atomics, Ecowaste has plans to build a commercial scale SCWO facility to join its pilot scale facility. It has contracts with the military to destroy existing arsenals of chemical warfare agents and stockpiles of unusual solid-rocket propellant.<sup>48</sup>

2. General Atomics Corporation (GA). GA is the prime contractor for Navy and Air Force SCWO research.

3. GeneSyst International, Inc. GeneSyst international is involved with subsurface SCWO reactor research, but haven't yet developed a commercial scale project.

4. Modar, Inc. (Natick, MA) Modar Inc., along with its research and development partner ABB Lummus Crest (Bloomfield, NJ), has developed the patented MODAR process, a high-temperature, above-ground currently in the pilot-plant stage. Research, in conjunction with MIT, is addressing corrosion and clogage problems. Corrosion occurs on the walls of the reactor due to the extreme conditions necessary. Clogage problems

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<sup>47</sup> Earnest F Gloyna, Ibid., 1993.

<sup>48</sup> Vinod K. Jain, Ibid., 1993.

may occur due to the large volume of salts that are precipitated out. MODAC is also involved in developing a supercritical reactor for NASA to deal with the problem of human wastes in outer space.<sup>49</sup> The MODAR system meets EPA Best Available Control Technique, and Lowest Available Emissions Rate, and doesn't require further air pollution devices.<sup>50</sup>

5. Modell Development Corporation (MODEC) (Framingham MA). A MODEC 5 ton (dry weight) per day pilot plant is currently nearing the construction stage with a commercial scale unit in the planning stages.

6. Oxidyne, Inc. (Dallas, TX). Principally, Oxidyne Inc. is involved with subcritical subsurface wet oxidation. However, this company has developed a supercritical deep-well oxidation process which consists of a 10,000 to 12,000-foot-deep reactor that becomes thermally self-sufficient at very low CODs, due to the large heat-transfer surfaces within the well.

The following private companies are involved in subcritical oxidation:

1. Vertech (Netherlands) This company focuses on subcritical subsurface reactor development. A commercial scale facility for treating municipal sewage has been constructed in the Netherlands. Air Products and Chemicals is the US licensee for Vertech products<sup>51</sup>.

2. Vertox/Oxidyne/CMC (Dallas, Texas). This company, proceeding in the last few years through a series of name changes, focuses on subcritical subsurface deep-well

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<sup>49</sup> Hong, Glenn T., Patrick K. Fowler, William R. Killilea, and Kathleen C. Swallow, "Supercritical Water Oxidation: Treatment of Human Waste and System Configuration Tradeoff Study", SAE Technical paper #87144, 1987.

<sup>50</sup> ABB Lummus Crest Technical Profile, MODAR Tech SCWO Process 1990, p. 1-2.

<sup>51</sup> Ernest F. Gloyna and Lixiong Li, Ibid..

systems. Funding constraints halted a deep-well (5000 feet) project already under construction in the city of Houston for the treatment of domestic sludge<sup>52</sup>.

3. Zimpro Passavant Environmental Systems, Inc. (Rothschild, WI). This company developed the Zimpro Process for subcritical oxidation over three decades ago--the process has been utilized ever since<sup>53</sup>. It is currently being used at over 186 facilities worldwide.

4. Kenox Corporation (North York, Ontario, Canada). A commercial Kenox wet oxidation system is currently being demonstrated at a drum washing plant in Mississauga, Ontario. With an initial COD of 250,000 mg/l, approximately 8,000–10,000 gal/day of highly alkaline wastewater are reduced 80 to 90% in terms of COD<sup>54</sup>.

The following federal and non-profit agencies are involved in sponsoring supercritical water oxidation research and development projects, both directly and indirectly:

1. Battelle Pacific Northwest Research Labs (Richland WA)
2. Defense Advanced Research Projects Agency (DARPA)
3. Los Alamos National Laboratories (Los Alamos, NM)
4. National Aeronautics and Space Administration
5. Sandia Livermore National Laboratories
6. US Army
7. US Department of Commerce
8. US Air Force
9. US Department of Energy
10. US Environmental Protection Agency

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<sup>52</sup> Earnest F. Gloyna and Lixiong Li, *Ibid.*

<sup>53</sup> Earnest F. Gloyna and Lixiong Li, *Ibid.*

<sup>54</sup> "Kenox Wet Oxidation Process", *The Hazardous Waste Consultant*, May/June 1988, p. 4.40–4.41.

## 11. US Navy

### 3.4.3. Development of Other AOPs

The development of other AOPs is being conducted by a wide variety of private companies, both in the US and abroad. Within the individual technology sections, various companies are discussed. The following companies—five located within the United States and seven abroad—are involved in either the manufacturing of ultrasonic equipment or are pursuing research in this area<sup>55</sup>:

1. Advanced Sonics Processing Systems (Woodbury, Conn.);
2. Arc Sonics Inc. (Burnaby, British Columbia, Canada);
3. Branson Ultrasonics Corp. (Danbury, Conn.);
4. Dawe Ultrasonics Ltd. (Hayes, England);
5. Heat Systems, Inc. (Farmingdale, New York);
6. Kerry Ultrasonics Ltd. (Hitchin, England);
7. Lewis Corp. (Oxford, Conn.);
8. Martin Walter Ultraschalltechnik GmbH (Straubenhardt, Germany);
9. Sodeva (Bonne-sur-Menoge, France);
10. Sonics and Materials (Danbury, Conn.);
11. Telsonic (Bronshofen, Switzerland);
12. Undatim Ultrasonics S.A. (Louvain la Neuve, Belgium).

### 3.5. Market Attractiveness to the Construction Industry

This section will look at the market attractiveness to the construction industry of chemical oxidation technologies. This will be accomplished by examining three aspects of

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<sup>55</sup> Wayne Grinthal with Gerald Ondrey, "Ultrasound: Seen But Not Heard", *Chemical Engineering*, October 1992, p. 37-41.

the industry: the strategic attractiveness of the industry, the cost effectiveness for the customer and the suitability to the construction industry.

### **3.5.1. Strategic Attractiveness**

The strategic attractiveness of chemical oxidation technologies will be a function of the technology and its purpose. Due to fragmentation of the AOPs, this section will focus on the strategic attractiveness of SCWO and WO. The market is defined as the construction of large (non-mobile) SCWO and WO waste-treatment facilities. The market is still emerging, but any medium to large construction company will have the capability to enter the market. However, because the risks involved are relatively high and to enter the market requires working in conjunction with the holders of the patents, there are some, although not extensive barriers to entry. The threat of alternatives depends on the nature of the waste stream and the regulatory environment. If TETF are required, the only alternatives to SCWO are thermal oxidation devices, which, due to widespread opposition to their use, is a limited threat. Similarly, if the waste stream is a mixed waste, the options are limited. For low-COD wastes, for which WO is possible but not thermally self-sustaining, there are other options, and so the threat of alternatives is higher. The supplier's threat—or the holder of the patent—is the most serious, and potentially could be quite large. The buyer's threat, on the other hand, is again a function of the nature of the waste stream. For certain types of waste, there is the option of transporting the waste to other treatment facilities, and will be a function of the overall price. For other types of waste, there is little such option. Overall, the strategic attractiveness of this market is medium.

### **3.5.2. Cost Effectiveness for the Customer**

AOPs offer low-cost alternatives for traditional disposal methods. In particular, SCWO and WO offer two comparatively low-cost methods with which to deal with extremely hazardous sludges, wastewaters and groundwater leachates. Both are totally

enclosed, and as such can be classified as totally enclosed treatment facilities, under the EPA TETF program. As concerns about further pollution from environmental restoration programs grow, this will be increasingly advantageous. The competitiveness of other AOPs will be a function of the nature of the waste, the size of the facility, the site location and other site- and waste-specific characteristics.

### **3.5.3. Suitability for the Construction Industry**

The suitability for the construction industry for chemical oxidation facilities will largely a function of size. Any small, mobile treatment unit—designed, for instance, to decontaminate groundwater contaminated with solvents at a shutdown factory—will be less in the ken of a construction company than large, permanent facilities, such as the one described in the case study. Most of the technologies described above are amenable to larger facilities. This is certainly the case with both SCWO and WO, and with most of the AOPs. Such facilities can be designed in conjunction with established treatment areas or be all inclusive centers for the treatment of specific types of waste streams. Most of such facilities would have to be operated in conjunction with the patent holder or as licensed facilities, and the design and construction well within the expertise of medium to large construction companies. However, the construction company must be willing and able to deal with the large amounts of risk and potential liability that comes from dealing with hazardous waste.

### **3.6. Investment Requirements**

Research and development for all these systems is being conducted by a combination of public and private sources. Government aid continues to be forthcoming; see the Market Characteristics section for a summary of public and non-profits involved in SCWO and WO research. Most of the research costs on AOP research and development are being borne by private companies. There aren't any large capital costs for a full-service

construction company to enter this market; however, the technologies themselves, will, for the most part, have to be licensed from the holder of the patent or work in conjunction with the vendor. All the new and emerging technologies are patented.

This market is extremely appropriate for a full-service construction company with environmental remediation capabilities. AOPs can usually be designed and constructed as unit processes at one stage of an industrial or municipal facility or as a comprehensive treatment unit as is the case for groundwater remediation projects. SWCOs and WOs are comprehensive treatment methods. However, for some waste streams, further treatment (usually municipal wastewater treatment) is possible, following WO.

### **3.7. Case Study**

The following case study illustrates the use, costs and effectiveness of an advanced oxidation process at a municipal wastewater treatment center.

#### **3.7.1. Electron Beam Treatment System: Miami, Florida<sup>56,57</sup>**

The Electron Beam Research Facility was constructed in 1984 as a part of the Virginia Key Wastewater Treatment Plant in Miami, Florida, and was accepted into the US Environmental Protection Agency's Superfund Innovative Technology Evaluation (SITE) Emerging Technology Program in June, 1990. This facility can treat on the order of 170,000 gallons per day, and can be used to decontaminate a wide variety of aqueous solutions and waste streams, including sludges of up to 8% solids, groundwater, leachates, secondary wastewater, and drinking water. Although this system was designed to treat drinking water and secondary effluent, it can accept truckloads of aqueous waste (in 6000 gallon aliquots), allowing for the broader spectrum of wastes. This system is effective in

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<sup>56</sup> EPA/540/R-92/077, Ibid., p. 240.

<sup>57</sup> "Electron Beam Treatment Destroys Toxic Organics", Ibid., p. 1.11-1.13.

the treatment of many different organic contaminants including trihalomethanes, chlorinated solvents, aromatics found in gasoline, chlorobenzene and dichlorobenzenes, phenol, and dieldrin.

The facility centers around a 1.5 megavolt (1.5 MeV), 50 mA ICT electron accelerator. Other important features of the treatment facility are a five-ton crane, voltage regulator, capacitor bank, and step-up transformer, to provide electricity for the accelerator; an influent spreader, to regulate the width and thickness of the influent stream; a sampling area for the effluent; control centers for the ICT and the influent; and an exhaust system.

The capital costs for the entire system were \$2,300,000, which, when annualized over a ten-year period with a 10% capital recovery factor (see Table 3.10), translates to \$382,500 per year. Although operating costs will vary somewhat of the waste stream, for irradiation of trichloroethylene-contaminated water, the capital costs consume just over fifty percent of the total costs of the system. The major operating expense was the price of labor, with electricity and maintenance fees being the other two significant costs. The overall treatment costs is \$9.33 per thousand gallons.

**Table 3.10 Capital and Operating Costs for E-Beam Irradiation of TCE-Contaminated Water<sup>58</sup>**

	Unit Costs	Costs	Percent of Total Costs, Annualized (%/yr.)
<b>Capital costs</b>			
Electron accelerator		\$1,850,000	42.7
Support facility		\$500,000	11.5
<b>Total Capital Costs</b>		<b>\$2,350,000</b>	
<b>Annualized Capital Costs</b>	<b>10%, 10-yr. capital recovery factor</b>	<b>\$382,500/yr.</b>	<b>54.2</b>
<b>Annual Operating Costs</b>			
Operating labor	\$20.00/hour	\$157,700/year	22.3
Electrical power (150 kw)	\$0.07/kwh	\$82,800/year	11.7
Water (2000 gph)	\$1.25/1000 gal	\$19,700/year	2.8
Maintenance	\$8.00/hour	\$63,100/year	8.9
<b>Total Annual Operating Costs</b>		<b>\$323,300/yr.</b>	<b>45.8</b>
<b>Total Annual Costs</b>		<b>\$705,800/yr.</b>	<b>100</b>

In the irradiation of aqueous streams, the accelerator produces a beam of high-energy electrons directed at an aqueous waste stream. As the voltage is produced, electrons are generated, accelerated to 95% the speed of light, and focused into a 48-inch (122 cm) wide horizontal beam. At this facility, the beam is characterized as having 75 kW of power with a theoretical irradiating dose of 987 krads and an actual irradiating dose of around 650 krads, due to system losses and inefficiencies of the system. While the beam itself is a form of ionizing radiation, no residual radioactivity can be detected.

Directed at a 48-inch wide, 0.3 inch (0.8 cm) thick, falling stream of wastewater, the energy from the electrons is absorbed by the wastewater, forming a slew of slower, lower-energy (less than 50 electron volts) electrons. These electrons in turn react with certain compounds, both inorganic and organic, in the waste stream, forming principally four highly reactive species: aqueous electrons ( $e^-_{aq}$ ), hydrogen radicals, ( $H\cdot$ ), hydroxyl radicals ( $OH\cdot$ ), and hydrogen peroxide ( $H_2O_2$ ). These four species, in turn, react rapidly

<sup>58</sup> "Electron Beam Treatment Destroys Toxic Organics", Ibid., p. 1.12.

with organics in the waste stream, producing CO<sub>2</sub>, H<sub>2</sub>O, salts, and very low concentrations of certain organic acids and formaldehydes. The removal efficiency of the contaminant will be a function of the nature of the contaminant, the initial concentration of the contaminant, and the dose of ionizing radiation received, with higher efficiencies associated with lower initial concentrations of the contaminant, lower overall concentrations and higher doses of radiation. Removal efficiencies at various doses of ionization are shown in Table 3.11.

**Table 3.11 Removal Efficiencies for Electron Beam Irradiation of Various Water Contaminants<sup>59</sup>**

Contaminant	Removal Efficiency (%)	Required Dose (krads)
<b>Drinking Water</b>		
Chloroform	83	650
Bromodichloromethane	>99	80
Dibromochloromethane	>99	80
Bromoform	>99	80
<b>Wastewater</b>		
Carbon tetrachloride	>99	50
Trichloroethylene (TCE)	>99	500
Tetrachloroethylene (PCE)	>99	500
trans-1,2-Dichloroethene	93	800
cis-1,2-Dichloroethene	98	800
1,1-Dichloroethene	>99	800
1,2-Dichloroethene	60	800
Hexachloroethene	99	800
1,1,1-Trichloroethane	89	650
1,1,2,2-Tetrachloroethane	88	650
Hexachloro-1,3-butadiene	98	800
Methylene chloride	77	800
<b>Groundwater treatment</b>		
Benzene	>99	650
Toluene	97	650
Chlorobenzene	97	650
Ethylbenzene	92	650
1,2-Dichlorobenzene	88	650
1,3-Dichlorobenzene	86	650
1,4-Dichlorobenzene	84	650
m-Xylene	91	650
o-Xylene	92	650
Dieldrin	>99	800
Total phenol	88	800

In conclusion, electron beam irradiation provides a relatively efficient method to eliminate organic contaminants from aqueous solutions.

<sup>59</sup> "Electron Beam Treatment Destroys Toxic Organics", Ibid., p. 1.13.

### **3.8. Conclusions**

This report has examined the field of chemical oxidation technology from the point of view of the construction industry. In particular, the focus was on two smaller areas: high temperature and pressure oxidation systems (SCWO and WO) and advanced oxidation processes. Because these technologies reduce the toxicity of hazardous organics, without producing secondary pollution or transferring the pollution to another media, their use is promising. Within these areas, the individual technologies were discussed at length. Potential markets and market size; stage of development; and social, legal and regulatory concerns were also addressed. Investment requirements were indicated, and the market attractiveness for the construction industry was analyzed. A case study looked at an actual application of a large-scale advanced oxidation treatment facility, the electron beam treatment center in Miami, Florida. In conclusion, both high temperature and high pressure oxidation systems and advanced oxidation processes show extreme promise to fulfill niches in the environmental remediation market.

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## **Chapter 4 Ion exchange**

### **4.1. Introduction**

**Ion exchange is the chemical process of exchanging ions in solution for those sorbed on certain types of solid matrices. The first observation of the ion exchange properties of certain soils was noted in a report to the Royal Agriculture Society in Great Britain in 1850. Two scientists noted that when a solution of ammonium sulfate was filtered through such soils the effluent contained calcium sulfate. Commercially, ion exchange has been in use since 1905, when a German scientist removed hardness from water with a zeolite soil filter. In the United States, commercial use of ion exchange has its root in a synthetic zeolite manufactured by the Permutit Company in New York State in 1913<sup>1</sup>. Since then, ion exchange has progressed far beyond simple zeolite filters. A plethora of ion exchange resins have been developed, and a wide variety of complete systems have been designed to remove any and all ions that might exist in a given solution.**

**Ion exchange is currently utilized for a wide range of industrial, commercial, and municipal purposes. Among these many uses are the supply of fresh drinking water, the production of ultra-pure water needed for the manufacture of pharmaceuticals and high-tech electronic devices and for circulation in industrial boilers and cooling systems, and the recovery of heavy metals from industrial processing. General categories of use include water softening, reduction of alkalinity, deionization of the water, condensate polishing, desalination, reduction of organic matter, recovery of mineral acids and bases, recovery of heavy metals, and removal of radioactive material and radionucleotides from solution and raw drinking water sources. Furthermore, within each of these categories the range of uses varies tremendously. For example, heavy metal recovery spans from**

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<sup>1</sup> "Ion Exchange Primer", Sybron Chemicals Bulletin, Sybron Chemicals Inc., undated, p. 2.

measures taken to achieve minimal compliance with discharge permits, to the production of water used to manufacture delicate devices, to the capture of these metals in order to reuse or resell them. Deionized water, on the other hand, is used for a broad variety of purposes including academic research, beverage preparation, cosmetics manufacture, electrochemical processes, irrigation, nuclear reactors, photography, batteries and textile processing<sup>2</sup>. Use of ion exchange in water and wastewater treatment include water softening and nitrate removal in drinking water systems; currently, ion exchange is the most common method for removing nitrate from drinking water in the United States, in use at approximately fifteen water treatment plants nationwide<sup>3</sup>. Heavy metal removal and other advanced, or tertiary, treatment processes in municipal wastewater treatment and ion removal in industrial wastewater treatment, the treatment of hazardous wastes and internal plant water recycle systems can be accomplished by ion exchange.

## **4.2. Technology description**

### **4.2.1. General Descriptions**

Ion exchange is the removal of an ion, either positively or negatively charged, from an aqueous solution by a physical exchange with an ion trapped in a matrix. Exchanges, also known as resins, can be natural or synthetic, and either organic or inorganic. Furthermore, resins can exchange either anions, cations, or both. There are four main types of ion-exchangers: cation exchangers, anion exchangers, mixed ion exchangers, and specific ion exchangers.

Naturally occurring ion exchangers are mostly zeolites, a type of soil. Zeolites are naturally occurring crystalline aluminosilicates with cation exchange properties. Formed from volcanic ash which has reacted within an aqueous environment, zeolites, as well as

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<sup>2</sup> "If you use water", Rohm and Hoss Bulletin IE-1-54C, April 1974, p. 26.

<sup>3</sup> Dennis Clifford and Xiaosha Liu, "Ion Exchange for Nitrate Removal", *Journal AWWA*, April 1993, p. 135.

clays, can be mined with a simple bulldozer or front end loader. On a microscopic level, zeolites, also known as molecular sieves, are a series of very complicated geometrically precise interconnected channels and cavities of three to ten Angstroms in size. Within the three-dimensional tetrahedral  $\text{SiO}_4$  and  $\text{AlO}_4$  is a fixed negative charge and cations with dispersed charge. These natural zeolites are still used for a wide variety of purposes.

Table 4.1 gives a few example of zeolites.

**Table 4.1 Selected Naturally Occurring Zeolites<sup>4</sup>**

Zeolite	Chemical Composition
Analcite	$\text{Na}(\text{SiAlO}_6)_2 \cdot \text{H}_2\text{O}$
Chabazite	$\text{CaNa}(\text{SiAlO}_6)_2 \cdot 6\text{H}_2\text{O}$
Clinophlolite	$[(\text{Na}_2\text{O})_7\text{CaO}(\text{H}_2\text{O})_{1.5}(\text{MgO})_{0.5} \cdot \text{Al}_2\text{O}_3 \cdot (85-105)\text{SiO}_2 \cdot (60-70)\text{H}_2\text{O}]$
Harmatone	$\text{KBa}(\text{Si}_5\text{Al}_2\text{O}_{14}) \cdot 5\text{H}_2\text{O}$
Heulandite	$\text{Ca}(\text{Si}_3\text{AlO}_8) \cdot 5\text{H}_2\text{O}$
Natrolite	$\text{Na}_2(\text{Si}_3\text{AlO}_{10}) \cdot 2\text{H}_2\text{O}$
Montmorillonite	$\text{Al}_2(\text{Si}_4\text{O}_{10}(\text{OH})_2) \cdot n\text{H}_2\text{O}$

Source: B.A. Bolto and L. Pawlowski, p. 6.

These are used for a wide variety of purposes in water and wastewater treatment and other industrial applications. Clinophlolite, for example, is used for the recovery of ammonia from sewage effluent as well as the recovery of radioactive waste from aqueous solutions. Chabazite, on the other hand, is used in the purification of natural gas<sup>5</sup>.

Synthetic zeolites—synthetically manufactured aluminosilicates with ion exchange capacities—have been designed to improve or modify naturally occurring zeolites and include Linde molecular sieves-Type 3A, 4A, and 5A--, Type Y, Type X, and ZSM (pentasils) series<sup>6</sup>.

Using zeolites as a general model, other synthetic resins—not necessarily based on aluminosilicates as zeolites are—have been developed and synthesized to improve and

<sup>4</sup> B.A. Bolto and L. Pawlowski, *Ibid.*, p. 6.

<sup>5</sup> D.E. Vaughan, "The Synthesis and Manufacture of Zeolites", *Chemical Engineering Progress*, Vol. 84, No. 2, February 1988, p. 25 - 31.

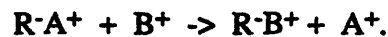
<sup>6</sup> R.G. Anthony, C.P. Philip, and R.G. Dosch, "Selective Adsorption and Ion Exchange of Metal Cations and Anions with Silico-Titanates and Layered Titanates", *Proceeding of the Fifth Annual Conference on Emerging Technologies: Metals, Oxidation, and Separation*, Gulf Coast Hazardous Substance Research Center, 1993.

expand exchange capacity and other properties of ion exchangers. Currently, while zeolites are used to some extent, these synthetic resins have become the norm in the wastewater and water treatment areas.

This section will explain ion exchange chemistry, and describe the general characteristics of ion exchangers and ion exchange systems.

#### 4.2.2. General Ion Exchange Chemistry

Ion exchange is a stoichiometric chemical exchange between ions in solution and those on the resin. Like other similar reactions, the law of mass action can be used to approximate chemical behavior. For a negatively charged cation exchange resin ( $R^-$ ),  $B^+$ , a cation in solution, is exchanged, in a reversible reaction, for  $A^+$  on the resin:



During regeneration, the reaction is reversed:



Furthermore, the law of mass action can be applied as an equilibrium reaction:

$$K_s = (R^-B^+)(A^+) / (R^-A^+)(B^+).$$

$K_s$ , the selectivity coefficient, will be a function of the ions in solution, the resin, and the ions being exchanged. In non-selective ion exchangers, this reaction will proceed forward as long as equilibrium conditions favor the reaction and there are ions ( $R^-A^+$ ) left on the resin. When all available exchange sites on the resin have been filled, contaminant ions will be seen in the effluent of the ion exchanger, a situation known as breakthrough. With selective ion exchangers, the situation is somewhat different in that the law of mass action does not necessarily hold. In such cases, lattice forces and steric

effects play a very important role in determining which ion will be able to exchange; selectivity can be caused by excluding the entry of a given cation into the pore structure of the resin<sup>7</sup>. When all sites are filled, breakthrough will occur. With both selective and non-selective exchangers, it becomes necessary to regenerate the resin when breakthrough occurs, or optimally, slightly before it occurs.

Because less energy is required to exchange the ion originally on the resin for one in solution, regeneration is not as simple as the ion exchange process and requires concentrations of the regenerant to be orders of magnitude higher than those seen in the ion exchange process. Typically, it consists of three steps: loosening, or preparing, the exchanger for regeneration; flushing the system with regenerant, or regeneration proper; and finally washing away the excess solution of regenerant.

The preparation step consists of backwashing the resin bed. This causes the bed to expand and also washes away any particulate matter that might have been trapped among or within the beads. Following this, regenerant is washed over the bed for a period of thirty to ninety minutes. The regenerant used, concentration and contact time will be a function of the type of resin (see Table 4.2).

**Table 4.2 Properties of Regenerants<sup>8</sup>**

Resin Type	Exchange Site	Regenerant	Conc. (%)	Contact Time (min.)
Cation	H <sup>+</sup>	H <sub>2</sub> SO <sub>4</sub>	1 - 8	30 - 45
Cation	H <sup>+</sup>	HCl	4 - 10	30 - 45
Cation	Na <sup>+</sup>	NaCl brine	10 - 26	30 - 45
Anion	OH <sup>-</sup>	NaOH	2 - 4	60 - 90

Adapted from: Leonard J. Lefevre, p. 72-74.

In processes other than complete demineralization, weak base ion exchangers can be regenerated with solutions other than sodium hydroxide. NH<sub>4</sub>OH, Na<sub>2</sub>CO<sub>3</sub>, and NaCl

<sup>7</sup> R.G. Anthony, C.P. Philip, and R.G. Dosch, Ibid..

<sup>8</sup> Leonard J. Lefevre, "Resins for Industrial Water Treatment", *Plant Engineering*, October 22, 1987, p. 72-74.

are a few possibilities. Mixed bed resins, those with both cation and anion exchange beads, can also be regenerated, with greater cost and effort.

Regeneration will not result in 100% replacement of exchange sites, or a return to original exchange capacity. The resin will have a tendency to hold certain ions for which it has great affinity. While high concentrations of regenerant will help to mitigate this situation, above a certain concentration the return, in terms of increased performance, environmental harm, and downtime and disposal fees, is not worth the cost. Manufacturers specifications will state an expected lifetime for the resin, for instance three years or both in terms of time and volume of water treated. The actual performance will be a function, however, of operating conditions.

If, as commonly occurs both in municipal and industrial wastewater treatment, more than one ion exists in the solution, the exchange with the ions on the resin will be determined by the affinity, or energy of displacement, of the ion for the resin. The higher the affinity for a resin, the lower the energy required to exchange and the higher the likelihood it will exchange. In the case of organic material, adsorption properties as well as ion-exchange properties, will determine displacement in the resin. For the various categories of resins, Table 4.3 shows affinity series for ions commonly found in wastewater.

**Table 4.3 Qualitative Affinity of Common Ions for Various Resin Types<sup>9,10</sup>**

<b>Sulphonic Acid Resins (Strong Acid Cation Exchanger)</b>	<b>Carboxylic Acid Resins (Weak Acid Cation Exchanger)</b>
Ca <sup>2+</sup> > Fe <sup>2+</sup> > Mg <sup>2+</sup> > NH <sup>4+</sup> > Na <sup>+</sup> > H <sup>+</sup> Fe <sup>3+</sup> > Al <sup>3+</sup> > Ca <sup>2+</sup> Ac <sup>3+</sup> > La <sup>3+</sup> > Y <sup>3+</sup> > Ba <sup>2+</sup> Th <sup>4+</sup> > La <sup>3+</sup> > Ce <sup>3+</sup> > Na <sup>+</sup> Th <sup>4+</sup> > Hf <sup>4+</sup> ≥ Zn <sup>2+</sup> Mg <sup>2+</sup> > Be <sup>2+</sup>	H <sup>+</sup> > Ca <sup>2+</sup> > Mg <sup>2+</sup> > K <sup>+</sup> > Na <sup>+</sup>
<b>Quaternary Ammonium Resins (Strong Base Anion Exchangers)</b>	<b>Polyamine Resins (Weakly Alkaline Anion Exchangers)</b>
HSO <sub>4</sub> <sup>-</sup> > NO <sub>3</sub> <sup>-</sup> > CrO <sub>4</sub> <sup>2-</sup> > Br > SCN <sup>-</sup> > Cl <sup>-</sup> > HCO <sub>3</sub> <sup>-</sup> > HSiO <sub>3</sub> <sup>-</sup> > OH <sup>-</sup>	OH <sup>-</sup> > SO <sub>4</sub> <sup>2-</sup> > CrO <sub>4</sub> <sup>2-</sup> > NO <sub>3</sub> <sup>-</sup> > PO <sub>4</sub> <sup>3-</sup> > MoO <sub>4</sub> <sup>2-</sup> > HCO <sub>3</sub> <sup>-</sup> ≥ Br > Cl <sup>-</sup> > F <sup>-</sup>
<b>Chelating Resin - Imidodiacetic Acid Type</b>	<b>Chelating Resin - In an Acetate Buffer</b>
Cu <sup>2+</sup> >> Pb <sup>2+</sup> > Fe <sup>3+</sup> > Al <sup>3+</sup> > Cr <sup>3+</sup> > Ni <sup>2+</sup> > Zn <sup>2+</sup> > Ag <sup>+</sup> > Co <sup>2+</sup> > Cd <sup>2+</sup> > Fe <sup>2+</sup> > Mn <sup>2+</sup> > Ba <sup>2+</sup> > Ca <sup>2+</sup> >>> Na <sup>+</sup>	Pd <sup>2+</sup> > Cu <sup>2+</sup> >> Fe <sup>2+</sup> > Ni <sup>2+</sup> > Pb <sup>2+</sup> > Mn <sup>2+</sup> >> Ca <sup>2+</sup> > Mg <sup>2+</sup> >>> Na <sup>+</sup>

Adapted from: B.A. Bolto and L. Pawlowski, p. 22-23; and Leonard J. Lefevre, p. 70-74.

The rate limiting step for ion exchange has been found to be a function of the concentration of ions in solution. At concentrations less than 0.001M (1 mM), diffusion of the ion across the static 10 μM thick film that separates the bulk solution from the matrix of the resin is the limiting step. Above 0.1 M, it is diffusion through the matrix of the resin (between these concentrations, both of these rates are critical in determining the overall rate). Increasing the flow across the resin bed which concomitantly decreases the thickness of the static film will increase the rate of ion-exchange in the first case.

Temperature increases or a change of resin type (to a resin with a low degree of crosslinking which slows particle diffusion) can increase the rate in the second case.

<sup>9</sup> B.A. Bolto and L. Pawlowski, *Ibid.*, p. 22-33.

<sup>10</sup> Leonard J. Lefevre, "Resins for Industrial Water Treatment, Part 1: Types, Structure, Operations, Properties", *Plant Engineering*, October 22, 1987, p. 70-74.

#### 4.2.4.3. Characteristics of Ion Exchangers

Ion exchangers have a number of important interconnected characteristics that describe the theoretical and actual performance of a resin. This section defines various operating parameters and also notes physical properties of interest in the resin.

Total ion exchange capacity. Also known as absorptivity and full exchange capacity, this is the concentration of fixed charges in the resin; or, in other words, the number of equivalents of fixed charges per volume of wet resin available for exchange with ions in solution. This describes the theoretical maximum or saturation number of ions that can be exchanged between solution and resin.

Operating ion exchange capacity. Also known as working ion exchange capacity, this describes the ability of a wet resin to exchange a given ion under actual working conditions. Thus, operating ion exchange capacity is a function of the age and extent of regeneration of the resin, the type of exchange reaction, the equipment used and existing physical conditions.

Reversibility. This describes the ability of the resin to regenerate itself by carrying out the reaction in the reverse direction. On any given resin, there are only a given number of ions that can be exchanged between resin and solution. Once these are depleted, breakthrough will occur. This is noted by the appearance of the ion to be exchanged in the effluent of the exchanger. At this point the resin will have to be regenerated. This three stage process consists of running the surface reactions in reverse. For example, a strong acid cation exchanger will be regenerated by washing thoroughly with an acid or sodium chloride solution.

Leakage. This describes the amount, or concentration of dissolved solids, including ions, that flow out of the resin bed due to equilibrium conditions being skewed in all or part of

the resin bed. This occurs when certain ions are dislodged prematurely—prior to regeneration—from exchange sites due to the presence of a more favorable ion, usually because an upstream ion has dislodged another ion. Ions with higher affinity will displace those with lower affinities. When leakage reaches a certain concentration, it is time to regenerate the ion.

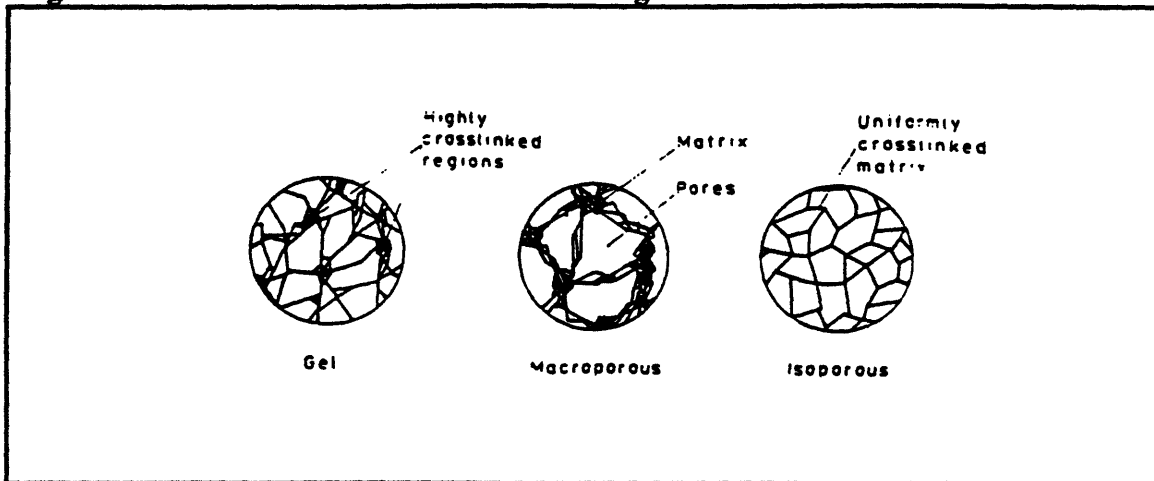
The chemistry of ion exchange occurs on the beads that comprise the resin. The physical properties of importance : particle or bead diameter, moisture content, degree of swelling, pH range, maximum and minimum temperatures, turbidity and chlorine tolerance, backwash rate and period, service and regeneration rate, rinse volume, life expectancy, level of crosslinking, shipping weight, and cost. These are largely determined by the chemical composition of the resin and the exchange groups on the matrix.<sup>11</sup>

Ion exchange resins are usually a matrix of pores connected by cross-linking copolymers. The size of the pore and the degree of crosslinking help determine much of the behavior of the resin. The three most common structures for resins, as shown in Figure 4.1, are gels, isoporous resins, and macroporous resins, with the former two the most widely used commercially.

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<sup>11</sup> B.A. Bolto and L. Pawlowski, *Ibid.*, p. 22-33.

**Figure 4.1 Various Structures of Ion Exchangers<sup>12</sup>**



Source: B.A. Bolto and L. Pawlowski, p. 9.

The primary differences of importance between these resins is the size of the pores, the degree of crosslinking and the mechanical strength. Most ion exchange resins used in municipal and industrial water supply systems are synthetic spherical gels or macroporous beads with a diameter of roughly 0.5 mm, a moisture content of 35 to 60%, and a level of crosslinking of 8 to 20%. Impregnated with additional charged groups, these beads are usually styrene/divinyl benzene (DVB) or acrylic acid copolymers.<sup>13</sup> Strong acid cation exchangers use sulphonic ( $\text{SO}_3\text{-H}^+$ ) groups, while weak acid exchangers are created by the addition of carboxylic groups ( $\text{-COOH}$ ). Strong base exchangers, on the other hand, are manufactured by the addition of quaternary ammonium groups ( $\text{-}^+\text{NR}_3\text{OH}$ ) and come in two basic types: Type I and Type II. Weak base exchangers by polyamides, either tertiary ( $\text{-NR}_2$ ), secondary ( $\text{-NHR}$ ), or primary ( $\text{NH}_2$ ).<sup>14</sup>

Strong acid cation resins can exchange ions with any type of cation, either strong or weak. The cations, either hydrogen or sodium, on the resin tend to exchange easily

<sup>12</sup> B.A. Bolto and L. Pawlowski, *Ibid.*, p. 9-10.

<sup>13</sup> Leonard J. Lefevre, *Ibid.*, p. 70-74.

<sup>14</sup> B.A. Bolto and L. Pawlowski, *Ibid.*, p. 11-18.

with whatever cation in solution that comes along. Easily regenerated and hence more economical for treating such water quality problems as hard, alkaline water<sup>15</sup>, weak acid resins will only exchange with ions associated with alkaline ions. Both Type I and Type II strong base resins can exchange with any anion in solution. Type I resins, however, is more efficient at removing carbonic and silicic acids from solution; while Type II resins, the more easily regenerated and higher exchange capacity of the two, are the more economical choice for the removal of nitrates and sulfates from a water supply. With characteristics more accurately described as absorbers rather than exchangers and a regeneration ability that surpasses all other anion exchangers, weak base ion exchangers excel at the removal of strong acids such as hydrochloric, nitric and sulfuric<sup>16</sup>.

In contrast to the general ion exchangers described above, specific ion exchangers are designed to remove a specific ion from solution. Usually they become necessary when a more general cation or ion exchanger cannot remove a specific ion because its affinity for that ion is lower than its affinity for other ions that exist in solution. Both the imidoacetic ( $-\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$ ) and thiol active groups ( $-\text{SH}$ ) are often utilized for this purpose. Table 4.4 delineates specific groups selective for removing specific ions from solution.

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<sup>15</sup> Leonard J. Lefevre, *Ibid.*, p. 73.

<sup>16</sup> Leonard J. Lefevre, *Ibid.*, p. 73.

**Table 4.4 Ion Exchangers Containing Specific Groups Selective for Particular Ions<sup>17</sup>**

<b>Ion</b>	<b>Specific Group or Exchanger</b>
Ammonium	Clinophlolite (inorganic matrix)
Arsenic	Fluorone
Beryllium	Diallyl phosphate
Bismuth	Pyrogallol
Boron	N-Methylglucamine (Rohm and Haas Amberlite XE-243)
Calcium	Gallic acid Imidodiacetic acid
Cesium	Diallyl phosphate Methylene sulphonic acid (Bayer-Lewatit DN and Diamond Shamrock Duolite C-3)
Cobalt	8-Hydroxyquinoline $\beta$ -Diketone
Copper	Ethelynediaminetetra-acetic acid Diphenylthiourea 8-Hydroxyquinoline Anthranilic acid $\beta$ -Diketone Ethelynediaminetetra-acetic acid Phosphonic acid (Duolite ES-63) Amidoxime (Duolite CS-346)
Cyanide	Anion exchanger (Rohm and Haas Amberlite XE-275 for ferrocyanide)
Germanium	Fluorone
Gold	Polyhydric phenols Polyisothiuronium (Ayalon SRAFION-NMRR)
Iron	Alginate acid Diallyl phosphate Hydroxamic acid m-Phenylglycine Thiol (AKZO Chemical Co.) Anthranilic acid
Lead	Pyrogallol (AKZO Chemical Co. - IMAC T-73)
Magnesium	Alginate acid Phenyldiaminoacetic acid

Source: B.A. Bolto and L. Pawlowski, p. 18-19.

<sup>17</sup> B.A. Bolto and L. Pawlowski, *Ibid.*, p. 18-19.

**Table 4.4 (Cont.) Ion Exchangers Containing Specific Groups Selective for Particular Ions<sup>18</sup>**

Ion	Specific Group or Exchanger
Nickel	8-Hydroxyquinoline β-Diketone
Nitrate	Ethelynediaminetetra-acetic acid
Palladium	Alkylated amidines
Platinum	Aminophenol and nitro groups Polyisothiuronium (Ayalon SRAFION-NMRR)
Potassium	Guanidine
Silver	Dipicrylamine Thiol
Strontium	Aminocarboxylic acid
Thorium	Diallyl phosphate
Titanium	Arsonic acid
Uranyl oxide	Chromotropic acid
Zinc	Schiff base - dinitrophenol Anthranilic acid
Zirconium	Phosphonic acid Phosphonic acid

Source: B.A. Bolto and L. Pawlowski, p. 18-19.

Finally, hydrous metal oxide gels of Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, ThO<sub>2</sub>, SnO<sub>2</sub>, MoO<sub>3</sub> and WoO<sub>3</sub> have been developed. These ion exchangers are amphoteric, cation exchangers above their isoelectric points and anion exchangers below them. Properties of these gels are highly dependent on their preparation; however, synthesis procedures have been developed for gels of ferric oxides, titanates, niobates and tantalates for use in neutralizing and decontaminating nuclear wastes<sup>19</sup>.

#### 4.2.4. Ion Exchange Systems

Ion Exchange is a chemical process that is used commercially to remove ions from an aqueous solution. In a municipal or industrial treatment stream, ion exchange is an advanced treatment, or tertiary, unit process. In industrial and municipal wastewater treatment, it will be preceded by other processes that will remove particulates, suspended

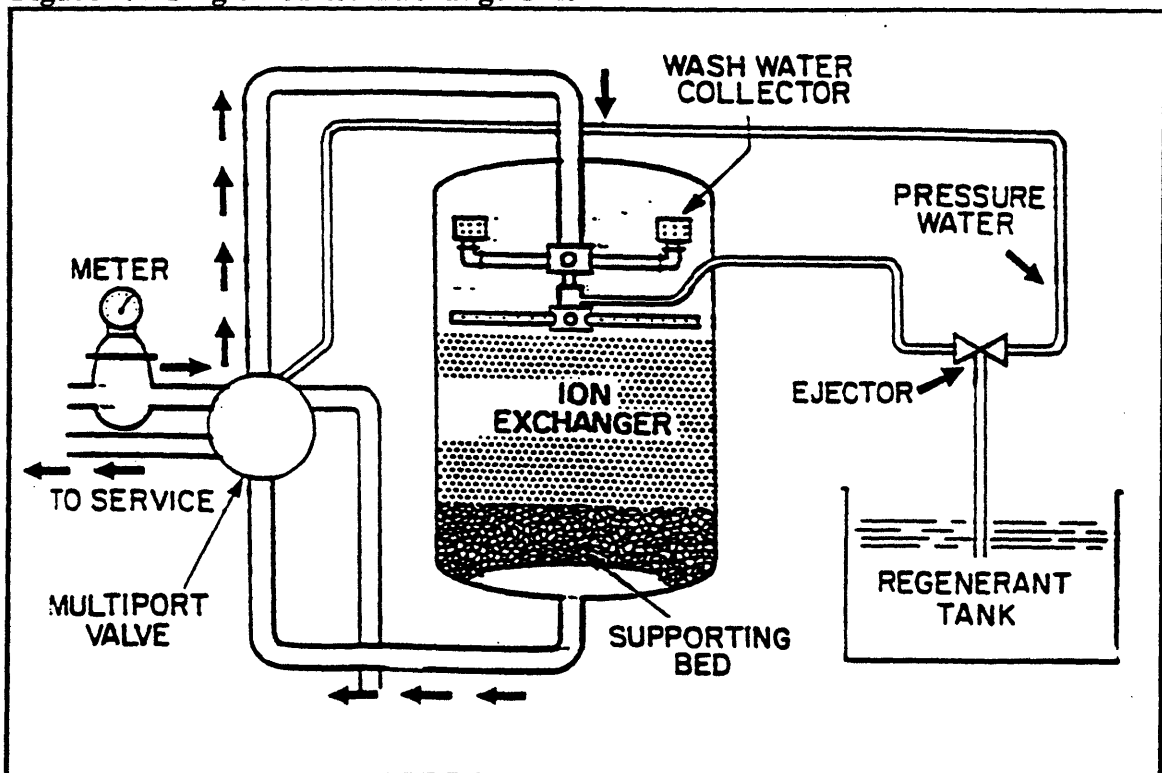
<sup>18</sup> B.A. Bolto and L. Pawlowski, *Ibid.*, p. 18-19.

<sup>19</sup> R.G. Anthony, C.P. Philip, and R.G. Dosch, *Ibid.*

solids, and colloids as well as some dissolved solids. In the production of ultra-pure water---as is needed for the manufacture of electronics and pharmaceuticals---aeration, clarification, coagulation, filtration, and reverse osmosis will precede ion exchange.

In order to carry out ion exchange on a large scale, an ion exchange system (see Figure 4.2) is needed. The basic components of such a system are an ion exchange tank, an inlet distribution system, an outlet collector, the ion exchange resin and a supporting bed for the resin. Furthermore, to allow for regeneration of the resin, a regeneration tank and distribution system are also necessary. Accompanying these two parts are a bevy of pipes, valves, gauges, and other such accouterments.

Figure 4.2 Single Bed Ion Exchange Unit<sup>20</sup>



Source: "Ion Exchange Primer", p. 5.

The actual configuration of an ion exchange system will be a function of the requirements of the process water produced. These systems will range from the

<sup>20</sup> "Ion Exchange Primer", Ibid., p. 5.

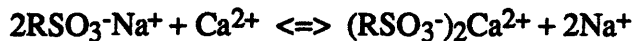
relatively simple to the complex. The following section gives examples of specific uses of ion exchange and requirements of those systems.

#### 4.2.5 . Specific Ion Exchange Systems

Ion exchange is a well established method for a number of different water quality problems including water softening; nitrate, heavy metal and radionucleotide removal; and the complete demineralization of water. Ion exchange systems range from the relatively simple to the quite complex. The complexity of the system will be a function of the requirements of the output as well as the quality of the influent. This next section discusses in more detail certain water quality and wastewater recycle problems amenable to treatment by ion exchange.

##### 4.2.5.1. Water Softening

Until quite recently, the most common use of ion exchange in the drinking water industry was for water softening. Municipalities requiring water softening, the removal of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions from public water supplies:



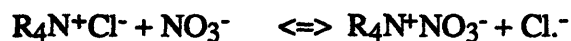
will only need single-bed systems.

##### 4.2.5.2. Nitrate removal

In agricultural areas, the necessity of removing nitrate from drinking water supplies is becoming more and more urgent as nitrates from fertilizers and livestock contaminate ground water supplies. Nitrates and nitrites in the drinking water put infants, fetuses, and pregnant women at risk. At concentrations higher than 10 mg/l  $\text{NO}_3^-$ -N (weight of nitrogen content) or about 45 mg/l  $\text{NO}_3^-$  (ionic weight per unit volume) in drinking water, approximately one in five infants will come down with

nitrate-induced methemoglobinemia, popularly known as "blue baby syndrome", while below this benchmark level there is no significant risk<sup>21</sup>. The nitrate from the drinking water is reduced to nitrite, primarily by bacteria living in the colon. While these bacteria also exist in adults, because infants have a higher pH in their stomachs than adults, the bacteria there are able to thrive. Nitrite is capable of oxidizing hemoglobin, eliminating the major oxygen-transport system within the body. As the body becomes starved for oxygen, the sufferer will show signs of bluish lips and skin, overall weakness, an elevated pulse rate and tachypnea<sup>22</sup>. Some studies have shown that babies born to women who drank water with nitrate levels over 5 mg/l are prone to birth defects; however, a recent literature review suggests that levels of 10 mg/l is enough to prevent teratogenic effects from nitrate<sup>23</sup>. A third concern is the production of N-nitrosoamines in the stomach, as a result of reactions of secondary amines with nitrite, the reduction product of nitrate. While no conclusive evidence has proven these N-nitrosoamines to be carcinogenic in humans, they have been proven carcinogenic in animals and are known to be among the most carcinogenic compounds around<sup>24</sup>. Ion exchangers can be effective in removing nitrates and nitrites from the drinking water supply. They can be used either at the treatment plant scale or in the home to protect human health.

At the treatment plant scale, nitrate removal is also achieved by a single-bed system, consisting of a strong base ion exchanger in the chloride form:



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<sup>21</sup> Howard Hu and Nancy Kim, "Drinking-Water Pollution and Human Health", in Critical Condition: Human Health and the Environment, Eric Chivian, Michael McCally, Howard Hu, and Haines (eds.), MIT Press: Cambridge, MA, 1993, p.35.

<sup>22</sup> Howard Hu and Nancy Kim, 1993, p. 35.

<sup>23</sup> Howard Hu and Nancy Kim, 1993, p. 36.

<sup>24</sup> Edward C. Anton, Jeffrey L. Barnickol, and Dean R. Schnaible, Nitrates in Drinking Water: Report to the Legislature, Report No. 88-11WQ, State Water Resources Control Board, State of California, October, 1988, p. 7.

Just prior to nitrate breakthrough, the chloride resin can be regenerated with 0.5–2.0 N NaCl solution. Disposal of the nitrate-contaminated brine is the most significant problem with this approach to nitrate removal. Moreover, if sulfate ion also exists in the raw water, it will be exchanged before the nitrate ion at typical ionic strengths ( $I \leq 0.01$  N), due to a higher affinity for sulfate ion by standard resins. Finally, elevated chloride levels may lead to certain health effects and increased corrosiveness of the water<sup>25</sup>. The disposal problems can be partially alleviated by regenerating the column with a closed circuit continuous upflow sludge blanket biological denitrification reactors instead of a chloride solution.

#### 4.5.4.3. Ammonium Ion Reduction

In order to comply with NPDES discharge permit limits for nitrogen in the form of ammonia, ammonium ion can be removed from filtered secondary effluent at POTWs, advanced wastewater treatment facilities, and industrial sites. Following a filtration process in order to maintain the zeolite, removal is accomplished by a single bed ion exchange reactor used in conjunction with an air stripping column. This sequence maximizes the total ammonium removed and recovers the ammonia. The natural zeolite clinophlolite, with an exchange capacity of 2 meq/g, is used inside the exchanger, and removes from 90 to 97% of the ammonium ions<sup>26</sup>. While synthetic zeolites with higher exchange capacities have been developed, they have yet to be utilized in wastewater treatment plants for this purpose. Nitrates, nitrites, and organic nitrogen, however, are not affected by this process. The final component of the system is a regenerant unit. At neutral pHs, regeneration can be facilitated by a sodium chloride brine; at higher pHs, alkaline solutions such as sodium or calcium hydroxide are required. While these are more efficient, such alkaline regenerants may cause precipitation of hydroxides or

<sup>25</sup> Dennis Clifford and Xiaosha Liu, *Ibid.*, p. 135–136.

<sup>26</sup> W. Wesley Eckenfelder and Yerachmiel Argaman, "Principles of Biological and Physical/Chemical Nitrogen Removal" in Richard Sedlak (ed.), Phosphorus and Nitrogen Removal from Municipal Wastewater, Second Edition, p. 40.

carbonates within the column<sup>27</sup>. Ammonia is usually removed from the brine by air stripping. However, it is also possible to remove the ammonium ion by precipitating it out of solution as ammonium sulfate by neutralizing the brine with sulfuric acid<sup>28</sup>.

While removing ammonium ion by ion exchange can be 55% more costly than biological treatment, it is also more reliable and achieves higher rates of removal<sup>29</sup>. Because it can be turned off and off without harm to the system, it can be used for "peaking"; that is, for removing ammonia only during those periods when it is necessary. For instance, during low-flow conditions, a POTW may need to remove ammonia in order to comply with its NPDES permit. An ion exchanger has the flexibility to allow for this. Another POTW, with a year-round need to remove ammonia, may opt for a biological system, due to the lower costs.

Ion exchange is being used for this purpose at Denver's full-scale potable water reuse demonstration plant. This 1 mgd plant aims to show that the unchlorinated effluent following secondary treatment at a POTW could be used for direct, potable reuse. As one of over a dozen unit processes, a selective ion exchange system is being used to remove ammonium ion from the waste stream. In conjunction with this are associated regeneration and ammonia recovery processes. Facilitating removal of the ion is a natural zeolite clinophlolite exchanger. Regeneration is accomplished by using a 2% NaCl brine to clean the spent media. Air stripping then removes the ammonia from solution, followed by more than 40 steps in order to recover the ammonia. Overall, these systems have not been without problems, and were plagued by operational, mechanical and electrical problems which prevented smooth, non-interrupted operation<sup>30</sup> early on.

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<sup>27</sup> W. Wesley Eckenfelder and Yerachmiel Argaman, *Ibid.*, p. 40.

<sup>28</sup> Rational Use of Water and Its Treatment by the Chemical Industry, Economic Commission for Europe, United Nation Report ECE/CHEM/78, New York, 1991, p. 65.

<sup>29</sup> ECE/CHEM/78, *Ibid.*, p. 65.

<sup>30</sup> William C. Lauer, Stephen E. Rogers, and Jean M. Ray, "The Current Status of Denver's Potable Water Reuse Project", *Journal AWWA*, July 1985, p. 56-57.

#### 4.2.5.4. Removal of Radionucleotides

Ion exchange can be used to remove a number of radionucleotides, including various isotopes of uranium and radium, from aqueous solutions. One example of this is the removal of uranium and radium from contaminated groundwater used for drinking water. It has been estimated that 300,000 people in the lower 48 states receive water with higher than 10 pCi/L uranium. These people are served by approximately 2,000 different community drinking water supplies, with the highest average concentrations occurring in the Rocky Mountain states<sup>31</sup>. Reduction in the concentration of radionucleotides—uranium, radium and radon— can be achieved by conventional treatment with coagulation-filtration, lime softening, ion exchange, adsorption, aeration and reverse osmosis. Radium is removed with cation exchangers, while uranium removal requires anion exchangers, with disposal problems existing from the brine of both systems. Ion exchange is the best option for small-scale plants for both radium and uranium reduction, with process efficiencies reported of between 95+ and 99%<sup>32</sup>. While these reductions are larger than those typically achieved by more conventional methods of treatment such as coagulation-filtration and lime softening, cost factors and economies of scale make these other options the best choice for large-scale plants. Typical costs for cation exchange are \$0.30–\$0.80/1000 gallons, while for anion exchange this increases to between \$1.60 and \$2.10/1000 gallons.<sup>33</sup>

Another large-scale use for ion exchangers in wastewater treatment facilities is for the removal of soluble radionucleotides from mixed waste wastewater. Mixed waste is a catchall term for all wastes that consist of a mixture of chemically hazardous components (re: the EPA definition of chemically hazardous) and radioactive components. It has

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<sup>31</sup> Robert T. Jelinek, Ronald L. Clemmer, and Frank J. Johns, "Uranium Removal from Drinking Water Using a Small Full-Scale System", EPA/600/2-89/012, April, 1989, p. 5.

<sup>32</sup> Technologies for Upgrading Existing or Designing New Drinking Water Facilities, Office of Drinking Water, US EPA, EPA 625/4-89/023, p. 143.

<sup>33</sup> In 1982 dollars; EPA/625/4-89/023, Ibid., p. 143.

been estimated that between 100,000 m<sup>3</sup> and 180,000 m<sup>3</sup> of mixed waste are currently in storage at various Department of Energy sites nationwide, and that between 8,000 and 20,000 m<sup>3</sup> are still being produced annually. To deal with on-site stored mixed waste at Oak Ridge National Lab, for example, two separate ion exchangers are being utilized in one centralized wastewater treatment facility, the LLLW (Low-Level Liquid Waste) plant, one to remove Cesium-137 (<sup>137</sup>Cs) and a second to remove Strontium-90 (<sup>90</sup>Sr) from the liquid effluent. A second treatment facility on-site uses naturally occurring zeolite ion exchangers to remove nitrates and heavy metals before the wastewater can be discharged to surface water. Compounding the problem, the spent ion exchangers from the LLLW plant, contaminated with either <sup>137</sup>Cs and <sup>90</sup>Sr ions, are classified as mixed waste and must be disposed of—in accordance with all State and Federal environmental regulations, including the Resource Conservation and Recovery Act (RCRA), the Land Disposal Restrictions (LDRs), and those specific to military and Dept. of Energy (DOE) facilities, such as the Federal Facility Compliance Agreements—or treated in a mixed waste (solid) treatment facility<sup>34</sup>.

#### 4.2.5.5. Activated Alumina<sup>35,36</sup>

Activated alumina is a highly effective method for removing fluoride, selenium(IV) and arsenic(III) from solution. While greater than 80% removal efficiency is achieved for all three of these contaminants, the primary use in the drinking water industry for activated alumina is fluoride removal from fresh groundwater. Because activated alumina will not remove total dissolved solids (TDS), sodium or chloride, it is not feasible for use on salty or brackish groundwater. Other uses for activated alumina include the removal of these contaminants from industrial wastewater.

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<sup>34</sup> W.D. Bostick and W.H. Hermes, "Control of Regulated Metals at DOE Oak Ridge Reservation Sites", *Proceeding of the Fifth Annual Conference on Emerging Technologies: Metals, Oxidation, and Separation*, Gulf Coast Hazardous Substance Research Center, 1993.

<sup>35</sup> Gary S. Logsdon, Thomas J. Sorg, and Robert Clark, "Capability and Cost of Treatment Technologies for Small Systems", *Journal AWWA*, June 1990, p. 62–65.

<sup>36</sup> EPA/625/4–89/023, *Ibid.*, p. 149–151, p. 206–208.

Activated alumina is a commercially available anion exchanger highly specific for fluoride, arsenic, and selenium. It operates by exchanging hydroxyl ions, supplied from the regenerant and flushed through the system prior to use, with the contaminant, such as fluoride.

Activated alumina systems consist of units for pretreatment, contact with the activated alumina, regeneration, and storage and neutralization of the regenerants plus a series of valves, controls, pipes, pumps and storage facilities. While pretreatment for activated alumina requires the removal of suspended solids, it is relatively insensitive to the presence of dissolved solids. The actual treatment might require pH adjustment, depending on the contaminant to be removed. Fluoride, for instance, is optimally removed at a pH between 5 and 6, which can be achieved by the addition of an acid to the influent. Like other ion exchangers, activated alumina systems are operated on demand, allowing them to be utilized only as flow and influent concentration dictate. Furthermore, these systems can be designed with either upflow or downflow operating and regeneration systems. Regeneration of the activated alumina media is achieved by sodium hydroxide. Up to 20% of the activated alumina is lost annually during regeneration, adding considerably to the cost of the system. Directly following regeneration, leached aluminum could possibly contaminate the product water for short duration of time. This can be mitigated by flushing the column prior to treating contaminated water.

As with other ion exchange columns, the disposal of the regenerant brine with and spent activated alumina might present additional environmental and waste management problems. Rectifying these issues may result in higher costs to the facility, which will be passed along to the consumer.

#### 4.2.5.6. Metals Removal

The removal of heavy metals from wastewater, and in particular industrial wastewater, is often necessary in order to comply with recent revisions to the Clean Water Act and the Resource Conservation and Recovery Act (RCRA). The heavy metals of primary concern vary from industry to industry and include cadmium, chromium, copper, iron, lead, mercury, nickel and silver. Other metals that may be added to this list include aluminum, arsenic, cobalt, manganese, molybdenum and selenium<sup>37</sup>. While ion exchange was not designated as the best demonstrated available technology (BDAT) from which the treatment standards were derived, any EPA-approved technology, including ion exchange, capable of meeting these standards can be utilized. Table 4.5 shows the maximum concentration allowed for discharge of various metals. For metals with more than one standard based on various processes, wastewater standards are listed.

**Table 4.5 Maximum Concentration Allowed for Discharge of Selected Metals<sup>38,39</sup>**

Metal	Concentration (mg/l)	Metal	Concentration (mg/l)
Arsenic	0.79	Lead	0.04
Barium	1.0	Mercury	0.03
Cadmium	0.2	Selenium	1.0
Chromium	0.32	Silver	0.29 (24 hr.)
Copper	1.0		

Source: Maung Min, et al, p. 64–65, and William Fries and David Chew, p. 32.

Depending on the ionic charge of the metal, the metal ion can be removed from solution—wastewater, sludge leachate, contaminated groundwater—by either cation exchange or anion exchange. Removal efficiencies achievable by ion exchange for selected heavy metals are shown in Table 4.6.

<sup>37</sup> Yi-Chu Huang and S. Sefa Koseglu, "Separation of Heavy Metals from Industrial Waste Streams by Membrane Separation Technologies", Proceedings from the 5th Annual Symposium on Emerging Technologies: Metals, Oxidation, and Separation, Gulf Coast Hazardous Substance Research Center, Feb. 25–26, 1993.

<sup>38</sup> Maung Min, Richard Barbour, and Jou Huang, "Land Ban Technologies, Impacts and Implications", *Pollution Engineering*, July 1991, p. 64–65.

<sup>39</sup> William Fries and David Chew, "Get the Metal Out!", *Chemtech*, February 1993, p. 32.

**Table 4.6 Removal Efficiencies Achievable for Selected Metals by Ion Exchange<sup>40,41</sup>**

Metal	Removal (%)	Metal	Removal (%)
Arsenic (V)	<90	Copper	<95
Barium	>90	Lead	<95
Cadmium	>90	Selenium (Activated Aluminum)	<95
Chromium (III)	<90	Silver	>90
Chromium (IV)	>90		

Adapted from: *Chemical Engineering*, Vol. 95, No. 16, 1988, p. 76; and EPA/625/4-89/023, p. 144.3.

These removal rates can be improved by using ion exchange in conjunction with other technologies, such as electrowinning, which can allow for removal efficiencies for some heavy metals of upward of 99 percent.

Lastly, cyanide (CN<sup>-</sup>), while not a metal, is utilized in many of the same processes as certain heavy metals, and also amenable to treatment by anion exchange. Because of this, the treatment of cyanide by ion exchange will be included in this section.

In accordance to 40 CFR Part 261(RCRA), ion exchange can be used to treat a number of metal-bearing RCRA hazardous waste streams, including wastewaters and sludge leachates contaminated by metals and cyanides. These waste streams are produced by a wide variety of industries including electroplating; production of paints, inks and dyes; steel and iron manufacturing; lead smelting and zinc production; silicon production and the manufacture of photographic products. These wastewaters and leachates have been classified by production process and/or contaminant. In the lexicon of this act, toxicity characteristic (TC) wastes are deemed D-wastes; listed hazardous wastes from non-specific sources, F-wastes; and listed hazardous wastes from specific sources, K-wastes. Annually, 3860 generators produce 3, 685 x 10<sup>6</sup> gallons of D-wastes; 2091 generators produce 3,920 x 10<sup>6</sup> gallons of F-wastes; and 402 generators produce

<sup>40</sup> *Rational Use of Water and Its Treatment by the Chemical Industry*, Economic Commission for Europe, United Nation Report ECE/CHEM/78, New York, 1991, p. 64.

<sup>41</sup> EPA/625/4-89/023, *Ibid.*, p. 143.

219 x 10<sup>6</sup> gallons of K-wastes<sup>42</sup>. Many of these wastewaters and sludge leachates are amenable to treatment by ion exchange, as shown, respectively, in Tables 4.7 and 4.8.

**Table 4.7 Metal-Bearing RCRA Wastewaters Amenable to Ion Exchange<sup>43</sup>**

EPA Hazardous Waste No.	Hazardous Waste Description	Hazardous Constituents
D004	Toxicity Characteristic (TC) waste	Arsenic
D006	Toxicity Characteristic (TC) waste	Cadmium
D007	Toxicity Characteristic (TC) waste	Chromium
D008	Toxicity Characteristic (TC) waste	Lead
D009	Toxicity Characteristic (TC) waste	Mercury
D011	Toxicity Characteristic (TC) waste	Silver
K062	Spent pickle liquor generated by steel-finishing operations of facilities within the iron and steel industry	Hexavalent chromium, lead
K100	Waste leaching solution from acid leaching of emission control dust/sludge from secondary lead smelting	Hexavalent chromium, lead, cadmium

Source: E.R. Krishnan et al.

<sup>42</sup> E. Rodha Krishan, Ronald J. Turner, et al., "Overview of Metals Recovery Technologies for Hazardous Wastes", Proceedings of the National Research & Development Conference on the Control of Hazardous Materials, Feb. 20-22, 1991, Anaheim, CA in *The Hazardous Waste Consultant*, Vol. 9, No. 3, May/June 1991, p. 1.22-1.28.

<sup>43</sup> E. Rodha Krishan, Ronald J. Turner, et al., *Ibid.*, p. 1.22-1.28.

**Table 4.8 RCRA Metal-Bearing Sludge Leachates Amenable to Ion Exchange<sup>44</sup>**

EPA Hazardous Waste No.	Hazardous Waste Description	Hazardous Constituents
F006	Wastewater treatment sludges from electroplating operations except from the following processes: 1. Sulfuric acid anodizing of aluminum 2. Tin plating on carbon steel 3. Zinc plating (segregated) on carbon steel 4. Aluminum or steel-Al plating on carbon steel 5. Cleaning/stripping associated with tin, zinc and aluminum plating on carbon steel 6. Chemical etching and milling of aluminum	Cadmium, hexavalent chromium, nickel, cyanide (complexed)
F008	Plating bath residues from the bottom of plating baths from electroplating operations where cyanides are used in the process	Cyanide (salts)
F019	Wastewater treatment sludges from the chemical conversion coating of aluminum	Cyanide (salts)
K002	Wastewater treatment sludge from the production of chrome yellow and orange pigments	Hexavalent chromium, lead
K003	Wastewater treatment sludge from the production of molybdate orange pigments	Hexavalent chromium, lead
K004	Wastewater treatment sludge from the production of zinc yellow pigments	Hexavalent chromium
K005	Wastewater treatment sludge from the production of chrome green pigments	Hexavalent chromium, lead
K006	Wastewater treatment sludge from the production of chrome oxide green pigments (anhydrous and hydrated)	Hexavalent chromium
K008	Oven residue from the production of chrome oxide green pigments	Hexavalent chromium
K065	Surface impoundments solids contained in and dredged from surface impoundments at primary lead smelting facilities	Lead, cadmium
K066	Sludge from the treatment of process wastewater and/or acid plant blowdown from primary zinc production	Lead, cadmium
K069	Emission control dust/sludge from secondary lead smelting	Lead, cadmium
K090	Emission control dust or sludge from ferro-chromium silicon production	Chromium

Source: E.R. Krishnan et al.

Besides satisfying RCRA requirements, ion exchange allows for the recycling of metals. In the electroplating industry, ion exchange allows companies to remove and recycle cadmium, chromium, copper, nickel, silver and zinc from the rinse water from the

<sup>44</sup> E. Rodha Krishan, Ronald J. Turner, et al., *Ibid.*, p. 1.22–1.28.

plating bathes; while in the photography industry, it is used to recover silver. This allows the companies to save money, while satisfying environmental regulations.

One example of an ion exchange system is designed to remove and recycle copper from the effluent of a manufacturer of printed circuit boards. Preceded by a two-step filtration process, the first system, the primary recoverer of the copper, consists of two beds of strong acid, sulfonic ion exchange resins (Amberlite IR-122, Duolite PCA-13) and a type I, strongly basic, quaternary ion exchange resin (Amberlite IRA-400). The first cation exchanger removes the copper and is regenerated with sulfuric acid. The second cation exchanger is designed to remove sodium and some organic matter and regenerated with hydrochloric acid. The anion exchangers, or third bed, remove sulfates, chlorides, fluoborates, organics, and ethylenediaminetetraacetic acid (EDTA) and are regenerated by a caustic solution. The regenerants from the final two stages are neutralized and discharged.

Following regeneration of the first cation exchanger, the copper is removed from the acid by an electrowinning unit. The regenerant waste from the electrowinning process is sent to a second ion exchanger, a copper scavenge system. This system consists of a metal-specific chelating ion exchange resin (Duolite PCC-718, Amberlite IRC-718) which allows for the removal and concentration of the remaining  $\text{Cu}^{2+}$  ions left in solution.

The entire system has been in operation since April 1991 and allows for the recovery of 99% of the copper in metallic form. The deionized water produced by the entire system is recycled back to the manufacturing facility<sup>45</sup>.

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<sup>45</sup> William Fries and David Chew, *Ibid.*, p. 32-35.

#### 4.2.5.7. Complete Deionization

Complete demineralization—the removal of all ions—requires a number of resin beds in series, each performing a specific task. At least one strong cation bed, a CO<sub>2</sub> degasser, and one strong anion bed are required, as well as the appropriate recovery units in order to regenerate each individual bed. An optional third mixed ion bed is necessary for polishing of the effluent in cases where high quality water is desired. Each increase in complexity brings along an increase in both the total capital cost of the system and in the operating costs.

#### 4.2.5.8. Small-Scale Drinking Water Facilities

When used for water treatment for small systems, ion exchange is often comparable in costs with traditional methods of water treatment that depend on economies of scale to make them cost effective. With new regulations for drinking water being promulgated, small drinking water facilities, with production rates of 100,000 gpd, face more stringent regulations than currently present. These communities, however, only have a small population base to bear the brunt of the cost. For these communities, ion exchange is often overall the most cost effective method for water treatment. Table 4.9 shows the cost of water treatment by ion exchange for such communities.

**Table 4.9 Estimated Capital and Operating Costs for Small-Scale Ion Exchangers for Water Treatment<sup>46</sup>**

Process	Capital Cost <sup>A</sup> (\$)	Energy <sup>B</sup> , Maintenance, Materials, and Labor <sup>C</sup> Costs (\$/year)	Cost for Chemicals (\$/year)	Total Operating Costs (\$/year) (\$/1000 gal)
0.10-MGD Cation Exchange	150,000 (94 cu ft resin in both tanks)	3,300 (regenerated every other day)	5,200 (400 mg/l hardness as CaCO <sub>3</sub> )	8,500 0.23
0.10-MGD Anion Exchange	115,000	4,900 (regenerated every other day)	5,400	10,300 0.28
0.10-MGD Activated Alumina	104,000 (for fluoride removal)	10,800 (12-day regeneration cycle)	3,800	14,600 0.4
1.0-MGD Anion Exchange	395,000 (McFarland, CA plant)		49,000	49,000 0.134

A: Amortization of capital at 10% interest over 20 years.

B: Based on a cost of \$0.07/kW for electricity.

C: Based on a cost of \$11.00/hour for labor.

Based on: Gary S. Logsdon et al.

### 4.3. Regulatory and Social Acceptability

#### 4.3.1. Legal and Regulatory Issues

Ion exchange is not a mandatory technology for any treatment need. However, it can be used in many instances to achieve Maximum Contaminant Levels (MCL) allowed for various ions. Examples of these were given in Section 4.2.5.6.

Pertinent major federal legislation governing facilities using ion exchange are recent amendments to the Clean Water Act and the Safe Drinking Water Act, and the Resource Conservation and Recovery Act. Additional state and local regulations also apply.

<sup>46</sup> Gary S. Logsdon, Thomas J. Sorg, and Robert Clark, *Ibid.*, p. 62.

#### **4.3.2. Associated Liability**

The associated liability of ion exchange systems comes from meeting discharge limits, disposal issues, and safety issues. If the ion exchanger fails to meet discharge limit, the facility is at risk for litigation for endangering human health of the environment. Careful monitoring can alleviate such danger. Depending on the contaminant removed, the disposal of the regenerant and spent exchangers can be the most serious drawback to this technology. Worker safety is a concern because of the caustic and acid regenerants used. Furthermore, removing spent ion exchange resins—for instance, if they are contaminated with low levels of radioactivity—can put the worker at increased risk. Care and caution can help mitigate but not eliminate associated liabilities.

#### **4.3.3. Public Opinion**

Currently, the public does not have any opinion about ion exchange and so is unlikely to halt the construction of an ion exchange unit on the site of a municipal or industrial wastewater facility. Some controversy might arise concerning the disposal of spent ion exchange media. The federal government has supported the use of synthetic and natural zeolite ion exchangers in various DOE projects; and local governments have utilized ion exchangers in groundwater decontamination projects.

#### **4.3.4. Political Acceptability**

Ion exchange is, where it is cost effective, an acceptable technology to deal with water quality problems. It has been used in local, state and federal projects, as well as in private industry. Examples of these are outlined in Section 4.3.5, 4.7.1 and 4.7.2.

#### **4.3.5. Related Public Health and Environmental Issues**

The major environmental hazards associated with ion exchange are the disposal of the brines and the spent resins. The brines produced can be either acidic or caustic

residues with concentrated amounts of certain ions. Depending on which ions were exchanged, these solutions are potentially hazardous waste. For instance, if the exchanger is removing heavy metal ions from solution, then the metals will have to be precipitated from solution or the spent regenerate effluent will have to be disposed of in accordance with all applicable local, state and federal regulations concerning the disposal of heavy metals. If, on the other hand, the ion exchanger is used to remove radionuclides from a water or wastewater stream, then the spent regenerant and the spent ion exchanger will be radioactive. Disposal will have to be in accordance with all environmental regulations concerning radioactive waste. Furthermore, the spent ion exchange resin will have to be disposed of properly. Again, depending on the use of the resin, this might require further treatment or disposal of at an approved facility.

In some cases, non-hazardous brines can be disposed of via an ocean outfall. In arid regions of the country, brines can be evaporated to concentrated salts via membrane-lined lagoons. In most areas of the country, disposal problems remain one of the challenges and impediments toward using ion exchange.

With the proper care, negative health effects to workers involved in the installation and the maintenance of an ion exchanger can be minimized. Workers involved in the production of ion exchange resins have an occupational health risk of contracting malignant neoplasms of the trachea, bronchus and lung<sup>47</sup>.

#### **4.4. Market Characteristics**

This section describes the general market conditions and the key companies involved in ion exchange in this country.

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<sup>47</sup> Dean B. Barker and Philip J. Landrigan, "Occupational Exposures and Human Health", in Critical Condition: Human Health and the Environment, MIT Press: Cambridge, MA, 1993, p. 79.

#### 4.4.1. General Market Characteristics

The market for ion exchangers can be analyzed from a number of different angles. Included might be the annual production and sales of resins, equipment and construction of overall systems. Because the base of these systems are the resins, the production and sales of resins reflect the overall health of the market.

In terms of overall sales of ion exchange resins, the total ion exchange market is now in excess of \$550 million per year. Broken down geographically, American and European sales each account for \$220 million/year, Japanese sales for \$75 million/year, and all other locales for the remaining \$75 million/year<sup>48</sup>. Expressed in terms of production, the total world output is, 4.3 billion lb./year (160,000 m.t./yr.)<sup>49</sup>.

Market growth for the ion exchange resins ranges considerably as a function of the end use of the resin, from nearly stagnant to a healthy eight percent yearly growth rate. The fastest growing markets, at 5 to 8% per yr., are for specialty applications like semiconductor production and food processing. Slightly slower, at 2 to 5 % per year, is the market for demineralization ion exchangers. The market for resins used in mining shows a rate of growth of only 0.5% per year while the market for water softening is basically stagnant<sup>50</sup>.

#### 4.4.2. Manufacturers of Resins and Systems

While a number of smaller companies manufacture ion exchange resins for specialty purposes and at low production levels (over 25 companies are listed in the Parker guide as manufacturers of ion exchange manufacturers). However, the larger companies, in addition to manufacturing the resins, also perform a great deal of research

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48 "Ion Exchange: A new sphere of action", *Chemical Engineering*, Sept. 1992, p. 67.

49 "Ion Exchange: A new sphere of action", *Ibid.*, p. 67.

50 "Ion Exchange: A new sphere of action", *Ibid.*, p. 67.

and development, leading to large improvements in the overall performance of resins and ion exchangers. The key US manufacturers of ion exchange resins are:

- Dow Chemical Co. (Midland, MI),
- Purolite Co. (Bala Cynwyd, PA),
- Rohm and Haas Co. (Philadelphia, PA; also known as R & H),
- Sybron Chemicals Inc. (Birmingham, NJ).

Resins from these five companies are often fairly interchangeable. These resins are known as Dowex (Dow Chemical Co.), Purolite (Purolite Chemical Co.), Duolite and Amberlite (Rohm and Haas Co.), and Ionac (Sybron Chemicals Inc.). The following tables show equivalent resins—anion, cation, mixed bed and nuclear grade—from the various companies and divisions. Table 4.10 compares the anion exchange resins and Table 4.11 compares cation exchange resins.

**Table 4.10 Anion Exchange Resins (Equivalents)<sup>51,52</sup>**

Dow Chemicals Dowex	Sybron Chemicals Ionac	Purolite Co. Purolite	Rohm & Haas Amberlite	Rohm & Haas Duolite
SBR	ASB-1	A-600	IRA-400	A-109
SBR-P	ASB-1P/A-540	A-400	IRA-402	A-101D
SAR	ASB-2/A-550	A-300/A-300E	IRA-410	A-102D/A-104
-	-	A-850	IRA-458	A-132
MSA-1	A-641	A-500	IRA-900	A-161
MSA-2	A-651	A-510	IRA-910	A-162
-	A-642	A-500P	IRA-904	-
MWA-1	AFP-329	A-100	IRA-93/94	A-378
-	-	A-103	-	A-392
DOWEX 66	-	A-104	-	-
DOWEX II	-	A-444	-	-
SBR	NA-38	NRW-600	IRA-78	ARA-366
-	-	A-845	IRA-68	-
-	-	A-501P	IRA-938	-
-	-	A-520E	-	-
-	-	A-870	IRA-478	-
WGR/WGR-2	A-305	-	-	A-30G/A-30B/ A-340

Adapted from: "Closest Competitive Equivalents to Ionac Ion Exchange Resins", p. 1; and "Purolite Ion Exchange Resins", p. 6.

51 "Closest Competitive Equivalents to Ionac Ion Exchange Resins", Sybron Chemical Bulletin, Undated, p. 1.

52 "Purolite Ion Exchange Resins", Purolite Company Bulletin D0030, May 1992, p. 6.

**Table 4.11 Cation Exchange Resins (Equivalents)<sup>53,54</sup>**

Dow Chemicals Dowex	Purolite	Sybron Chemicals Ionac	Rohm & Haas Duolite	Rohm & Haas Amberlite
HCR-S/HCR-W-2	C-100(Na <sup>+</sup> )	C-249/C-298	C-20/C-225	IR-120/130 IR-120+
HCR-S	C-100H	C-267	C-20 (H <sup>+</sup> )	IR-120 (H <sup>+</sup> )
HGR/HGR-W2	C-100X10	C-250/C-299	C-20X10/ C-225X10	IR-122/IR-132
MSC-1	C-150	CFP-110	C-26	IR-200/252
DOWEX 88	C-155	-	C-280	
CCR-2	C-105	CC	C-433	IRC-76
-	C-106	CNN	C-464	DP-1
-	NRW-100	NC-10	-	IRC-77
HGR-W2	-	C-299C	-	IR-132C

Adapted from: "Closest Competitive Equivalents to Ionac Ion Exchange Resins", p. 1; and "Purolite Ion Exchange Resins", p. 6.

Consisting of both anion exchange resins and cation exchange resins are mixed bed resins. These resins are typically for purposes which require extremely high quality water such as in the pharmaceutical, electronics, nuclear and power industries. Table 4.12 compares the mixed bed resins available from various manufacturers.

**Table 4.12 Mixed Bed Resins (Equivalents)<sup>55,56</sup>**

Dow Chemicals Dowex	Purolite	Sybron Chemicals Ionac	Rohm & Haas Duolite	Rohm & Haas Amberlite
MR-3	NRW-37	NM-60	ARM-381	IRN-150
-	-	NM-75	ARM-381D	-
-	-	NM-65	-	-

Adapted from: "Closest Competitive Equivalents to Ionac Ion Exchange Resins", p. 1; and "Purolite Ion Exchange Resins", p. 6.

Certain of these anion, cation, and mixed-bed resins provide the high quality water required by the nuclear industry and for the reduction in radioactivity of wastes. Table

53 "Closest Competitive Equivalents to Ionac Ion Exchange Resins", Sybron Chemical Bulletin, Undated, p. 1.

54 "Purolite Ion Exchange Resins", Ibid., p. 6.

55 "Closest Competitive Equivalents to Ionac Ion Exchange Resins", Ibid., p. 1.

56 "Purolite Ion Exchange Resins", Ibid., p. 6.

4.13 shows the various nuclear grade cation, anion and mixed bed resins available from the major producers.

**Table 4.13 Nuclear Grade Resins (Equivalents)<sup>57,58</sup>**

<b>Dow Chemicals Dowex</b>	<b>Purolite</b>	<b>Sybron Chemicals Ionac</b>	<b>Rohm &amp; Haas Duolite</b>	<b>Rohm &amp; Haas Amberlite</b>
<b>Cation Resins</b> HCR-S HGR	- -	NC-10 NC-11	ARC-351 -	IRN-77
<b>Anion Resins</b> NA-38 -	A-650U A-600U	NC-11 NM-65	ARA-366 -	IRN-78
<b>Mixed Bed Resins</b> MR-3		NM-60 NM-75 NM-65	ARM-381 ARM-381D	IRN-150

Adapted from: "Closest Competitive Equivalents to Ionac Ion Exchange Resins", p. 1; and "Purolite Ion Exchange Resins", p. 6.

Companies that manufacture ion exchange resins outside the United States include:

- Akzo Chemie BV (Amersfoort, The Netherlands),
- Ayalon Water Conditioning Co. (Haifa, Israel),
- Bayer AG (Leverkusen, Germany),
- Chemapol NP (Prague, Czech Republic),
- DISA Ltd. (Middlesex, United Kingdom),
- ICI Australia Operations Pty Ltd. (Melbourne, Australia),
- Mitsubishi Kasei Co. (Tokyo, Japan),
- Nippon Soda Co., Ltd. (Tokyo, Japan),
- Nitrokemia Ipartelepek (Fulzfoegyartelep, Hungary),
- Tulsi Industries (Tulsi Bhavan, India),
- Unitika Ltd. (Osaka, Japan),
- VEB Chemiekombinat (Bitterfeld, Germany).

Key manufacture of ion-exchange systems (North America) include:

<sup>57</sup> "Closest Competitive Equivalents to Ionac Ion Exchange Resins", Ibid., p. 1.

<sup>58</sup> "Purolite Ion Exchange Resins", Ibid., p. 6.

- ARI Technologies, Inc. (Palantine, IL).
- Bio-Recovery Systems, Inc. (Las Cruces, NM),
- Clack Corporation (Windsor, WI),
- Infilco Degremont Inc. (Richmond, VA),
- Ozone Research & Equipment Corp.,
- Serck Baker Inc. (Huntington Beach, CA),
- Tetra Technologies Inc. (Houston, TX),
- US Filter / IWT (Rockford, IL).

#### 4.4.3. Patents and Patentability

Each year about 1000 new patents are issued, with approximately one third of these patents given to Mobil Research and Development Lab. These patents fall roughly into the five distinct categories listed below:<sup>59</sup>

- i) **New Zeolites.** This group includes the discovery or synthesis of unique zeolites which differ in chemical composition and topology from previously known zeolites.
- ii) **New Expanded Chemical Composition.** Patents granted in this category are given to known structures, including naturally occurring minerals.
- iii) **Synthesis Methods.** These patents are granted for new processes for the synthesis of new or existing zeolites.
- iv) **Activation/Regeneration Methods.** These include any new material or process for regenerating resins which have become deactivated with use.
- v) **Applications/Processes.** By far the largest group, this category includes any new use or process for any new or existing zeolite.

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<sup>59</sup> D. E. W. Vaughan, "Synthesis and Manufacture of Zeolites", *Chemical Engineering Prog.*, Volume 84, #2, February 1988, p. 25-31.

Patents are often granted in this field before the publication of any scientific publication describing its effect because of competitiveness. Resins are also highly patented.

#### **4.5. Market Attractiveness to the Construction Industry**

The use of ion exchange continues to grow in both the public and the private sector. There are three main reasons behind this growth, the first being increased regulatory control over industrial and municipal effluent discharges. As the cost and difficulty in discharge increases, the incentive to use high tech, albeit expensive, options for water treatment also increases. The second reason are new drinking water standards. Recently, citizens and legislature have become increasingly concerned with the water quality of drinking water. On the federal level, this is reflected in new standards of recent amendments to the Safe Drinking Water Act. On the state level, new standards are being promulgated to protect citizens and reflect more regional concerns. In agricultural region, nitrates, of special concern to infants, children and pregnant women, are a widespread concern, easily dealt with by ion exchange, as is currently underway in California. The third reason for continued growth is the increased need for high quality water for industrial applications, such as the production of pharmaceuticals and electronic devices.

##### **4.5.1. Strategic Attractiveness**

The strategic attractiveness of a market for a construction company can be analyzed by looking at five different elements: market stability, the threat of entry, the threat of alternatives, the supplier's threat and the buyer's threat.

The overall market can be defined as the design and construction of ion exchange processes. The market is only low to moderately stable because a large number of construction companies have the capability to design and construct these systems.

Moreover, additional competition exists from larger full-service environmental consulting firms which have the capability to design and then contract out the work. For this reason, the threat of entry is high. Furthermore, the threat of alternatives is high. The threat of alternatives is great. Ion exchange is only one of a number of high-tech options that will remove ions from solutions. While these alternatives vary depending on the contaminant, they always exist; the parameters of the system will determine the cost-effectiveness of ion exchange versus the other possibilities.

There are four main suppliers of resins in this country and a plethora of suppliers of equipment. Therefore, the suppliers of the resins could hold considerable power and thereby take an advantageous position over a buyer. However, because these companies are still competing with each other for market share of the resin market, this is not likely. Furthermore, since development of better resins is still occurring, this will help competition in terms of increased differentiation with each other. The other main suppliers—for equipment—have too many players for substantial threat. Therefore, the overall threat from suppliers is low. The threat from buyers is medium. While other options do exist, it is in the buyers best interest to finish the project, and this requires the cooperation with the construction company. Upon completion, the buyer will be able to achieve industrial, environmental and health regulations, which will allow for lower overall cost.

#### 4.5.2. Cost Effectiveness for the Customer

The main customers for ion exchange facilities are drinking water facilities, POTWs and industrial facilities. Because sanitary wastewater is so dilute in regards to heavy metals, ion exchange is usually not a cost effective method for treating wastewater in Publicly Owned Treatment Works. However, for POTWs that receive industrial wastewater from a number of small industrial facilities, ion exchange might be a cost effective option as part of a pretreatment program, before primary treatment. It is also a

cost effective option for removing ammonia from wastewater for those facilities which only need it during certain times of the year; in those cases, biological treatment is not feasible. For drinking water facilities, it is a cost effective method for certain facilities to remove for the removal of nitrates, fluoride, hardness, and radionucleotides from the raw water. This is often a function of size, with ion exchange being quite cost effective for the small systems and less so for the larger ones. Ion exchange provides a cost effective method for removing heavy metals from industrial wastewater. Because of cost savings from recycling the metals, and reduced discharge and disposal fees, overall costs can be reduced by using ion exchange.

#### 5.4.3. Suitability for the Construction Industry

The market for the construction of ion exchange facilities, either at existing municipal or industrial sites or at new facilities, is judged suitable for a construction company to enter. Suitability for a construction company can be subdivided into four components: planning, design, construction and maintenance.

Planning of ion exchange processes will require water quality testing, site definition and planning, and possibly an environmental assessment of the impact of the facility. It will include planning options for disposal of the spent resin and regenerant brine. Planning is probably most effective if three parties are involved: the owners of the facility, an environmental consulting firm, and the construction company. The design work for the facility is well within the ken of a large construction company; however, a large environmental consulting firm will also be able to do the design work. The construction work will be dominated by the construction industry. The maintenance of ion exchange systems is left to the workers of the facility. Usually it is not a large expense and will be left to a few people. Because of this, it is particularly necessary that safety features, especially for the storage and use of the regenerants, be incorporated into the design.

## **4.6. Investment Requirements**

To be able to provide ion exchange services, a construction company will need to work with one of the suppliers of the resins, listed above. There are many suppliers of ion exchange equipment in the United States, the major ones of which are listed in Section 4.4. Research and development costs, for improvement in resins, will be borne by these companies. The US government is not providing money for installation of ion exchangers. Exceptions to this are for subsidies for studies on certain uses of ion exchange—removing radionucleotides from drinking water—and for uses of military and Department of Energy facilities. Entering this market will require little additional costs for the construction company.

While there is only a low to medium strategic attractiveness for this process, it is necessary for a construction company who is aiming to enter the environmental market to be acquainted with this technology, design and construction. Furthermore, because the investment costs are also low, there is addition incentive to enter.

## **4.7. Case Studies**

This section will present two cases studies designed to show the implementation and installation of ion exchange systems. Both case studies show the utilization of ion exchange to solve drinking water quality problems. Because the preparation of drinking water is, compared to industrial or sanitary wastewater treatment, a relatively simple process, choosing a drinking water facility allows ion exchange to be the main treatment. In sanitary facilities, it is one of many unit processes. For the sake of simplicity, the drinking water facilities were chosen for the case studies. The first is concerned with nitrate removal from a contaminated raw water supply in California. Like many groundwater sources in agricultural districts, this water supply is contaminated with

nitrates. Currently, ion exchange is the most popular method to remove nitrate from groundwater. The second case study centers around the removal of uranium from drinking water. Similar to nitrate contamination, uranium in groundwater can be removed by ion exchange. Unlike nitrate removal, the disposal issues are quite severe and give some insight into such challenges.

#### 4.7.1. Nitrate Removal: McFarland, California.

Nitrate contaminated groundwater is a widespread problem in the state of California. Statewide, the sources for this are leachate from agriculture, animals, and poultry; septic tank waste from individual households; effluent from POTWs, industries and municipalities; and runoff from industry, agriculture and urban areas<sup>60</sup>. While certain areas within the state have a high natural occurrence of nitrates in the soil, these are of minor impact, as water from those regions isn't used significantly for drinking water.

The major source of nitrate in the groundwater is from agricultural activities. In particular, the application of nitrogen-based fertilizers has led to widespread contamination of the groundwater. The total amount applied statewide nearly doubled between 1965 to 1980, increasing from 342,142 to 631,065 tons in only fifteen years. Estimates suggest that approximately 35% of the nitrogen applied as fertilizer is removed as leachate or runoff. In some regions of the state, the groundwater contamination is so severe that farmers no longer need to apply fertilizers to their fields because the nitrate concentration in the groundwater is high enough to provide adequate nitrogen to their crops<sup>61</sup>.

A second major contributor is confined animal lots such as barn yards, dairies, and poultry/turkey ranches. Runoff, animal wastes and wash water all lend to the

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<sup>60</sup> Edward C. Anton, Jeffrey L. Barnickol, and Dean R. Schnaible, *Ibid.*, p. 35.

<sup>61</sup> Edward C. Anton, Jeffrey L. Barnickol, and Dean R. Schnaible, *Ibid.*, p. 36.

problem, as nitrates from these sources leach into the soil and percolate through to the groundwater. As with other agricultural sources, this tends to affect shallow water aquifers more than deep well aquifers. Exceptions to this are from improperly constructed wells that draw from deep well aquifers and allow flow between shallow and deep water areas.

As discussed more completely in Section 4.2.5.2 of this report, nitrates and nitrites in the drinking water put infants, fetuses, and pregnant women at risk. At concentrations higher than 10 mg/l  $\text{NO}_3^-$ -N (weight of nitrogen content) or about 45 mg/l  $\text{NO}_3^-$  (ionic weight per unit volume) in drinking water, approximately twenty percent of all infants will come down with nitrate-induced methemoglobinemia<sup>62</sup>. Some studies have shown that babies born to women who drank water with nitrate levels over 5 mg/l  $\text{NO}_3^-$ -N are prone to birth defects; however, a recent literature review suggests that levels of 10 mg/l  $\text{NO}_3^-$ -N is enough to prevent teratogenic effects from nitrate<sup>63</sup>. A third concern is the production of N-nitrosoamines in the stomach. While no conclusive evidence has proven these N-nitrosoamines to be carcinogenic in humans, they have been proven carcinogenic in animals and are known to be among the most carcinogenic compounds around<sup>64</sup>.

In order to protect public health, the State of California has a Maximum Contaminant Level (MCL) for nitrate in drinking water of 45 mg/l (10 mg/l  $\text{NO}_3^-$ -N). The direct economic consequences of this are manifested in the need to construct additional facilities, either to be built separately or in addition to existing facilities. Orange County, CA has estimated that the cost of nitrate removal is \$375 per million gallons. Overall, in 1986, \$48,706,000 was requested to the state Department of Health by small and large facilities to help come into compliance with the MCL for nitrate<sup>65</sup>.

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<sup>62</sup> Howard Hu and Nancy Kim, *Ibid.*, p. 35.

<sup>63</sup> Howard Hu and Nancy Kim, *Ibid.*, p. 36.

<sup>64</sup> Edward C. Anton, Jeffrey L. Barnickol, and Dean R. Schnaible, *Ibid.*, p. 7.

<sup>65</sup> Edward C. Anton, Jeffrey L. Barnickol, and Dean R. Schnaible, *Ibid.*, p. 8.

However, this amount does not take into account utilities that did not request funds from the state or households that draw drinking water from private wells.

Coming into compliance with the MCL can be accomplished in many ways. Nitrate can be removed from a contaminated source, water can be purchased from another source, or a contaminated source can be blended with a cleaner source such that the resulting mix meets the standard. Methods that are moderately to highly successful at removing nitrate from water include ion exchange, reverse osmosis, and biological treatment. Conventional treatment, lime softening, powdered activated carbon (PAC) and granular activated carbon (GAC) all remove less than 20% of the  $\text{NO}_3^-$  in the supply, and so are only useful if the contamination is quite mild.

McFarland, California is an agricultural community of about 5,200 people located in northern Kern County in the San Joaquin Valley. McFarland is located on a discontinuous belt of highly contaminated groundwater located in the eastern portion of the San Joaquin Valley. This belt stretches from Fresno County south into Tulare County and continues still further south into Kern County, comprising large tracks of land that have been farmed for many decades. Estimates predict that it takes up to 60 years of significantly reduced levels of applied fertilizers to affect the groundwater<sup>66</sup>, suggesting that the situation has yet to reach its apex. In fact, only 49 square miles in Kern County in 1958 exceeded the state MCL for nitrate; however, by 1979, this had increased to 372 square miles<sup>67</sup>, and continues to increase. In 1986, under the California Safe Drinking Water Bond Law of 1986, the Department of Health received loan applications from 14 small systems in Kern County and 2 large ones for the solution of nitrate problems<sup>68</sup>. To put this in perspective, only 2 counties had more small systems and 3 counties had more large systems apply for loans at that time.

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<sup>66</sup> Edward C. Anton, Jeffrey L. Barnickol, and Dean R. Schnaible, *Ibid.*, p. 36.

<sup>67</sup> Edward C. Anton, Jeffrey L. Barnickol, and Dean R. Schnaible, *Ibid.*, p. 25.

<sup>68</sup> Edward C. Anton, Jeffrey L. Barnickol, and Dean R. Schnaible, *Ibid.*, p. 11.

Due primarily to contamination from agriculture and manure, the water supply system for McFarland draws 1 mgd from 4 contaminated wells. In the early 1980s, nitrate concentrations in these wells averaged 16 mg/l NO<sup>3-</sup>-N (70.4 mg/l NO<sup>3-</sup>), and ranged from 6.8 NO<sup>3-</sup>-N (30 mg/l NO<sup>3-</sup>) to 22.1 NO<sup>3-</sup>-N (97 mg/l NO<sup>3-</sup>). In 1983, the utility decided on ion exchange because of removal efficiency and ease of use to deal with the problem, followed by blending with raw water at a ratio of 7 to 3 (treated to raw water). The three stages of the ion exchange process were anion exchange (Duolite A101D resin), regeneration with 6% NaCl brine, treatment of the brine via discharge to a POTW.

Three reaction basins, 1.8 m (6 ft.) in diameter and 3 m (10 ft.) tall, were designed for ion exchange. With this design, one reaction tank is always undergoing regeneration and two are in operation at all times. Surface loading rates are 6.13 l/sec/m<sup>2</sup> (9.03 gpm/ft<sup>2</sup>), with a treated water flow rate of 15.77 l/sec (250 gpm).

This process results in treated water with nitrate concentration of 2 to 5 mg/l NO<sup>3-</sup>-N (8.8 to 22.0 mg/l NO<sup>3-</sup>). This is then blended at a ratio of 7 to 3 with raw water to produce a final product which averages 7 mg/l NO<sup>3-</sup>-N, with a range of 6 to 10 mg/l NO<sup>3-</sup>-N (26.4 to 44 mg/l NO<sup>3-</sup>).

Construction costs for the plant are listed in Table 4.14. The major component is the cost of the ion exchange vessels (31.5%), followed by onsite construction costs (22.9%). Engineering costs were 16.0% of the total.

**Table 4.14 Construction Costs for McFarland, CA Ion Exchange Plant<sup>69</sup>**

Component	Costs (\$)	Costs (%)
Ion exchange unit vessels	111,741	31.5
Onsite construction	81,154	22.9
Resin	56,610	15.9
Engineering	46,388	14.3.1
Brine tank	18,700	5.3
Other	40,045	14.3.3
<b>Total</b>	<b>354,638</b>	<b>100.1</b>

Modified from: EPA 625/4-89/023, p. 208.

The regeneration process consists of a quick rinse, slow rinse and resin reclassification. Using 981 kg (2,162 lb) of salt daily during continuous operation, this produces 2.27 l/sec (36 gpm) of saturated brine and 12 (190.5 gpm) of dilute waste. The cost of this salt requires over 26%, and the largest, of the operating expenses for this plant (see Table 4.15). With a resin replacement rate of 20% per year results in the second largest operating expense for the plant. The cost of the salt and resin total just over 50% of the operating expense; power, labor, and regular operating and maintenance costs are the other major costs.

**Table 4.15 Operation and Maintenance Costs for McFarland, CA Ion Exchange Plant<sup>70</sup>**

Component	Costs (¢/1000 gal)	Costs (%)
Salt	4.3.4	26.6
Resin Replacement (20%/year)	4.3.2	25
Power	2.2	17.2
Normal operation and maintenance	1.9	14.8
Operating labor	1.3	10.2
Miscellaneous	0.8	6.3
<b>Total</b>	<b>12.8</b>	<b>100.1</b>

Modified from: EPA 625/4-89/023, p. 208.

This brine is then discharged to a POTW, where it is diluted by other waste streams and then flows into aeration lagoons. Lastly, the aerated solution is spray irrigated onto fields of animal-feed crops and cotton.

<sup>69</sup> EPA/625/4-89/023, Ibid., p. 208.

<sup>70</sup> EPA/625/4-89/023, Ibid., p. 208.

In conclusion, nitrate can be removed from groundwater by ion exchange. This was shown for a 1 mgd plant in McFarland, California.

#### 4.7.2. Uranium Removal: Coal Creek, Colorado.<sup>71</sup>

The presence of radionuclides in drinking water presents a public health risk to approximately 300,000 people, serviced by over 2000 different water utilities in the lower 48 states. The radionuclides of concern are uranium, radium and radon, and can be removed from water a number of different ways. These include conventional treatment with coagulation-filtration, lime softening, ion exchange, adsorption, aeration, and reverse osmosis. To remove radium or uranium, the best choice for small plants is ion exchange. For radium, cation exchangers are used; and for uranium, either anion or cation exchangers can be used. However, because cation exchange resins only remove uranium effectively (pH less than 7), anion exchange is used for this purpose.

With intentions of protecting human health, the Safe Drinking Water Act of 1974 required EPA to write primary, though non-enforceable, drinking water standards. The National Interim Primary Drinking Water Standards, while addressing radium and gross alpha activity, didn't include standards for either radon or uranium. In 1986, amendments to the Safe Drinking Water Act required EPA to promulgate maximum contaminant level goals (MCLGs), as well as enforceable MCLs. An MCL will be set for uranium, as well as other radionuclide.

Because of potential radiotoxicity and chemotoxicity, uranium presents a public health risk. Of primary concern, both the structure and the function of the kidney is affected by ingested uranium, with symptoms including both inflammation of the organ and changes in the composition of the urine. In order to prevent damage to the kidney, recommendations for MCLs range from 35 µg/l to 100 µg/l, depending in part on the

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<sup>71</sup> Robert T. Jelinek, Ronald L. Clemmer, and Frank J. Johns, *Ibid.*, p. 1-36.

percentage of uranium ingested assumed to be attributable to drinking water. It is likely that the MCL for uranium will be in the range of 10 to 40 pCi/L.

The most serious challenge for all technologies that remove radionuclides from drinking water is disposal. In particular, the disposal of radioactive sludges, brines and spent resins is an unresolved problem. Currently, only three states—Nevada, South Carolina and Washington—have commercial radioactive waste disposal sites in operation. At the time this system was designed, the Colorado Department of Health—the regulating body for the disposal of radioactive material in that state—allowed a total concentration of  $9 \times 10^{-4}$   $\mu\text{Ci/ml}$  of  $\text{U}_{234}$  and  $1 \times 10^{-3}$   $\mu\text{Ci/ml}$  of  $\text{U}_{238}$  to be present in wastewater discharged to a sewer, with a total daily quantity limit of 1000  $\mu\text{Ci}$ . Finally, Federal and State Radiation Control Regulations, at that time, did not address certain key issues, among them disposal of brines and sludges containing radionuclides removed from community water supplies. Since then, regulations have become more stringent, and these may not apply today.

Coal Creek, Colorado School District chose to participate in the EPA study to test the efficacy of a full-scale anion exchange plant for uranium removal that led to the design and construction of this system. The radiochemical water quality of the Coal Creek Well was characterized as having a Gross Alpha Activity of 50–60 pCi/L, uranium concentration of 0.024 mg/l,  $\text{U}_{234}/\text{U}_{238}$  Activity Ratio of 4.3.6, and a  $\text{Ra}_{226}$  Activity level of 1.9 pCi/l.

The ion exchange process—the design criteria are listed in Table 4.16—for Coal Creek draws 10 gpm raw water from the ground and pumps it first through prefilters, next through the ion exchange system, and finally into a storage tank. Protective of the ion exchange system, the disposable prefilters remove any particulate larger than 1  $\mu\text{m}$ ; when these filters become clogged, the system automatically shuts down until they are removed and replaced. The anion exchanger consists of two Ionac A642 anion

exchangers in parallel. As an additional safety measure, they are arranged in this fashion to prevent breakthrough of uranium into the drinking water supply. Finally, the treated water flows into a vented storage tank. This venting allows any radon in the water to blow away. The other major component of the system is the regeneration system, consisting of a brine tank, and pumping and storage facilities for the regenerant wastewater.

**Table 4.16 Design Criteria for Uranium Removal System**

<b>Component</b>	<b>Criteria</b>
Well pump capacity	38 l/min (10 gpm)
Prefilters	2 spiral wound filters, operated in parallel with 1 $\mu$ m pores
Ion exchange capacity	2 Hydromax pressure vessels, operated in parallel, D = 0.4 m, 1.32 m high (16" x 52")
Resin	Sybron Ionac A642, 85 l/vessel, 0.6 m in depth
Loading cycle before regeneration	60,000 Bed Volumes
Brine tank	D = 0.6 m x 1.04 m high (24" x 41" high) 255 kg (560 lb) NaCl storage capacity
Regenerant wastewater tank	1.9 m <sup>3</sup> (500 gal) volume

A conservative decision from the Drinking Water Section of the Colorado Department of Health requires regeneration of the Coal Creek system to occur once every two months, despite the design capacity of once every three months based on the ion column size and system flow rates. The decision to require more frequent regeneration was based on meeting the 1 mCi maximum daily amount of radioactive material that may be discharged to a sanitary sewer. With a regeneration frequency of once per three months, the total amount of radioactivity from regenerating the columns was 80  $\mu$ Ci, well below the 1 mCi limit of the Department of Health. However, due to concerns from an unproved facility, the more frequent regeneration requirement was imposed.

The regeneration process removes the uranium ions from the resin with a saturated NaCl brine. It consists of a backwash of the media with the brine to dislodge any particulate matter from the media and a rinse cycle, to remove the brine from the

resin. Following regeneration, this uranium-laden brine is stored in a 1.89 m<sup>3</sup> (500 gallon) Nalgene storage tank until it can be pumped into a transport truck and taken to the West Jefferson County Junior High School Wastewater Treatment Plant for disposal.

Table 4.17 outlines typical plant performances by looking at uranium analysis for four separate dates. The uranium content of the raw water is on the order of 43 µg/l, while the treated water shows a reduction to 0.3 µg/l. This performance is typical of the system, which had >99% removal of uranium and between 84 and 94% removal of gross alpha activity for most of the operation. On February 3, 1988, the system was regenerated for the first time. The elevated concentration of uranium suggests that the rinse cycle was insufficiently short, and the uranium was not completely removed from the resin. This was fixed in later runs.

**Table 4.17 Results of Specific Uranium Analyses**

Sample Type (Date)	U <sub>234</sub>	U <sub>238</sub>	Average Ratio U <sub>234</sub> /U <sub>238</sub>	Uranium Concentration (µg/l)
Raw water (October 6, 1987)	31.2 29.3	8.04 8.42	4.3.68	39.7
Raw water (Nov. 18, 1987)	29.3 31.2	8.94 8.78	4.3.43	47.7
Treated water, after column one, before regeneration (February 3, 1987)	0.057 0.038	0.022 0.017	2.34	0.3
Treated water, after column one, after regeneration (February 3, 1988)	146 162	39.0 50.1	4.3.49	320

With elevated levels of uranium in the effluent and the sludge, the effects of adding the regeneration wastewater to the wastewater treatment plant can be seen in Table 4.18. These concentrations are quite high and could be a concern, should state or federal regulations change. However, after four months without wastewater from the ion

exchange plant, the uranium concentrations and the gross alpha activity of the effluent and sludge have returned to normal.

**Table 4.18 Fate of Regeneration Wastewater at Wastewater Treatment Plant**

Sample Date	Description	Uranium Concentration (µg/l)		Gross Alpha (pCi/l)	
		Effluent	Sludge	Effluent	Sludge
September 2, 1987	After regeneration wastewater was introduced	5	46	23±6	58±7
October 7, 1987	After regeneration wastewater was introduced	43	2455	---	---
February 2, 1988	No regeneration wastewater had been introduced for 4 months (background)	14	0.5	18±5	160±17

The capital costs of this ion exchange system—including equipment, engineering and construction—totaled \$8,900 in 1986, and are summarized in Table 4.19 in terms of actual cost and percentage of total cost.. However, these figures do not reflect the total capital costs of such a system due to the exclusion of certain preexisting components to the system such as the construction of the well, the well pumps and the building that houses the system. If these were included, the costs of this system would be considerably more expensive.

**Table 4.19 Capital Costs for Uranium Removal System**

Component	Cost (\$)	Cost (%)
Ion exchange system: prefilters, ion exchange columns, resin, brine tank, manual and automatic valves, pressure gauges, piping and appurtenances	3,800	42.7
Regenerant wastewater system: regenerant wastewater tank, wastewater pump, and hose	1,000	11.2
Labor for installation (160 hours)	2,100	24.3.6
Engineering: assist in ordering equipment, observe installation, permitting, record drawing, O&M manual	2,000	22.5
<b>Total Capital Cost</b>	<b>8,900</b>	<b>100</b>

The total operating and maintenance (O& M) costs for the Coal Creek uranium removal system are about \$6.70/1000 gallons treated. This cost can be divided into two main components: routine O & M costs and disposal costs. Routine O & M costs, \$4.30/1000 gallons treated, include the labor for routine operation, regeneration and sampling; sample analysis; prefilter and resin replacement; salt for the brine solution; and the electricity. Disposal costs, \$2.70/1000 gallons treated, include the cost of transporting the brine as well as the cost of analyzing the effluent and the sludge from the wastewater treatment plant for uranium. These costs do not reflect the design criteria of regeneration following 60,000 bed volumes treated (approximately once every three months), but instead are the actual costs for the imposed requirement of regeneration every other month. At design performance, the overall costs could be reduced to \$5.50/1000 treated. The routine O & M costs are on par with other small systems, while the treatment costs are higher than those not dealing with radioactive contaminants. Moreover, should regulations change, requiring alternate means of disposal of the uranium-laden brine, the disposal costs, and hence the overall costs, could increase significantly. Lastly, with environmental laws becoming more stringent, the likelihood that a company involved would be involved in long-term cleanup plans and expenses exists.

In conclusion, uranium can be removed from groundwater by ion exchange, as was demonstrated by a small plant at Coal Creek, California. As disposal regulations tighten for sludge and wastewater effluent, costs and risk will increase.

#### **4.8. Conclusions**

This report outlines the basic uses, theory and components of ion exchange. Since early in this century, ion exchange has provided a method for increased water quality. Currently, ion exchange is used in the areas of municipal and industrial water and wastewater treatment as a method to remove undesired ions from aqueous solutions.

Applications include the removal or reduction of nitrates, ammonium ion, alkalinity, hardness, radionucleotides, and heavy metals from water. The resulting water is cleaner, safer, and of higher quality.

This technology component of this report outlined the basics of ion exchange chemistry, characteristics of ion exchangers, and various ion exchange systems for the solution of common water quality problems. In the regulatory section, various aspects concerning the acceptance of ion exchange by the public and government were address. Furthermore, additional legal and environmental liabilities were discussed. It was noted that the disposal of spent regenerant and ion exchange resins could present the largest challenge to the widespread use of ion exchange. Disposal issues are a function of the contaminant; the spent regenerant and resins might be classified as radioactive and/or hazardous, if radionucleotides and/or heavy metals were exchanged. The market for ion exchangers was analyzed; general market characteristics, major manufacturers and patents were discussed. The market attractiveness to the construction industry was analyzed. It was noted that for a construction company which wants to enter full-scale the environmental market competence in this area is necessary. The investment requirements for entering will be low, another incentive. Lastly, two case studies, one on nitrate removal and the other on uranium removal, tied everything together.

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## **Chapter 5. Conclusion**

### **5.1 Conclusion**

Fresh water is a precious natural resource. Modern life depends on water for everything from drinking water, to enabling sanitation facilities to exist, to allowing agriculture to grow in the desert, to providing electric power. Almost every activity in modern society not only requires fresh water, but adds to the problem of water pollution. Daily life contributes to the sewage loads; runoff from agriculture contains pesticides, fertilizers, and nitrates; industrial wastewater is often contaminated by a wide variety of metals, solvents, and other organics.

However, due to a combination of environmental legislation and advances in technology, it is now possible to clean up even the dirtiest water. Some of these technologies merely transfer the pollution from one media to another; for instance, ridding the water of volatile organics by releasing them to the air. Then capturing the volatile organics in a carbon filter before they escape up the smokestack or out the window. Thus, the pollution was transferred twice, once from the water to the air, and again from the air to a solid media. The train of pollution continues. Other technologies, with the power of electricity behind them, separate pollutants such as metals out from the aqueous portion of the waste stream, enabling the contaminants and the water both to be recycled. However, this technology still comes at an additional environmental price—the harm to the environment from the production of electricity. While this is often ignored, the price is high: 2% of all electricity produced in the US is used to run wastewater treatment centers. As the treatment levels needed increase, the amount of electricity used will only grow higher. The train of pollution continues. Other technologies—chemical oxidation technologies—reduce the toxicity of the waste, by oxidizing virulent organics to CO<sub>2</sub>, H<sub>2</sub>O and inorganic salts, but still add to other forms of pollution by their dependence on

electricity. Natural systems are another story. They reduce the toxicity of the wastewater and other aqueous waste streams without the dependence on electricity. Because of this, they are not contributing to the pollution problem on the one hand, by claiming to solve it on the other. However, natural systems are only possible in areas where land is cheap, usually away from large population centers, and are only good for certain types of problems.

Zero discharge is the concept of total recycle and reuse of water, metals and organics within a factory or industrial facility. In a zero discharge world, either there is no effluent leaving the site or the effluent leaving the factory is not contaminated by solvents or other organics, metals, excess salts or other contaminants, but is as clean as the influent. Sludge from such a facility will be used, optimally, for beneficial reuse purposes. Advances in instrumentation now allow for the most minute concentration of contaminant to be detected, which can result in water contaminated by parts per billion being labeled as dirty, unacceptable, worthy of cleanup. While in concept, this is an attractive alternative, like many other concepts, it will be difficult to put into action, due to the costs of implementation. Each unit process, whether it is biological, physical or chemical in nature, adds additional costs to the overall budget. Whereas some processes, like ion exchange for metals, will result in cost savings due to the recycling of the metals, for the most part, there will be additional capital and operating expenses. Municipal wastewater treatment facilities can also be instrumental in zero discharge policies. Reusing and recycling wastewater—either for consumptive or environmental purposes—results in effluent that is far cleaner than effluent from secondary treatment centers. This translates to cleaner water downstream of the plant, and less pollution overall entering the environment.

The pollution control industry is regulatory driven and consumes around 2% of the US GNP. The water pollution control industry is driven primarily by the Clean Water Act, the Safe Drinking Water Act, and subsequent revisions. These acts have made the water

pollution control industry the largest of all the media. Without the impetus from the federal—and in some cases state—environmental legislation, this industry would be far smaller than it is now. Because it is regulatory driven, the pollution control market is to a certain extent a function of the whims of government and popular opinion. As long as the public, and behind the public the government, feels that environmental quality is important, the market will exist. As it currently stands, the market has an annual size of tens of billions of dollars, and because of its enormity and projections of future growth, seems worth entering. However, the current approach to solving environmental problems—the so-called end-of-the-pipe solutions such as ion exchangers and chemical oxidation devices—will not be in vogue forever. Eventually, environmental pollution control will be solved by process change and more natural solutions, ones that more closely mimic nature and are less heavily dependent on energy.

This thesis examined the water pollution control industry in regards to the construction industry. The issues surrounding wastewater reuse and recycle were discussed. Wastewater can be used for both consumptive and environmental purposes, including the replenishment of depleting groundwater sources, meeting water budgets and providing water for agriculture, industry, and recreational facilities in arid regions. In the United States, while wastewater is used extensively, its use for direct potable reuse has been limited to a few instances borne out of necessity. However useful wastewater is for certain purposes, if not carefully monitored, it can be destructive, to both public health and the environment. It can be damaging to human health by helping to spread contagious diseases, while to the environment, excess salts, metals, nutrients, or organics can be damaging. On the other hand, when monitored carefully, wastewater can be beneficial.

Methods to clean up municipal and industrial wastewater vary in their range, cost, effectiveness and other such variables. This thesis was separated into three general areas. The first was wastewater recycle and reclamation. In this chapter, three groups of

technologies were discussed: membrane separation processes, which act as sieves and capture all contaminants larger than a given pore size; aquifer storage recovery, which provides a relatively low-cost method for a community to expand its water supply, and natural systems, which are used to provide polishing for wastewater, without extreme dependence on electricity. The next general section was on chemical oxidation processes. These technologies are dual purpose. Not only do they have a future in wastewater treatment centers, but they are applicable to the destruction of hazardous organics, and so fall into the realm of technologies that help solve the problem of hazardous wastes. Furthermore, if the technologies are perfected a bit, some will be useful for dealing with the problem of mixed hazardous and radioactive waste, by oxidizing the hazardous components, leaving radioactive waste that can be commercially disposed of. The last section dealt with ion exchange. This technology not only removes ions from water and wastewater systems, it can be used as one of the many processes that can be used to deal with radioactive waste and mixed waste by removing radionucleotides from solution. The technologies were discussed individually; however, for a construction company to enter effectively the wastewater reuse and recycle market, a competence in not only these technologies, but others, would be necessary.

Relating these technologies to the construction industry, many variables were discussed. Those included the market characteristics; the attractiveness of the technologies or group of technologies to the construction industry; the legal, regulatory, and social environment surrounding the technologies; and the investment requirements of the technologies. For each technology, or technology group, a case study was included to illustrate certain problems, costs, and results in implementing the technology to solve a water pollution problem.

Water pollution can be prevented. The government and the general public both feel the prevention of further water pollution is a worthwhile goal. To meet this, industry and

municipalities alike will spend billions of dollars a year, opening up a large field to enter. Construction companies, by their very nature, have long been involved in the design, construction and implementation of large, public works projects. Water pollution control will continue to be a market for such companies, even as the focus shifts away from traditional secondary treatment centers, to ones that more adequately deal with the plethora of pollutants that are being generated every day and provide effluent that is clean and safe enough to drink.