OVERVIEW OF EMERGING PRODUCED WATER TREATMENT TECHNOLOGIES

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ABSTRACT

In many areas of the Rocky Mountain and Mid-Continent regions of the U.S., produced water management is a major factor in the feasibility of oil and gas field development. These are areas where the existing reinjection well capacities in some basins are not sufficient to dispose of growing volumes of produced water. Alternatives to reinjection include treatment of produced water streams to meet criteria for surface discharge, infiltration and beneficial reuse with brine volume reductions sufficient to extend the life of existing Class II reinjection wells. Over the past decade, a number of commercial and advanced technologies have been developed and deployed for the handling of produced waters. This presentation will provide an overview of emerging processes that have the potential of improving the economics of treating produced waters to meet objectives of brine volume reduction, surface water discharge, infiltration for groundwater recharge and beneficial use. Some major technical challenges include the control of soluble and free oils, the fouling of membrane-based desalinization processes, the control of elevated levels of soluble volatile acids, and the economical control of BTEX. Promising processing approaches to improve the economics of reaching treatment goals suitable to achieve certain water management objectives will be discussed.

INTRODUCTION

The production of oil, conventional natural gas and coal bed natural gas (CBNG) result in the co-generation of substantial flows of water from the hydrocarbon-bearing formation. Produced water streams are usually separated from the gas at or near the wellhead; because of the composition of these streams, they must be disposed of in a manner that is protective of human health and the environment. In general, produced waters are of high mineral content, containing total dissolved solids (TDS) concentrations in the range from 500-6,000 upwards to greater than 100,000 mg/l for coal bed natural gas and conventional non-associated gas, respectively.

Currently, 14-18 billion barrels of produced water are generated each year with the production of oil and gas in the U.S. (API, 2000; Veil, et al., 2004). In the natural gas industry, more than 60% by volume of produced water is presently reinjected (recycled) into specially designated reinjection horizons which are deemed to be geologically isolated from potential underground sources of drinking water. This produced-water reinjection percentage rises to greater than 90% when produced water from oil and gas operations are considered together; many producing formations are designed to employ water injection as a means of maintaining pressures and integrity of production operations. While the injection of produced water is both environmentally acceptable and economically manageable in most cases, certain areas of the U.S. (e.g. certain basins of the Rocky Mountain States and the Mid-Continental States) are already feeling the constraints of limited reinjection capacities and increased regulatory restrictions that make it necessary to consider alternative methods for cost-effective produced water management. It is conceivable that in future years, the oil and gas industry will be faced with the challenge of disposing of more than 1 billion barrels of produced water each year using methods other than deep well injection.

The purpose of this paper is to review the alternate produced water management options that are being considered by industry and regulators and to provide an overview of treatment processes that could emerge in the industry to support these alternatives, including those that are aimed at the beneficial use of these water streams.

BACKGROUND

The general nature of produced water production and composition as well as the environmental issues and current practices associated with the management of produced water streams are covered in several recent reviews (Veil, et al., 2004; Boysen, et al., 2002; Doran and Leong, 2000). Since produced waters represent more than 80 percent of the volume of wastes generated by E&P activities of the oil and gas industry, it is important that these streams are handled and disposed of in a manner that is protective of human health and the environment.

Regulatory Considerations

Environmental regulation of produced waters is addressed in three federal laws and a compliment of laws in various states; the websites where such regulations can be found is provided in the literature (Boysen, et al., 2002). Regulatory control of the injection of produced waters is governed by the Unerground Injection Control Program (UIC) of the Federal Safe Drinking Water Act. The purpose of

this act is to ensure that injected produced waters are confined in the injection zone in a manner that does not contaminate a water bearing geologic formation which is presently or may in the future serve as an Underground Source of Drinking Water (USDW).

Produced waters which are discharged to surface waters or the U.S. are regulated under the Federal Clean Water Act. Under this act, no effluent from an industrial operation may be discharged to surface waters except in accord with the provisions of a permit issued by the National Pollutant Discharge Elimination System (NPDES); NPDES permits are usually administered by the states. With respect to the onshore oil and gas industry, the only produced water discharges that can obtain an NPDES permit are those from a small daily volume stripper wells and produced water which is of sufficiently good quality to be acceptable for beneficial use in areas of the United States west of the 98th Meridian. No other onshore discharges of the oil and gas category can be permitted under the Clean Water Act except in very specific circumstances. For instance, water produced in association with CBNG production in Alabama is discharged based on regulatory considerations in that state.

It is important that the Resource Conservation and Recovery Act (RCRA) --- the third federal environmental statute impacting the oil and gas industry --- explicitly excludes E&P wastes, including produced waters, from inclusion under the hazardous waste management provisions of Subtitle C of the Act. It also states that residual salts derived from evaporation and demineralization of produced waters are included in the list of E&P exempt wastes. Like the Safe Drinking Water Act, federal law allows that the individual states can conduct hazardous waste programs that may be more stringent than federal RCRA. For example, California law does not exempt E&P wastes from its hazardous waste program; this means that an E&P waste stream that indicates a hazardous characteristic on contains a hazardous constituent can be regulated as a hazardous waste. Therefore, it is important to be as familiar with state-level programs as well as federal statutes in the evaluation of produced water options for a particular region.

Current Options in Produced Water Management

At least nine out of ten barrels of produced water generated from oil and gas fields are disposed via Class II injection wells. This means that the balance of these produced water streams will require options for beneficial use and/or disposal. In many basins of the U.S., the generation of produced water is already approaching maximum capacities for existing options of produced water disposal. Current options for dealing with this problem include water minimization that include techniques for blocking water from entering the well (e.g. mechanical blocking devices and water shut-off chemicals) and methods for preventing water from coming up to the surface (e.g. downhole oil/water separators) which are reviewed and described by Veil, et al. (1999) and Langhus (1996).

Regulations in the Rocky Mountain States of Wyoming, Colorado, New Mexico, Utah and Montana also recognize a number of above-ground produced water management alternatives, including evaporation, land application, surface discharge through the NPDES permit program, and a number of beneficial uses including irrigation, live stock ponds, maintenance of wetlands habitat, and aquifer recharge (Veil et al., 2004; Boysen et al., 2002). Nearly all of these options require compliance with water quality criteria; implementation of these options will therefore require, in many cases, the ability to upgrade water quality. Since water quality compliance is not inexpensive, producers are seeking more information on the economics of produced water management, disposal, and deployment of treatment technologies.

The technical and economic feasibility of implementing treatment technologies for transforming produced water into beneficial use water streams will depend upon the initial composition of the produced waters, the type of processing to be used, and the quality of the finished effluent that is needed to meet regulatory criteria for the targeted end use for the product water. Having a sustainable end use market is also important. As large parts of the continental United States suffer water shortages due to drought and/or population growth, reclamation of water from various sources (including produced water) will become increasingly important. It is, perhaps, fortuitous that produced water is often generated in large quantities within the arid regions of the U.S. Examples of good opportunities for beneficial use water markets may be found in the natural gas production areas of the Rocky Mountain region of the U.S., including the coal bed natural gas (CBNG) production fields of the Powder River Basin (PRB) of Wyoming and Montana. This sector probably represents the greatest initial opportunity for deployment of beneficial use systems since CBNG waters are generally low in total dissolved solids (TDS), organics and other constituents of regulatory interest and would be among the lowest cost to treat compared conventional produced water.

Produced Water Composition

Produced waters are highly varied in composition, a result that might be expected given that they arise from wide ranging formation characteristics, oil and gas hydrocarbon compositions, and a host of activities engaged by companies as a result of well development and maintenance. Examples of compositions of several produced waters compared to approximate water quality criteria required for several end uses of the treated water are shown in Table 1. A breakdown of the categories of constituents of concern in produced water is shown in Figure 1; this breakdown is organized to illustrate the potential opportunities of using certain processes to achieve produced water separations. Constituents can be considered to be divided into organic and inorganic compounds. Inorganic constituents in produced water generated in the field are either insoluble (examples include scale, precipitates, grit, inorganic colloids, etc.) or soluble. Soluble salts are comprised of anions and cations. Some examples of cations in produced water include the monovalent cations of sodium and potassium and the multivalent cations of iron, calcium and magnesium. Major anions include chloride, sulfate, carbonate and bicarbonate. Non-charged soluble inorganic species are also present; examples of these include silicate (H_4SiO_2) and Borate (H_3BO_3).

Organic compounds are either separable with gravimetric and deoiling technologies (oils and greases fall into this category), or they are soluble, requiring more complicated processing for removal. Soluble organic constituents can be divided into compounds that are dissociable into the ionic form (examples include phenol, mono-carboxylic acids and di-carboxylic acids) and into compounds that are not dissociable (such as non-ionic soluble oils and glycols).

In general, most produced waters are circum-neutral with pH values between 6 and 8. Buffering is usually provided through the presence of bicarbonate. In the normal storage and handling of produced waters, pH values will remain neutral unless caustics or acids are added in the course of treatment.

Treatment Requirements to Achieve Beneficial Use Goals

Growing interest among energy companies and the regulatory community in the conversion of produced water to water streams suitable for beneficial use, surface discharge and/or groundwater recharge points to an increased need for treatment that meets certain water quality criteria. In some cases, produced water may be of a “good quality” to begin with and may not require much treatment, if any, to

be considered for beneficial use. Examples of this situation may be found in coal bed natural gas fields where some of the produced water streams are naturally low in total dissolved solids and in organic content (Arthur, 2003). In most cases, however, treatment will be required to meet beneficial use effluent standards; in the majority of applications, the most pressing treatment needs would include one or more of the following:

- Oil and grease removal
- TDS reductions in product water
- Decreased concentrations of benzene
- Decreased concentrations of biological oxygen demand arising from soluble organics
- Control of suspended solids
- Reduction in brine volumes requiring disposal
- Control of total and fecal coliforms in final effluent stream
- Removal of special constituents of concern, such as boron, that restrict an end use (such as irrigation)
- Adjustment of the sodium absorption ratio parameter (SAR) to avoid clayey soil damage in land application (irrigation, infiltration, groundwater recharge, etc.).

In the management of produced waters generated on shore and off shore in past years, the first four items in the above list have been of highest priority as objectives in treatment. As attention is turned toward developing produced water as a source of beneficial use water supplies, the last four items in this list will become increasingly important.

A produced water management parameter of recent evolving importance among state regulatory agencies is the sodium absorption ratio or SAR. Sodium adsorption ratio (SAR) is a function of the ratio of sodium to the sum of calcium and magnesium cations; this parameter is defined by the following equation:

Equation 1.

$$SAR = \frac{[Na^{+}]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}}$$

where the concentrations are in meq/l. Highly "sodic" soils (those with SAR greater than 12) suffer from decreased water penetration; the specific SAR value at which soil damage begins depends on the nature of the soil itself. Optimum conductivity and SAR must be determined on a site-by-site basis. As seen in Table 1, acceptable SAR values depend on the end use for the produced water; criteria for SAR values are also controlled to a high degree by each state. In many cases, SAR numbers less than 6 with be required for beneficial use treatment systems. From the equation, it can be seen that reducing the SAR from high values to acceptable levels can be accomplished through processes that either decrease sodium or increase calcium and magnesium.

TREATMENT PROCESSES

Achieving current and future goals to reduce volumes of produced water brines directed at underground injection and to develop E&P sites as a new source of beneficial use waters will require implementation of treatment trains that utilize cost-effective unit processes. Treatment processes that have been commercially used in past decades in the oil and gas industry have focused mainly on the removal of oils and greases, scale control, and suspended solids and brine volume reduction using evaporation impoundments.

As treatment objectives focus on enabling higher value uses of produced water, such as irrigation, livestock watering, groundwater recharge, and habitat restoration, greater attention will turn toward processes that have even greater capability in the removal of contaminants and in water conditioning to meet certain water quality specifications for beneficial use. In addition to oil and grease and suspended solids removal targets, treatment objectives are now encompassing the removal of organic compounds to meet biochemical oxygen demand requirements for surface discharge (pursuant to compliance with NPDES permits). Agricultural beneficial uses for produced water (especially those emphasizing irrigation and watering of livestock) have generated greater interest in the application of treatments for the removal of constituents of toxicological significance such as BTEX and boron.

Achieving beneficial use, groundwater recharge and surface discharge treatment objectives will require in many cases the use of a combination of unit processes, since there is not a single unit process that is capable of performing all types of separation. Each unit process has its "niche" in terms of being able to perform certain treatments on produced water. These niches are illustrated in Table 2 which indicates the appropriate application of a number of unit processes that are potentially applicable to produced water treatment. From this table, it can be recognized that each process has application to a limited number of basic functions (e.g. deoiling, suspended solids removal, iron removal, desalinization, etc.)

Unit processes that are already applied or potentially applicable to produced water treatment are described in Tables 3-7; these tables classify unit processes according to their major functions or capability, but also discuss their stage of development in application to produced water as well as their strengths and limitations. From these tables, it is apparent that water treatment unit processes fall into at least one of the following general categories:

- Established processing
- Recently-deployed processing
- Emerging technology

"Established processing" is a category that covers unit processes that have been used for produced water treatment for many years (decades) in the oil and gas industry. These processes are well understood and have been of proven value and performance in their application to produced water treatment. Examples of such processes, all of which have served the industry very well for their intended purposes, include:

- API separator, deep bed filter, hydroclone, induced gas flotation, and sand filtration for suspended solids removal and deoiling;
- Aeration/sedimentation for iron removal and suspended solids control; and,
- Activated carbon for the adsorption of organic contaminants.

"Recently-deployed processing" encompasses unit processes that have been applied to produced water processing on a commercial scale mostly within the last decade. Treatment methods in this category have been applied to produced water in large scale operations at multiple locations for purposes

that represent another step beyond traditional produced water processing toward demineralization and water conditioning. These processes include:

- Precipitation and ion exchange for softening (i.e. removal of calcium and magnesium) and iron control;
- Water conditioning (chemical additions and ion exchange) for adjustment of the SAR parameter;
- Freeze thaw evaporation (FTE®) for the desalinization of produced water.

Extensive use of the first two of the above process categories in other industries has built a sizable information base on the design and operation of these treatments. For example, increased application of water conditioning for iron removal, softening and SAR control is being applied to areas where CBNG waters are processed for beneficial use. A photo of a produced water currently undergoing zeolite ion exchange treatment (for removal of barium and other scale-forming cations) in the Powder River Basin of Wyoming is shown in Figure 2.

More recently, freeze thaw evaporation (FTE®) has been commercially introduced at a number of sites where conventional produced waters are treated for brine reduction (Boysen, et al., 2002). The obvious limitation of this technology is that it must be deployed in the region U.S. with sufficient days of freezing weather as depicted in Figure 3. Costs for FTE and some conventional processes and produced water handling practices applied to produced water have been estimated by Boysen (2000) and Hackney (1996), respectively. The costs can be compared to the wide span of costs reported for Rocky Mountain Region for produced water disposal which range from $0.01 to over $5.00 per barrel (42 gallon) charged by commercial waste haulers (Boysen, 2000) to estimate the cost of water processing that can be commercially viable. These comparisons may also point to the need for certain “emerging technologies” to achieve reliably competitive costs in water handling and processing.

The "emerging technology" category covers unit processes that have been piloted or are in the experimental stage of development for application to produced waters. These are processes that may have extensive application to other industries or for other applications of water treatment, but have not yet been fully operational at full scale with the numbers of facilities that would classify the process as a commercial practice in the oil and gas industry. Processes belonging to this category include:

- Robust attached film biological processes that can tolerate elevated salinities;
- Reverse osmosis and electrodialysis for demineralization of produced water; and,
- Chemically enhanced ultrafiltration for improved removal of soluble oils.

PRODUCED WATER DEMINERALIZATION

Although there are produced water streams (such as some streams in coal bed natural gas (CBNG) areas) that do not need much treatment beyond suspended solids control minor electrolyte conditioning to achieve water quality objectives, the vast majority of produced waters require considerably more processing in order to reach goals of surface discharge, groundwater recharge or beneficial use. In most cases, the generation of water suitable for higher use will involve some degree of demineralization for the removal of TDS from the product water and for the reduction of brines requiring final disposal.

Reverse Osmosis Option

To pursue the option of demineralization, some energy companies have explored the use of reverse osmosis (RO) as a means of achieving brine volume reduction for CBNG waters and for conventional gas well produced water. A schematic of the RO process is shown in Figure 4. For both types of produced water, pilot tests have shown that although a 3:1 reduction of brine volume could be achieved, and although a deionized product stream of good quality water could be initially produced, many operational problems involving membrane fouling surfaced in the initial attempts in the field to deploy the technology (Lawrence, et al., 1995; Doran and Leong, 2000). These operational problems arise from the complex composition of the produced water and the effects of certain constituents on the membrane material. Free and dissolved oils collect on RO membranes causing them to lose their permeability. Particulates, including precipitates, tend to scour the surface of the membrane causing the filter material to break down mechanically. Soluble hydrocarbons including volatile acids and BTEX can promote the growth or microbial films on reverse osmosis membrane surfaces, causing them to lose their separation performance. These fouling problems are largely responsible for the lack of deployment success of RO in the oil and gas industry. Recent advances in applying rigorous preprocessing of produced water show potential of improving the reliability of RO in achieving economical brine reduction; successful preprocessing, is often complex and site specific.

The choice of RO for demineralization of produced waters is understandable given that RO is the predominant desalting technology in the United States; in 1997, there were approximately 2000 RO plants with a total capacity of 800 million gallons per day (MGD). Most of these plants were used to process brackish waters with and seawater to supplement water supplies for municipalities and industry. Under optimal conditions, the RO technology is applicable to the demineralization of waters with a wide range of salinities, from slightly brackish at TDS levels as low as 2,000 - 3,000 mg/l TDS to the ionic strength of seawater (35,000 mg/l TDS).

Electrodialysis Option

While there have been many tests of RO on produced waters, very little attention has been paid to the capability of the “other” desalinization process of electrodialysis or ED, especially as applied to the treatment of produced waters. There is, however, long-standing operational success with this process in other industrial and municipal applications; currently, there are 250 plants operating in the U.S. with a total capacity of about 40 MGD. Based on these applications, it would appear that ED seems to have its best fit with waters of moderate strength (3,000 - 15,000 mg/l TDS).

Electrodialysis is an electrically-driven separation conducted at very low pressure drops across the process (usually less than 25 psi) -- in contrast to RO which is a pressure-driven, size-exclusion filtering process.. The electrodialysis (ED) process, as applied to the treatment of salt water, depends on a number of principles. Soluble salts exist in water as ions, with positive and negative charges. This includes positively charged ions (cations) such as sodium, calcium, magnesium, and metals as well as negatively charged ions (anions) such as chloride, sulfide, sulfate, and bicarbonate. When electrodes are connected to an outside source of direct current, an electrical current is passed through the water and the ions migrate to the electrode of the opposite charge as shown in the schematic for ED of Figure 5.

To achieve good separation, the movement of ions (TDS) is controlled by the addition of selectively permeable membranes that form watertight compartments, as shown in Figure 6. Each anion transfer membrane allows only the transfer of negatively charged anions (e.g. chloride, sulfate,

bicarbonate, nitrate, sulfide, etc.). The cation transfer membrane (C) allows only the passage of positively charged cations (calcium, magnesium, sodium, potassium, metals, etc.). The membranes are electrically conductive and are impermeable to water flow, even under pressure.

Using this arrangement, concentrated and diluted solutions are produced in the spaces between the alternating membranes. The spaces between the membranes are called cells and two adjacent cells are called a cell pair. The conventional electrodialysis process consists of several hundred cell pairs and is called a membrane stack. In practice, the electrodialysis system is composed of a series of stacks. Periodically, chemicals can be passed through the stack to achieve a clean-in-place operation.

A commercial electrodialysis system used in the demineralization of water is shown in Figure 7. An electrodialysis processing train usually includes the following steps:

- Pretreatment
- Membrane Stack
- Low-pressure circulating pump
- Power supply for delivering direct current
- Post-treatment for water conditioning

Over the last thirty years, a number of features have been develop to improve the electrodialysis process. In the 1970's, the electrodialysis reversal (EDR) process was introduced into the commercial sector. The EDR process operates on the same principle as the conventional ED unit except for a couple of features. First, the brine and product channels are constructed identically; second, at intervals of several times an hour, the polarity of the electrodes is reversed and the flows are simultaneously switched so that the brine channel becomes the product water channel and vice versa. The reversal feature is useful in breaking up films, scales, and other deposits and flushing them out of the process before they can build up and foul the membranes. The EDR configuration, however, does add some added complexity in design and control. For many water treatment applications, effective clean-in-place operations can be accomplished with conventional automated chemical treatments.

Over the years, the electrodialysis has been applied to the processing of brackish saline waters to achieve partial demineralization to meet criteria for surface discharge or for water supply uses. Most of these applications did not require or utilize EDI. Although valuable for many industrial applications requiring the generation of ultra-high quality water, the performance of EDI is usually in excess of the levels of treatment required for upgrading brackish water or for the desalinization of produced waters, where effluents containing less than 500 mg/l would be environmentally acceptable.

The past successful experience in applying conventional electrodialysis and EDR processes to the demineralization of brackish waters strongly suggested that these same processes could play a role in providing useful separations of produced waters at a reasonable cost. This body of experience indicated that electrodialysis has the following potential characteristics that would facilitate its application to the treatment of produced waters:

- The ability to simultaneously separate a wide range of ionic constituents – not only sodium and chloride ions, but also barium, heavy metal cations and volatile acids (at neutral pH levels) that may comprise the majority of soluble organics in most produced waters.
- Applicability to the treatment of produced waters of moderate strength up to 15,000 mg/l TDS.
- The capability for high recovery of demineralized water where the product stream is more than 90 percent of the flow of the influent stream (compared to 50 to 70 percent with reverse osmosis).

- The possibility for increasing the brine volume reduction factor to 10:1 or more (compared to 3:1 with reverse osmosis).
- Good control over the degree to which salts are removed from the water stream through adjustments of flow and electrical energy inputs.
- Higher tolerance for higher levels of suspended solids compared with reverse osmosis (requiring less rigorous pretreatment for particulate removal).
- Low chemical use for pretreatment.
- Greater membrane life expectancy of 8-10 years for electrodialysis (compared with 1-2 years for reverse osmosis).

Electrodialysis may have application to a significant fraction of produced waters requiring beneficial use solutions. Many produced water streams, including most produced water streams in CBNG areas, contain modest levels of total dissolved solids that are less than 15,000 mg/l; these waters may only require partial demineralization to achieve good brine volume reductions and a demineralized steam suitable for surface discharge and/or beneficial use.

INTEGRATED PROCESSES FOR IMPROVED PERFORMANCE

The principal challenge of using either membrane-based demineralization process (i.e. whether implementing RO or ED) will be the protection of these processes from produced water constituents that can damage the membrane surfaces. Since the demineralization processes of RO and ED are fundamentally different, the nature and level of ancillary processing required to promote stable and economical operation will undoubtedly be different as well. Several fundamental categories of preprocessing will need to be considered with both demineralization processes; these include:

- Flow equalization
- Deoiling
- Suspended solids removal
- Soluble organics removal for biological growth control

In the handling of most conventional produced waters, all of the above pretreatment elements will likely be required. On the other hand, some produced waters have low natural levels of total petroleum hydrocarbons (TPH) that are below 0.1 ppm and total organic carbon levels below 5 ppm; examples of such streams can be found in many coal bed natural gas production basins. For lightly impacted produced waters, pretreatment steps involving deoiling and soluble organics removal may not be needed to protect demineralization processing.

Removal of suspended solids, oil and grease from produced water will, in most cases, be required before demineralization can be performed on produced waters. These processing steps depend, in large part, on the use of filtration technology. Filtration technologies operate on the basis of size exclusion; the appropriate choice of filtering technology will depend upon the particle size of the sought-after contaminant. The application niches of various filtering technologies relative to the sizes of particles that are removed are shown in Figure 8. All of these filters should be used within the context of performing pretreatments that are desired within the context of an “integrated” produced water treatment system.

An example of integrated processing for the implementation of reverse osmosis is shown in Figure 9; this flowscheme (developed by ARCO Western Energy) was used as the basis of a pilot plant that processed raw conventional oil field produced water to yield a demineralized product water stream. Produced water from the well field of interest was generated at a temperature of 160° F and contained about 5,800 mg/l TDS, 17 mg/l of soluble oils and grease, about 120 mg/l of TOC, trace levels of BTEX, and soluble silicates and boron at concentrations of 200 and 20 mg/l, respectively. Before being introduced into the reverse osmosis process, the produced water was subjected to considerable pretreatment for soluble oil removal (using the walnut shell filter), silicate removal to avoid abrasion (using the warm lime process), removal of soluble organics (using trickling filter biological treatment), suspended solids control (using a pressure sand filter), and a final softening step to remove calcium and magnesium to minimize the potential of forming calcium and magnesium carbonate precipitates under the high pressures of reverse osmosis.

The performance of this pilot scale treatment train is described by Doran and Leong (2000) for the 35-duration of its operation. In general, good demineralization performance was achieved with the RO unit; a product water of less than 150 mg/l TDS was generated and brine volume reduction of greater than 80 percent was achieved. However, pressure drop data from the RO process shows a degradation of performance occurred with each operating cycle between membrane cleanings, as depicted in Figure 10. An operational policy established that the RO would be operated until pressure drops across the membrane reached 450 psi, at which time, membrane cleaning and regeneration would be performed on the process so that the membrane would be able to operate at a virgin membrane pressure drop of 370 psi. The graph of Figure 10, though, shows that beyond the second cycle, pressure drops could not be restored to below 430 psi, substantially shortening operating time between cleanings by more than half. This rapid degradation of membrane performance is typical of oil and gas industry experience with the RO technology and may be explained by the performance of the processes that preceeded the RO. The walnut shell filter achieved less than 40% removal of the oil and grease (O&G), allowing more than 10 mg/l O&G to remain in the water stream. The trickling filter that received an influent stream total organic carbon concentration (TOC) of 95 mg/l only achieved an 8.4% removal of TOC, leaving 87 mg/l TOC to remain in the water stream. Thus, the inability of the preprocessing to perform efficient organic removals was responsible for up to 87 mg/l of TOC and 10 mg/l of O&G getting into the RO unit, which could possibly explain the rapid degradation of RO membrane performance. This RO degradation occurs after an initial 2-3 week period – about the amount of time required for microbial films to develop on surfaces.

This information, together with the body of experience with RO in the oil and gas industry, suggests that increased emphasis needs to be placed on high-performance preprocessing to remove oil and grease as well as total organic carbon to sustainable low levels and to minimize detrimental impacts to the expensive membrane components that carry out demineralization. Several emerging processes show promise in providing such improvements in preprocessing. Of course, activated carbon could achieve substantial reductions in TOC and O&G, but the GAC costs and/or regeneration expenditures would likely be excessive for these applications to organic concentrations above 10-40 mg/l. Experimental testing of ultrafiltration and micelle-enhanced ultrafiltration indicates oil and grease removals (from influent levels of 35-40 mg/l) of 90-99% and TOC removals of 80-95% were achievable, though permeate flux (L/m^2-hr) decreased gradually after each cleaning (Santos, 1997).

Alternatively, the GAC-FBR --- which is commercially available --- could be used to control soluble organics in produced water. The GAC-FBR is a biological process that uses a fixed microbial film which biologically converts dissolved organic compounds to harmless products such as carbon dioxide. The biofilm is attached to granular activated carbon granules inside the bioprocess (or "reactor"). This reactor configuration is usually operated in the aerobic mode in which oxygen from aeration is utilized by the biofilms to oxidize organic contaminants as the water flows over the cell mass.

The process can also be operated in the anaerobic mode, using nitrate to oxidize the organics to carbon dioxide. Both modes of GAC-FBR operation have been demonstrated as effective in efficiently removing BTEX and total organic carbon (TOC) from produced water at dissolved salt levels up to 15 percent.

Typical removals of BTEX achieved with the GAC-FBR process in pilot and full scale applications to produced water range from 95 to 99.8 percent and TOC (including volatile acids) is removed at efficiencies of 70-90 percent (Miller, et al., 1997). In the treatment of organics in water, the process seems to combine the high removal efficiency of adsorptive carbon with the destructive capability of biofilms to eliminate organic compounds and regenerate the carbon solid support. The amount of activated carbon added to the process on an annual basis is equal to the modest 3-6 percent of carbon lost from the reactor due to particle attrition. Most remarkable is the low volume of reactor that is required for treatment. The GAC-FBR typically operates at hydraulic loadings that are 25 to 50 times that of suspended culture systems; hydraulic retention times of 5 to 30 minutes are typical, compared to 6-8 hours or more for activated sludge processing. As such, the foot print of the GAC-FBR is less than 10% of the footprint required for conventional biological treatment, including trickling filter processing. Commercial history of this process with the beverage industry, the refinery industry and the utility industry shows that the GAC-FBR is economical to construct and to operate. This process also has considerable potential for pretreatment in the oil and gas industry to remove soluble organic acids, BTEX and soluble oils.

The GAC-FBR has been piloted in combination with induced gas flotation to provide pretreatment for an electrodialysis unit that was briefly tested at a conventional gas well in the Wind River Basin near Lysite, Wyoming (Miller, et al., 1997). Produced water at this site contained about 8,300 to 10,000 mg/l of total dissolved solids (TDS), comprised mainly of sodium, chloride, calcium and bicarbonate; these ions comprised approximately 93% of the dissolved inorganic salts. The produced water also contained 65 mg/l of oils and greases, and over 330 ppm of biological oxygen demand as measured with the standard 5-day test (BOD_5), 70% of which was made up of acetate and other volatile acids. The BOD_5 parameter is a predictor of the amount of oxygen required in natural streams to oxidize the organic carbon in a sample and it is proportional to the biodegradable total organic carbon (TOC). The goal was to treat the produced water to meet the NPDES criteria for surface discharge and to meet specifications for certain beneficial end uses of irrigation and livestock watering. To achieve these goals, the following unit processes were used in the pilot treatment train:

- Deoiling to remove oils and greases to achieve NPDES O&G limits and to protect downstream unit processes. This was accomplished with induced gas flotation.
- Dissolved organics removal. This was achieved with the use of two biological fluidized bed reactor (FBR) processes in series: 1) An anoxic, nitrate-consuming FBR to achieve large reductions in the soluble TOC; and, 2) An aerobic FBR to ensure efficient oxidation of soluble TOC and BTEX (i.e. benzene, toluene, ethylbenzene, and xylenes) to low levels.
- Partial demineralization to achieve NPDES criteria for total dissolved solids, chloride and sulfate.

The pilot system was operated over a 65 day period to obtain water quality data and treatment economics. A schematic and photo of the pilot process train are shown in Figures 11 and 12, respectively. Produced water flow to the induced gas flotation process and the FBR processes was 15 gpm. A split stream of treated water from the aerobic FBR was fed to the on-site electrodialysis (ED) unit which was designed and operated for batch recirculation flows of about 0.5 to 4 gpm, depending on the final TDS that was targeted for the effluent. The ED unit was operated in continuous mode for most of the 65 day period. Continuous operation was interrupted by twelve brief batch tests to evaluate determine the energy inputs necessary to achieve 5,000, 2,500 and 1000 mg/l of TDS. An acid wash was applied to

the membranes on a daily basis in accordance with the manufacturer's recommendation for maintenance. During the operational period, samples were collected throughout the pilot system to determine the effectiveness of each unit process in the treatment of Lysite produced water. At the conclusion of the 65-day test, the ED stack was dismantled and key electrode and membrane components were sent to the manufacturer for inspection.

Results from the electrodialysis field pilot system are summarized in Table 8. Overall, the integrated treatment system performed well throughout the 65-day operation. Membrane integrity tests performed by the vendor before and after the piloting period showed no significant impairment to the membranes in the ED stack. Consistent with the nature of conventional natural gas wells, the produced water contained elevated levels of oils and greases approaching 100 mg/l; however, the combination of induced gas flotation (using a coagulant dose of 5 mg/l) and biological treatment was able to reduce the oil and grease to 4 mg/l or less, as shown in Figure 13, which offered sufficient protection to avoid fouling of the ED unit. The "front-end" preprocessing was also able to achieve nearly 90% removal of soluble organics before the produced water was introduced to the ED stage. The ED unit was able to decrease the salinity of the product water from 9,000 mg/l to the desired target levels of 5,000, 2,500, and 1,000 mg/l TDS. Power costs required for each of these levels is shown in Figure 14 (based on an electricity price of 6 cents per KWh), based on actual electrical energy consumption required to reach each of the target TDS levels. These results showed that the Lysite electrodialysis pilot system was capable of demineralizing a conventional gas produced water stream from 9,000 mg/l to as low as 1,000 for only 3 cents per 42-gallon barrel; the cost of reaching 2,500 mg/l was about 1 cent per bbl.

Application of demineralization technology for the conversion of CBM produced water to beneficial use or surface discharge would likely involve less aggressive and, hence, lower-cost integrated processing. As previously mentioned, because CBM produced water is generally lower than conventional produced water in TDS concentration (less than 15,000 mg/l), electrodialysis could be applied at a reasonable cost for energy for demineralization. Having far lower levels of oil and grease (often below 2 mg/l) and total organic carbon (often less than 20 mg/l) would favor the use of a simpler flow scheme for the generation of beneficial use water.

Such a proposed scheme is shown in Figure 15 which consists of the use of flow equalization, induced gas flotation (optional -- needed only if free oil is present), pressure sand filter (for suspended solids removal), micelle-enhanced ultrafiltration (for soluble oil removal), electrodialysis (demineralization), adsorption using a regenerable sorbent (for BTEX control), and SAR adjustment through calcium addition. It is projected that this type of flowscheme would achieve very low levels of total and dissolved oils in the produced water before encountering the electrodialysis unit. This would greatly reduce oil and grease deposition on the ED membranes and require far less attention in terms of cleaning. It is also anticipated that the low concentrations of TOC would mainly be comprised of volatile acids which would be separated out of the water with the brine in the ED unit due to the dissociation of volatile acids to predominantly anionic ion form at a pH above 6.5. The flowsheme of Figure 15 would not generate large amounts of solid wastes requiring disposal but would generate small volumes of concentrated brines and liquid wastes that could be safely disposed of using injection into a Class II well. The processing of Figure 15 is currently under evaluation at the laboratory pilot scale under the support of DOE with performing organizations including the Colorado School of Mines (CERI Program), GTI, Argonne National Laboratories, and ALL Consulting.

FUTURE DEVELOPMENT NEEDS FOR EMERGING TECHNOLOGIES

As energy companies pursue the evaluation of options for on-shore produced water management as alternatives to conventional disposal, membrane-based desalinization will continue to receive attention as potential routes to brine volume reduction, regulatory compliance and the generation of beneficial use water streams. If membrane-based demineralization is to be successful, more development will be needed on a number of topics; some suggested areas follow:

- Identify effective preprocessing for produced waters to achieve reliable removals of free, dispersed and soluble oils to levels below 0.2 mg/l TPH. This may require fastidious attention to the implementation of a combination of processes that are able to deal with perturbations of oil concentrations in the influent stream and treat the stream to very low levels of oil and grease. This is critical to the protection of RO and ED units implemented for demineralization.
- Develop more effective clean-in-place techniques for RO treatment systems that allow membranes to operate for more than a year before replacement. Currently, it is difficult to operate RO on produced water for more than a month without significant degradation of separations performance.
- Explore the processing advantages of using of electrodialysis in combination with RO. The ED process combined with RO may be a means of controlling scale-forming divalent ions fed to RO and may offer energy saving advantages.
- Automate the systems. Sensors, computer controls, broad-band transmission of data collected from on-site data-acquisition and from strategically placed cameras can allow remote monitoring and intervention of many produced water treatment plants installed within a region.
- Continue to develop the information base on beneficial use management options, optimal water allocations, and environmental effects.

SUMMARY

In many regions of the U.S. (especially in the CBM basins), produced water management plays a major role in determining the economic feasibility of oil and gas field development. For on-shore production, the possibility of converting produced water to water streams that can be used for groundwater recharge, freshwater habitat (through surface discharge) or new beneficial use markets is becoming increasingly attractive to energy planners, regulators and other energy industry stakeholders.

As large parts of the continental United States suffer water shortages due to drought and/or population growth, opportunities may arise for reclaiming produced water for beneficial use. In particular, many produced waters, including most produced water streams in CBM areas, contain modest levels of total dissolved solids that are less than 20,000 mg/l; these waters may only require partial demineralization to achieve good brine volume reductions and a demineralized steam suitable for surface discharge and/or beneficial use. Surface discharge, groundwater recharge and proposed beneficial uses for produced water in the future (e.g. irrigation, livestock, industrial, etc.) will require, in most cases, a considerable effort to upgrade the quality of produced water to meet standards and specifications.

The economics and trade-offs of reclamation, of course, are determined by local conditions, including the volume and quality of produced water, the proximity of potential reclaimed water users, and

the robustness and applicability of treatment technologies. A number of established (conventional), recently-deployed and emerging water treatment technologies (and combinations thereof) will provide the basic tools for the engineer to use to meet future challenges and opportunities for produced water reclamation and management. In the area of using membrane-based demineralization (i.e. reverse osmosis and electrodialysis) to economically reach treatment goals, additional development and field testing will be needed to solve some persistent challenges and make this vision a reality.

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TABLES

Table 1. Typical Values for Produced Water Quality Compared to Some Criteria

Parameter	End Use Criteria (ppm)			CBM Water	Non-CBM (Conventional Gas Well) Water
	Drinking	Irrigation	Livestock		
pH	6.5 - 8	-	6.5 – 8	7 - 8	6.5 - 8
TDS, mg/l	500	2,000	5,000	4,000 – 20,000*	20,000 – 100,000
Benzene, ppb	5	5	5	< 100	1,000 – 4,000
SAR**	1.5-5	6	5-8	Highly Varied	Highly Varied
Na^+, mg/l	200	See SAR	2,000	500 - 2000	6,000 – 35,000
Barium, mg/l				0.01 – 0.1	0.1 – 40
Cl^-, mg/l	250	-	1,500	1,000 – 2,000	13,000 – 65,000
HCO_3^- mg/l	-	-	-	150 – 2,000	2,000 - 10,000

* Total Dissolved Solids (TDS) range estimated for the lower 50 percentile

** SAR = Sodium Absorption Ratio -- a function of a ratio of Na to Ca and Mg Levels.

Table 2. Unit Processes and Their Application to Produced Water Treatment.

Treatment Method	De-Oiling	Suspended Solids Removal	Iron Removal	Ca & Mg Removal Softening	Soluble Organic Removal	Trace Organics Removal	Desalination & Brine Volume Red	Adjust-ment of SAR	Silicate & Boron Removal
API Separator	✓	✓							
Deep Bed Filter	✓	✓							
Hydroclone	✓	✓							
Induced Gas Flotation	✓	✓							
Ultra-filtration	✓	✓							
Sand Filtration		✓							
Aeration & Sedimentation		✓	✓						
Precipation Softening				✓					✓
Ion Exchange			✓	✓					✓
Biological Treatment					✓				
Activated Carbon						✓			
Reverse Osmosis							✓		
Distillation							✓		
Freeze Thaw Evaporation					✓		✓		
Electrodialysis					✓		✓		
Chemical Addition								✓	

✓ = Indicates that the technology is applicable as a potential remedy as indicated by data collected from pilot or commercial scale units.

Table 3. Overview of Produced Water Treatment Processes for Deoiling (Oil and Grease Removal).

	Unit Process	Technology Description	State of Development	Strengths	Limitations
De-Oiling	API Separator (Rudolfs, 1971)	A gravity oil-water separator tank that is designed to promote the quiescent separation of water and free oil. Oil is mechanically collected as a floated material or as a settled mass in the process. Often used in conjunction with chemical pretreatment employed to break emulsions. Useful as a first-line treatment process. A variant of the process uses corregated plates to collect oil.	Very well established treatment process used in the oil and gas industry.	Performs well in the treatment of elevated oil concentrations at percent levels: achieves 50-99% removal of free oil. Particulates above 150 μ are removed.	Soluble components of the TPH parameter are not efficiently removed with the process. Free oil concns can be in the range of 15-100 ppm.
	Deep Bed Filter (Hensley, 1992; Santos, 1993)	A bed of sand or walnut shell granular media that is at least four feet deep in a vertical tank.	Well known and established technology in the oil and gas industry.	Able to remove small diameter oil droplets from produced water. Useful for polishing the effluent.	Soluble TPH components are not removed; not recommended for influent oil concns over 100 ppm.
	Hydroclone (Lawrence and Miller, 1995)	A device of cylindrical construction that is fitted with one or more tangential inlets which cause the fluid entering the cyclone to follow a circular path around the wall of the process. Rotation of the fluid generates a centripetal acceleration field which is thousands of times greater than earth's gravity. Heavier water and solids move toward the outer wall; lighter material moves toward the center and the light oil is rejected from the process.	Well know and established technology in the oil and gas industry.	Capable of reaching low levels of free oil below 10 ppm. Low space requirements. Lowest cost deoiling device in many cases. Removes particles larger than 15 μ.	Highly soluble oil components of TPH, such as naphthenic acids, are not removed. May not be able to meet NPDES permit effluent oil and grease limitations.
	Induced Gas Flotation (Lawrence, 1993)	Fine gas bubbles are generated and dispersed in a chamber to suspend particles which ultimately rise to the surface forming a froth layer. Foam containing the oil is skimmed from the surface.	Well known and established technology in the oil and gas industry.	Oil removals of greater than 93% have been demonstrated with chemical additions.	Does not remove soluble oil components.
	Ultrafiltration and Microfiltration (Santos, 1993)	Ultrafiltration is a membrane process that is capable of retaining solutes as small as 1000 daltons (1 dalton is 1/16 of the mass of an oxygen atom) while passing solvent and smaller solutes. Surfactant addition enhances oil removal. Operating pressures of 140-410 kPa (20-60 psi) are far lower than reverse osmosis pressures.	Widely practiced on a large scale in industry. Developmental for O&G applications. Micelle-enhanced version of this process is an emerging technology.	Compact. Removes about 85-99% of total oil. Effluent oil & grease can consistently be reduced to below 14 ppm.	Iron fouling can be a problem. Effective cleaning is critical to preventing membrane fouling and reduction in permeate flux

Table 4. Overview of Produced Water Treatment Processes for Primary Treatment (Suspended Solids Removal).

	Unit Process	Technology Description	State of Development	Strengths	Limitations
Primary Treatment	Sedimentation (Clark et al., 1977)	A long retention time tank or retention pond designed to establish quiescent conditions for settling of particulates.	Long established technology in the oil and gas industry.	Can be designed to handle large variations in flow. Removes large particulates;	Does not remove fine particulates.
	Multimedia Sand Filter (Clark et al., 1977)	Consists of a bed of stratified granular materials designed to achieve removals of particulate matter. Dual medium filter beds can be composed of: 1) sand and anthracite, 2) activated carbon and sand, 3) resin beads and sand, and, 4) activated carbon, sand and garnet. Continuous backwash features ensure ease of bed management.	Very well established in many industries for suspended solids removal.	Regeneration of the filter bed is automatic. Effective removal of large particulate matter and particulate matter that can be flocculated.	Does not remove fine particulates.
	Cartridge Filter (Cartridge Filter Website, 2004)	Process comprised of a tube support system that holds filter cartridges. Often used as a pretreatment device. Water is pumped through the filter under pressures lower than ultrafiltration.	Commercially available for application in the oil and gas industry.	Easy to maintain. Numerous cartridge types are available. Low pressure drops. Effective removal of particulates.	Does not remove fine particulates.

Table 5. Overview of Produced Water Treatment Processes for Iron Removal and Softening.

	Unit Process	Technology Description	State of Development	Strengths	Limitations
Iron Removal and Softening	Aeration and Sedimentation (Clark, et al., 1977)	Primarily for iron removal. Water is aerated, settled in a sedimentation tank and filtered. Soluble iron in the Fe^{2+} form is oxidized to Fe^{3+} which forms an insoluble iron hydroxide precipitate; the theoretical solubility of ferric (Fe^{3+}) is less than 5×10^{-6} mg/l as Fe. The oxidized iron floc is then removed by sedimentation and/or filtration.	Standard iron removal method used by many communities across the U.S.	Iron removal has considerable benefits in protecting downstream membrane processes (used for desalination) from iron fouling.	The pH needs to be adjusted to > 7.5 for good performance. Organics in the water compete for oxygen during aeration.
	Lime Soda Ash Softening (Clark, et al., 1977; AWWA, 1971)	In this process, hydrated lime or caustic soda is added to the produced water to adjust the pH to above pH 10. The following reaction results in the net removal of calcium: $Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O$	Conventional water softening practiced by municipalities and industry.	Well understood methodology. Effectively controls Ca and Mg hardness in water.	Large foot print. Needs considerable operating labor for chemicals handling and sludge disposal.
	Ion Exchange (Brown and Sheedy, 2002)	A process based on the ability of an ion exchange resin to exchange one ion from the water with another ion on the resin. For example, zeolite resins exchange sodium ions for calcium and magnesium ions that cause hardness in the water.	Used extensively in smaller water systems and in individual homes, and in industry.	Compact and low in cost in softening pretreated water streams.	Requires pretreatment (deoiling, precipitation softening, etc.) to avoid resin fouling.

Table 6. Overview of Produced Water Treatment Processes - Secondary Treatment (Soluble Organics Removal).

	Unit Process	Technology Description	State of Development	Strengths	Limitations
Secondary Treatment for Soluble Organics	Biological Treatment (Hickey, et al., 1999)	A number of biological processes have the capability to degrade dissolved oils, volatile acids and other soluble organics to carbon dioxide. An example of a biological process that is robust in treating produced water is the fluidized bed reactor that uses granular activated carbon as the solid support for microbial growth (the GAC-FBR process).	The GAC-FBR is commercially available equipment and has been successfully demonstrated for the treatment of produced waters up to 15,000 mg/l TDS.	Reasonable footprint. Highly versatile in the removal of organic compounds. Able to operate in the anaerobic, denitrifying and aerobic modes. Robust performance with many produced water streams. BTEX removal efficiencies exceed 98%.	High concentrations of total organic carbon over 100 mg/l may need a denitrifying mode of operation; this would require large process volumes and the handling of nitric acid and/or nitrates.
	Activated Carbon (Noll, K.E., 1992)	A fixed bed column that promotes the adsorption of organic compounds on the surface carbon media as the water passes through the column. Spent carbon media is usually regenerated off-site. Most often applied as a water polishing process for trace organics and some inorganic species.	Well established process in municipal and industry sectors. Best applied to organic concentrations below 20 ppm.	Excellent removal efficiencies with certain organic compounds; for example, removals of BTEX can exceed 99%.	Application to high organic concentrations over 100 ppm TOC causes rapid exhaustion of activated carbon.

Table 7. Overview of Produced Water Treatment Processes for Demineralization and Brine Volume Reduction.

	Unit Process	Technology Description	State of Development	Strengths	Limitations
Desalination and Brine Volume Reduction	Reverse Osmosis (Rousseau, 1987)	A membrane process capable of separating a chemical (solute) from an aqueous solution by forcing the water through a semipermeable membrane by applying a pressure greater than the osmotic pressure of the solute.	Processing more than 800 MGD at 2,000 plants in the U.S., RO is the predominant desalting technology used in the U.S. in the treatment of water --- developmental stage for O&G applications. New membranes and CIP are available.	Good track record with sea-water and brackish water. Small footprint. Handles a wide range of TDS concns. Organics and salts are removed	Demonstration test facilities exhibit: Membrane fouling due to: • Oil film on the membrane • Abrasion of membrane due to precipitates. • Poor water recoveries < 65%.
	Vapor Compression Distillation (Doran and Leong, 2000)	A process in which the heat for evaporating the water comes from the compression of vapor rather than the direct exchange of heat from steam produced in a boiler. The process includes a multiple-effect evaporator that uses a compressor to pull a vacuum on the vessel that induces the boiling of water at low temperatures of 40º to 60º C.	Commercially available at capacities of 120 to 120,000 bbl/d. Often utilized for resorts and industry. Also used for drilling sites where fresh water is limited. Not yet adapted for produced water.	High water recoveries of up to 98% can be achieved, even with concentrated feeds. Minimal fouling, scaling or plugging problems anticipated using the seeded slurry variant of VC.	For produced waters of low to medium TDS, VC distillation energy intensive compared to ED or RO. Volatile organic contaminants follow the product water.
	Freeze Thaw Evaporation (Boysen et al., 2002)	A process that combines the natural processes of freezing and evaporation to provide driving forces for the demineralization of produced water. Freeze crystallization and thawing cycles are used to concentrate salts into a reduced volume of brine with the concomitant production of demineralized water. Evaporation is used to further reduce brine volumes in the summer.	Commercial deployment of FTE is in its first decade. Performance data from two commercial-scale FTE facilities is available.	Low power requirements. Can often be retrofitted to existing evaporation facilities.	Only applies to areas of the U.S. that exhibit the required number of freeze days. Land required is significant. Operating labor is a cost driver.
	Electrodialysis (Kirk-Othmer, 1995; Rousseau, 1987; Tsai, et al., 1995)	An electrically-driven membrane separation process that is capable of separating, concentrating, and purifying selected ions from aqueous solutions. In this process, ions are transferred through ion-selective membranes by means of a dc voltage. Cation-exchange membranes are alternated with anion exchange membranes in stacks.	Commercially available since the 1960's and employed in a number of industries including food, chemicals, & pharmaceuticals. Not commercially used in oil and gas industry.	High water recoveries of > 92%. Lower pressure operation (<25 psi). Resistant to fouling.	Energy costs excessive with influent salt above 15,000 mg/l TDS. Does not remove BTEX or PAH's like naphthalene.

Table 8. Performance Results for the Integrated Electrodialysis Pilot Unit

Parameter	Influent	Effluent	Overall Removal, %
Oil and Grease	90	4	95.5
BOD_5 *	330	51	84.5
BTEX**	11	0.1	99.1
Total Dissolved Solids (TDS)	9,100	1,000***	88.9

* BOD5 = Biological Oxygen Demand measured in a five day test
** BTEX = Sum of benzene, toluene, ethylbenzene, and xylenes.
*** Generated at peak performance of the ED unit.

FIGURES

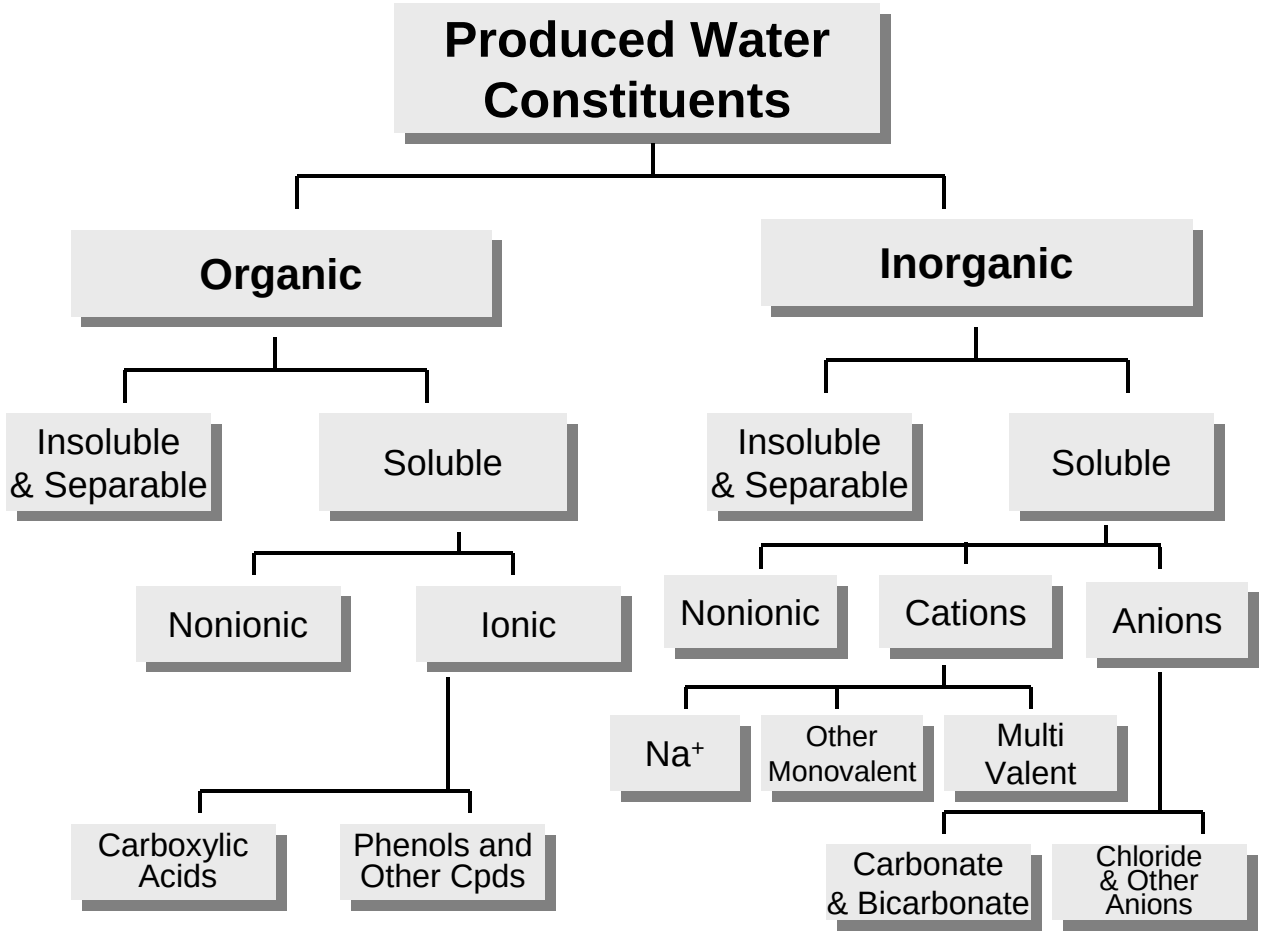

Figure 1. Breakdown of Produced Water Chemical Constituents.

Figure 2. Zeolite Ion Exchange Treatment of Produced Water in the Powder River Basin.

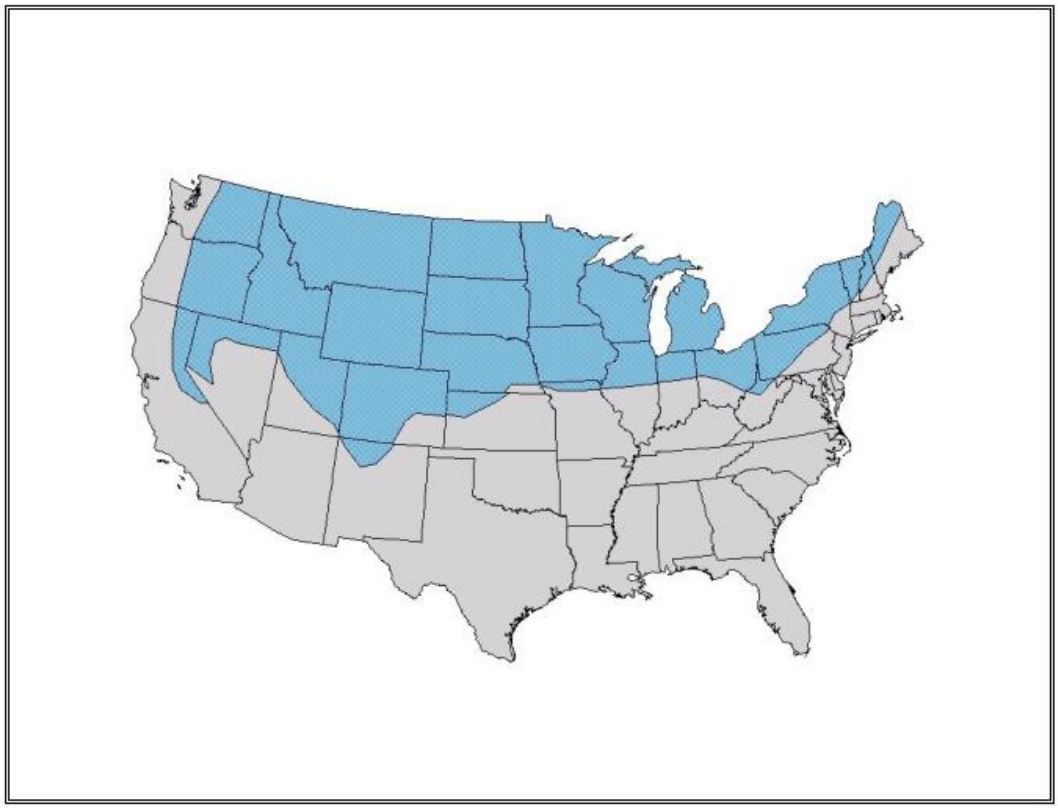

Figure 3. Northern Region of the U.S. Where Freeze Thaw Evaporation Technology Can Be Deployed.

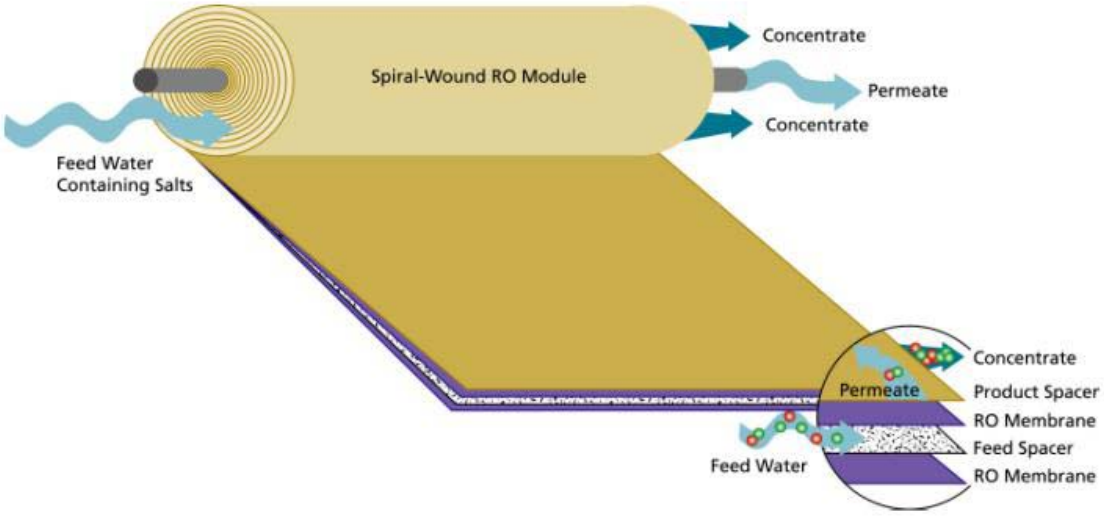

Figure 4. Schematic of Reverse Osmosis.

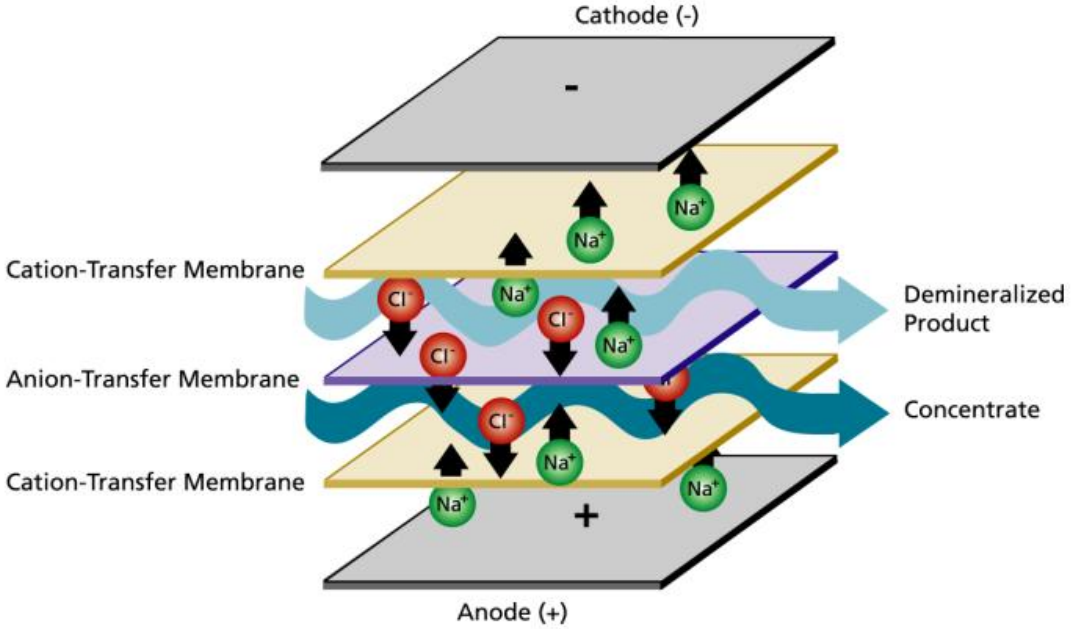

Figure 5. Schematic of Electrodialysis.

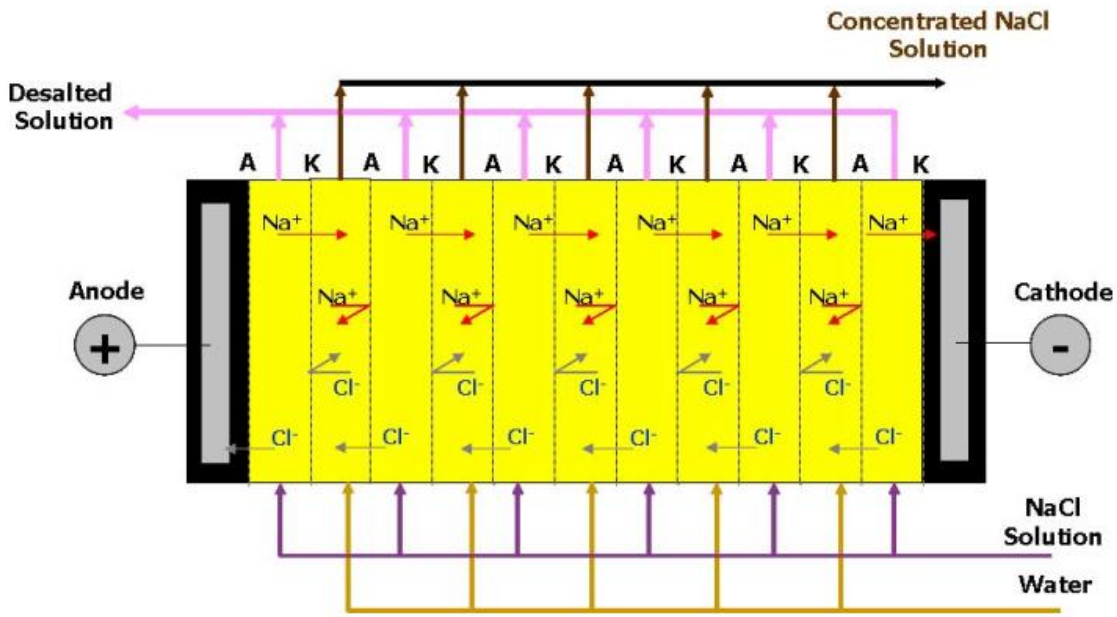

Figure 6. Diagram of an Electrodialysis Membrane Stack Applied to Produced Water Treatment.

Figure 7. Photo of a Commercial Electrodialysis Treatment System Applied to Water Treatment.

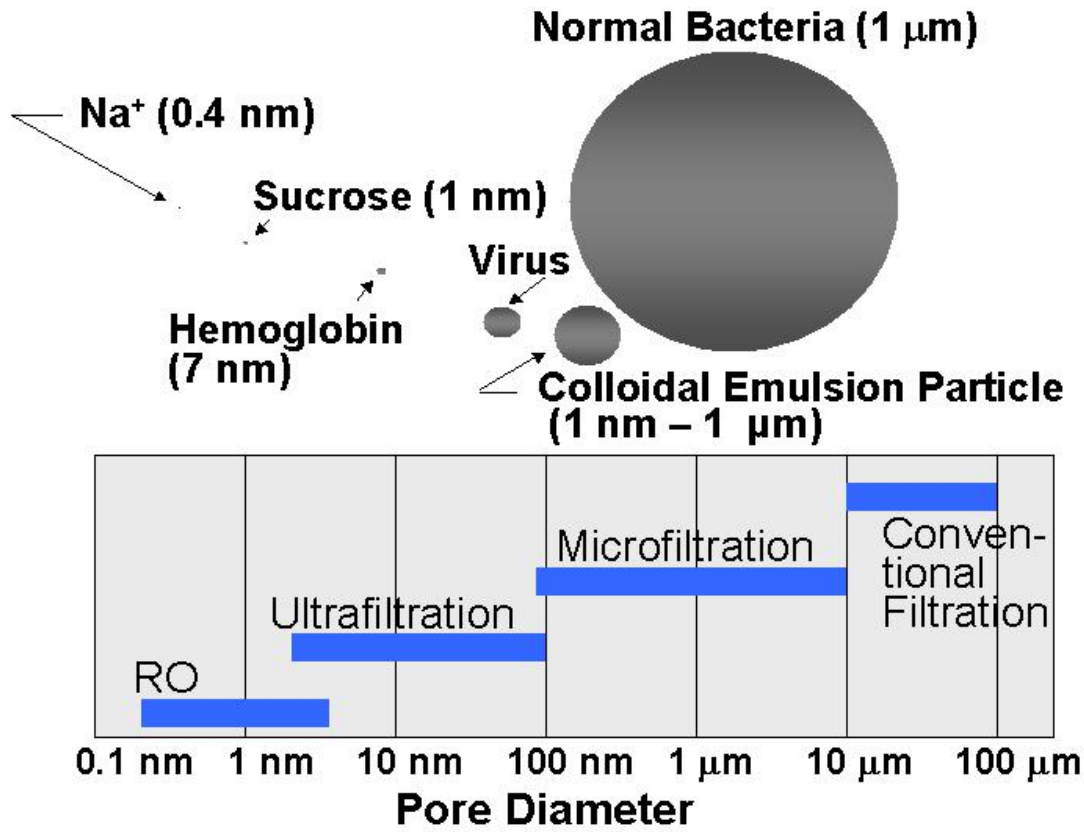

Figure 8. Particle Size Exclusion Ranges for Various Types of Filtering Technologies.

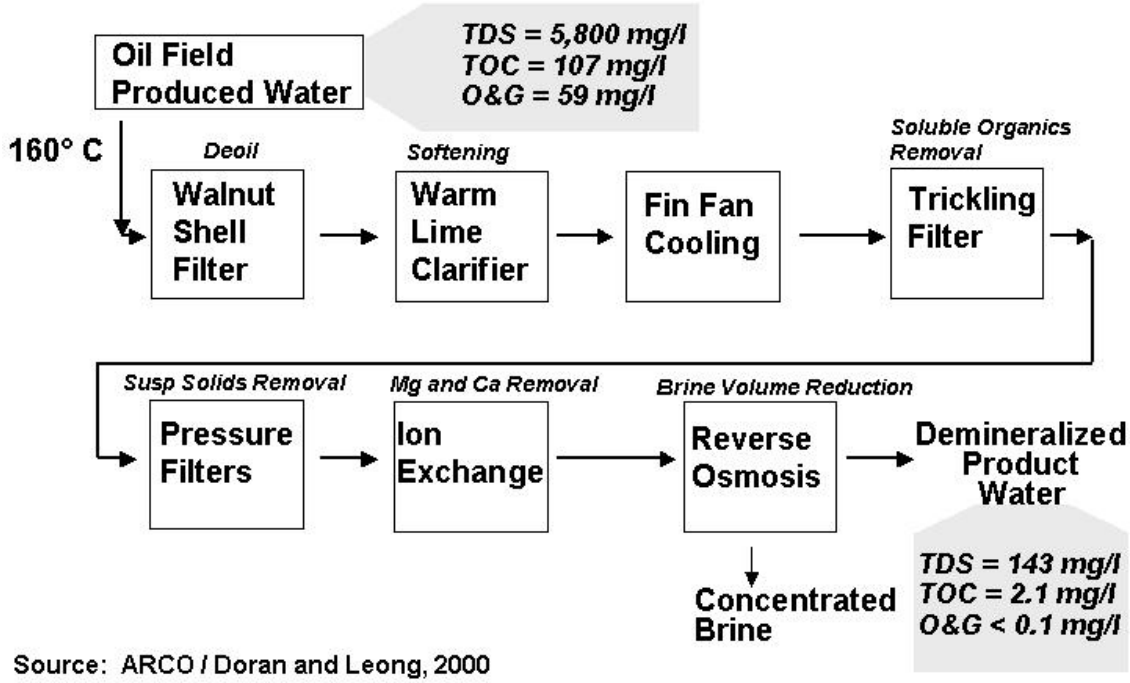

Figure 9. Schematic of the ARCO Pilot Scale Produced Water Treatment System.

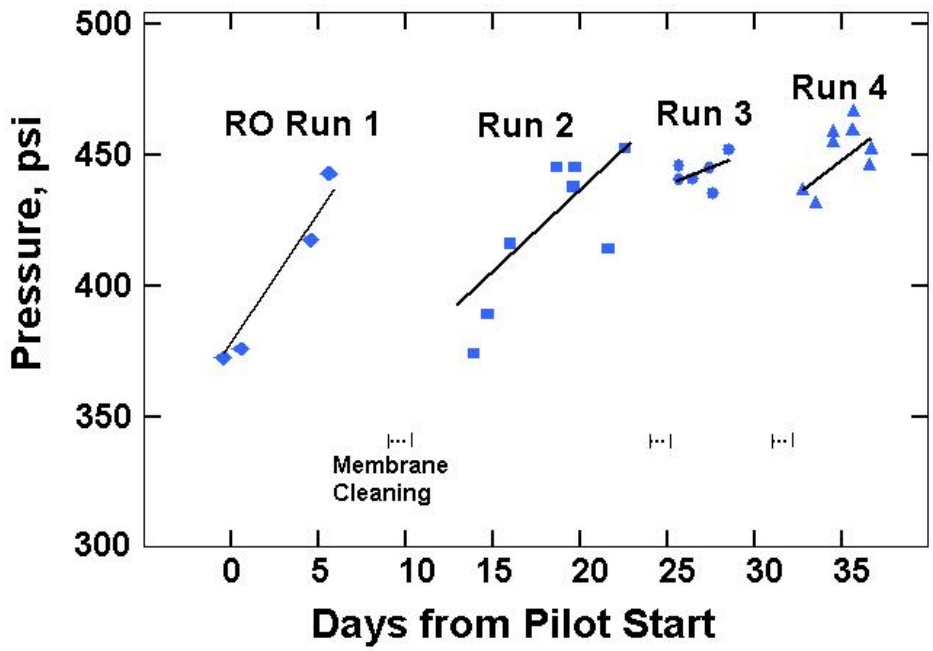

Figure 10. Pressure Drop Accumulation Profiles of the ARCO Reverse Osmosis Pilot Unit.

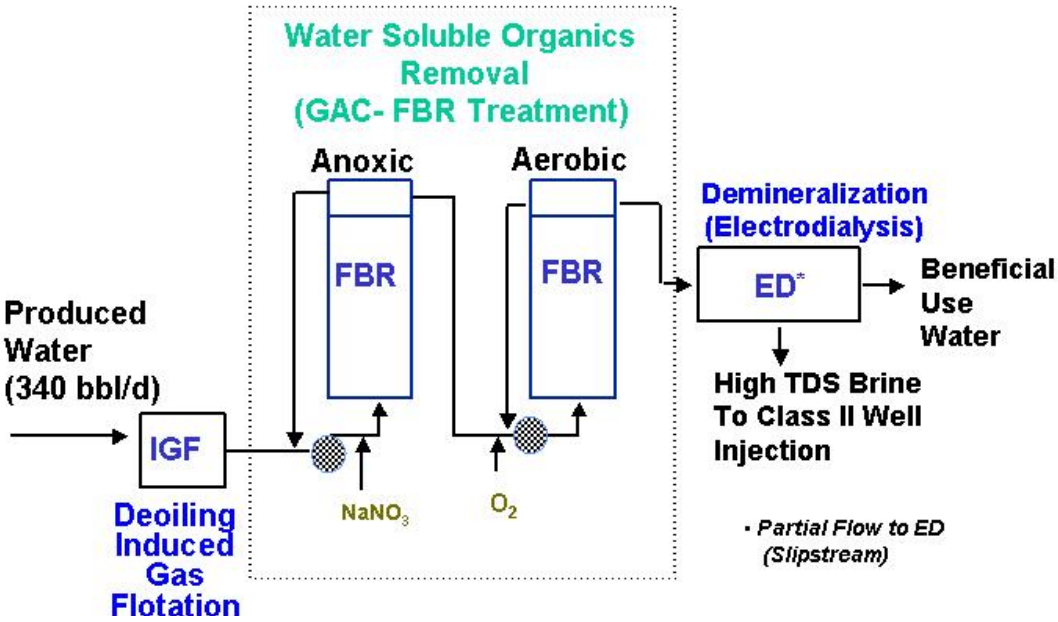

Figure 11. Schematic of the GTI Produced Water Treatment Pilot Plant Including the Induced Gas Flotation Process (IGF) and the Biological Granular Activated Carbon Fluidized Bed Reactor (GAC-FBR).

Figure 12. Photo of the GTI Produced Water Treatment Pilot Plant Including the Induced Gas Flotation Process (IGF) and the Biological Granular Activated Carbon Fluidized Bed Reactor (GAC-FBR).

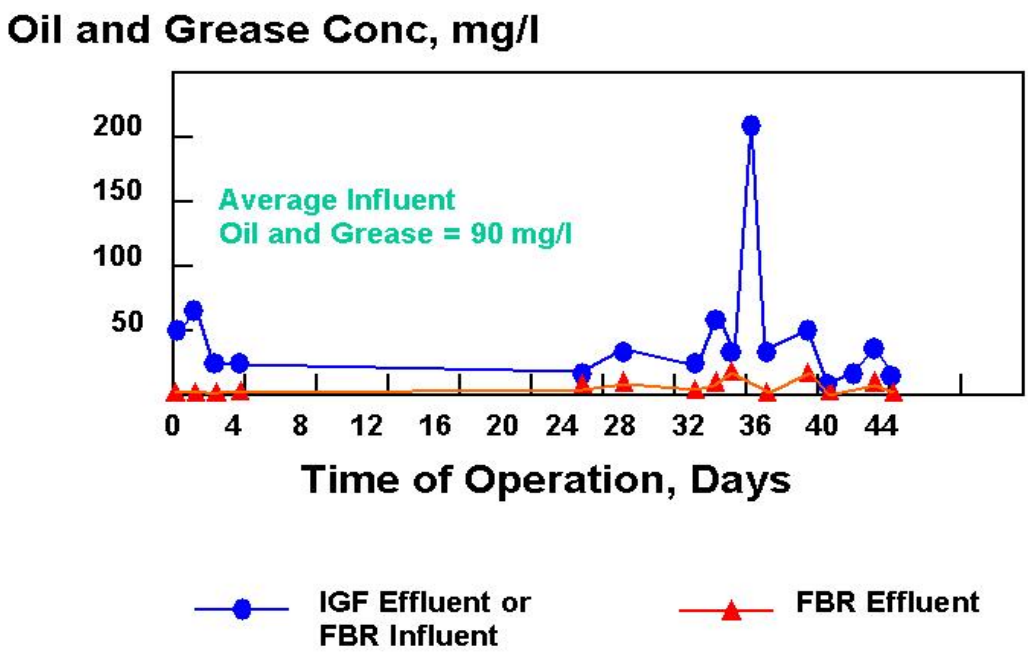

Figure 13. Oil and Grease Removal from Conventional Produced Water Using Induced Gas Flotation (IGF) and the Biological Granular Activated Carbon Fluidized Bed Reactor (GAC-FBR).

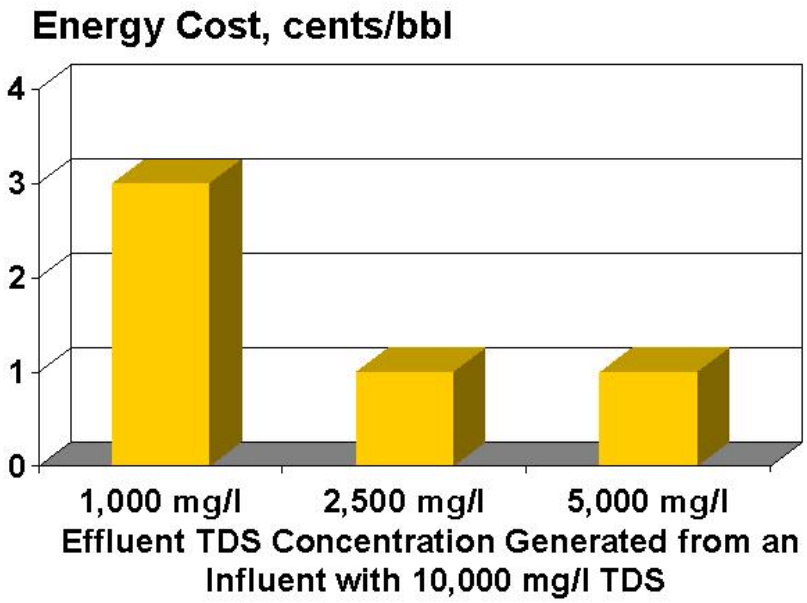

Figure 14. Power Cost Versus Effluent TDS Concentration Achieved with the Pilot ED Unit Treating Conventional Produced Water (Influent TDS = 10,000 mg/l).

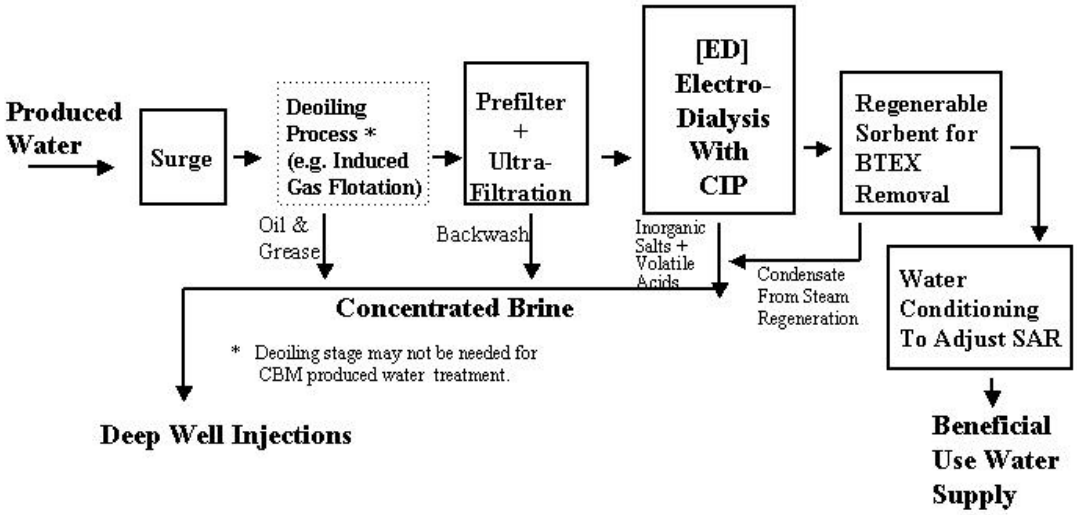

Figure 15. Schematic of the Integrated Produced Water Treatment System Using Electrodialysis.