

RECLAMATION

Managing Water in the West

Science and Technology Program Research Report

Produced Water Treatment Primer: Case Studies of Treatment Applications



U.S. Department of the Interior
Bureau of Reclamation

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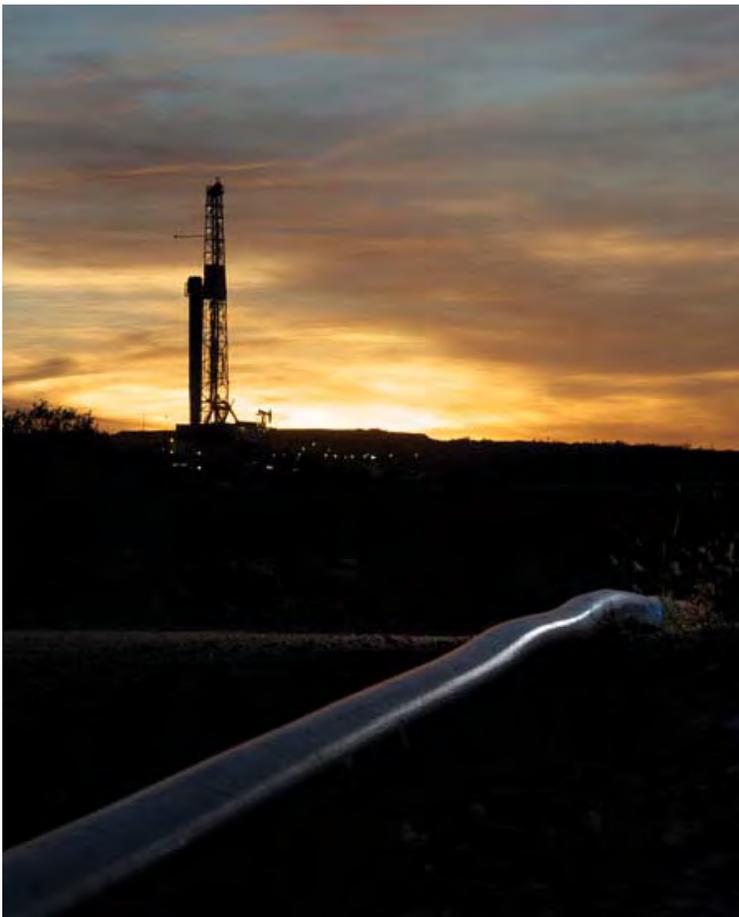
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by:

**Bureau of Reclamation
Technical Service Center
Water Treatment Group**

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The U.S. Department of the Interior protects America's natural resources and heritage, honors our cultures and tribal communities, and supplies the energy to power our future.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

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Acronyms and Abbreviations

bbl	Blue Barrel of Oil = 42 US gallons, 35 imperial gallons, or ~159 liters,
C	Celsius
Desal Plant	desalination plant
dP	differential pressure
EPA	United States Environmental Protection Agency
F	Fahrenheit
ft ²	square foot
gpd	gallon per day
gpm	gallon per minute
ISO	International Organization for Standardization
KW	kilowatt
kWh/kgal	kilowatts per thousand gallons
L/min	liters per minute
lb/in ²	pounds per square inch
LHS	load handling systems
LSI	Langelier Saturation Index
Mm	micrometer
m ²	square meters
m ³ /day	cubic meters per day
mgd	million gallons per day
mg/L	milligrams per liter
mL/hr	milliliters per hour
NTU	Nephelometric Turbidity Unit
ppm	parts per million
PVC	polyvinyl chloride
Reclamation	Bureau of Reclamation
RO	reverse osmosis
SDI	Silt Density Index
TDS	total dissolved solids
UF	ultrafiltration
USGS	U.S. Geological Survey
μS/cm	MicroSiemens per centimeter

Glossary of Terms

Anion: A negatively charged ion resulting from the dissociation of salts, minerals, or acids in water.

Anoxic: Waters without any dissolved oxygen.

Aquifer: Subsurface formation with sufficiently permeable to yield groundwater.

Basin: A closed geologic structure that the hydrocarbon is produced in.

Blending: Mixing treated water with untreated water.

Cation: A positively charged ion resulting from the dissociation of salts, minerals, or acids in water.

Coagulant: An agent that causes particles suspended in a liquid to coagulate (see coagulation).

Coagulation: To transform particulate matter suspended in a liquid into a soft or solid mass.

Coal bed methane/coal bed natural gas: A clean-burning natural gas found deep inside and around coal seams. Gas is produced by removing groundwater to reduce hydrostatic pressure and stimulate production.

Conductivity: The degree to which a specified material conducts electricity.

Contaminant: Any undesirable physical, chemical, or microbiological substance or matter in a given water source or supply.

Demineralization: Any process that removes mineral substances from water.

Direct filtration: A method of filtration where the feed stream is fed directly to the filtration media. In conventional terms, the conventional treatment train without sedimentation or clarification.

Disposal well: A well where produced water is injected into an underground formation for disposal.

Distillation: The process of heating water to evaporation and its subsequent condensation to purify the water.

Electrodialysis: A process in which ions are transferred through membranes from a less concentrated to a more concentrated solution as a result of direct current electrical potential.

Electrodialysis reversal: An automatic operating feature of some electrodialysis units that reverses the electrical potential applied to the two electrodes about every 15 minutes to promote cleaning of the unit.

Floc: A loosely clumped mass of fine particles.

Flocculation: The gathering of particles, by slow stirring, in water to bind them into larger aggregates to form a rapidly settling floc.

Flowback: Hydraulic fracturing fluids (see fracturing fluids) that return to surface after a hydraulic fracture is completed.

Fracturing fluids: Fluid mixture composed predominately of water with proppant and chemical additives used to induce and maintain fractures in the target formation.

Inorganic: Substances of mineral origin, such as sand, salt, iron, and calcium salts.

Ion: An electrically charged atom, radical, or molecule formed by the loss or gain of one or more electrons.

Ion Exchange: A chemical process where certain unwanted ions of a given electrical charge are absorbed on to resin, removed from solution, and replaced by less obtrusive ions of an equivalent charge.

Hydraulic fracturing: The process of injecting fluids into a target formation to induce fracturing through which oil or natural gas can flow.

Hydrocarbons: Organic compounds composed of a combination of carbon and hydrogen. They may or may not have other elements.

Media filtration: A type of filter that uses a bed of sand, crushed granite, or other material to filter water.

Membrane: A thin sheet of natural or synthetic material.

Microfiltration: The low pressure membrane filtration with a nominal pore size range from slightly below 0.1 micrometer (μm) to slightly above 1.5 μm .

Nanofiltration: A membrane process for removing hardness and other di-valent ions. Nanofiltration has a lower rejection rate for monovalent ions than multivalent ions and can operate at significantly lower operating pressures than reverse osmosis membranes.

Natural organic matter: Substances that come from animal or plant sources, and always contain carbon.

Naturally occurring radioactive material: Low-level, radioactive material naturally found in some geologic formations.

Oxidation: Adding oxygen, removing hydrogen, or removing electrons from an element or compound.

pH: Measurement of acidity (<7) or alkalinity (>7).

Photolysis: Process where light energy or photons decompose a chemical compound.

Pretreatment: Treatment units before the main treatment process which are necessary to remove compounds that are detrimental to the main treatment process.

Produced water: Water co-produced during oil and gas production.

Proppant: Silica sand or particles included in fracturing fluid used to keep fractures open and maintain permeability.

Raw water: Water in its natural state, prior to any treatment.

Recovery: The amount of permeate water attainable, expressed as a percent of the feed flow.

Pressure exchanger energy recovery: A device which captures hydraulic energy from the high-pressure reject stream and transfers this energy to low-pressure feed water.

Resins: A class of chemicals, many of which have ionic replacing properties to absorb specific ions (and release others) such as ammonia, nitrate, metals, etc. An anion resin adsorbs anions in the water, while a cation resin adsorbs cations in the water.

Reverse osmosis: A desalination technology using a semipermeable membrane and pressure to drive water from a higher concentration solution to a lower concentration solution.

Sedimentation: A process in which solid particles settle out of the water being treated in a clarifier or sedimentation basin.

Semi-permeable membrane: A film that allows passage of one component (i.e., water) while retaining others (i.e., salts and suspended solids) under the application of a driving force (i.e., pressure difference).

Scaling: A process where precipitation or crystallization of salt compounds or solids form a coating on working surfaces of a system.

Shale gas: Natural gas produced from low permeability shale formations.

Slick water: A water based fluid mixed with friction reducing agents, commonly potassium chloride.

Sparingly soluble salts: Salts that do not readily dissolve in water and when concentrated may precipitate out of solution (e.g. silicon dioxide, calcium sulfate, and barium sulfate).

Tight gas: Natural gas trapped in a hard rock, sandstone, or limestone formation that is relatively impermeable.

Total dissolved solids: All of the dissolved solids in the water. The residue after filtering of suspended solids and evaporation.

Total plant cost: The cost of treated water expressed in dollars per thousand gallons. Total plant costs includes the annualized capital equipment costs for all the unit processes, annual operations and maintenance costs, and various project related special costs.

Total suspended solids: The quantity of material removed by filtering, usually with either a Gooch crucible or a 0.45 μm filter.

Turbidity: The cloudiness of a fluid due to the scattering of light by individual particles (suspended solids), measured in units of Nephelometric Turbidity Units (NTU).

Ultrafiltration: A membrane filtration removing particles down to 0.001 μm in diameter, capable of removing bacteria, virus, and colloidal particles.

Water quality: The chemical, physical, and biological characteristics of water with respect to its suitability for a particular use.

Water reuse: Reclaiming wastewater for potable or non-potable uses.

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Introduction

This document catalogs advanced water treatment technologies currently used in the oil and gas industry. Each technology has varying positive and negative aspects with respect to chemical requirements, energy requirements, footprint, cost, and removal capability. General information is included on a number of categories of applied technologies, including: a brief technology description, applicable contaminants removed, removal mechanisms, and qualitative notes on advantages and disadvantages. Links to case study examples are provided to industry information on technology applications, operational experience, and performance data.

Background

Water treatment technologies offer opportunities for the oil and gas industry to reuse flowback water from hydraulic fracturing applications. This water reuse by the oil and gas industry offsets fresh water requirements and reduces demand on regional water systems.

Recent advancements in energy production technology, such as horizontal drilling, have greatly increased natural gas production in the United States. Hydraulic fracturing for gas production requires significant quantities of water per well site, making sustainable and available water supplies critical aspects of oil and gas well development. Furthermore, wells from horizontal drilling require more water than traditional vertical wells.

Oil and gas extraction also creates substantial quantities of “produced” waters with varying levels of contamination, which must be disposed through treatment or reinjection. Produced water coexists naturally with oil and gas deposits and is brought to the surface during well production. Produced water is extracted at an average rate of 2.4 billion gallons per day (gpd), and over 80 percent of production occurs in the Western U.S. (Clark and Veil, 2009). Produced water represents the largest waste stream associated with oil and gas production with estimates of almost 2.7 million acre feet per year.

Produced water is commonly re-injected for disposal due to its salinity, but in water-stressed areas, this water can be treated and managed for uses such as:

- Well drilling or hydraulic fracturing
- Emergency drought supply
- Livestock water
- Irrigation water
- Surface water augmentation
- Drinking water applications

Most produced water requires treatment to make it suitable for recycling or beneficial use. Produced water varies widely in quantity and quality, depending on the method of extraction, type of oil and gas reservoir, geographical location, and the geochemistry of the producing formation. Therefore, many different types of technologies exist to treat produced water. Furthermore the industry uses these technologies in both upstream and downstream applications. Also, as depicted in Figure 1, advanced water treatment technology can be used for:

- Treating alternative water sources for hydraulic fracturing
- Internal industry reuse on-site at decentralized facilities
- Beneficial use of produced water and flowback water for alternative applications off-site



Treatment (left column) and conveyance or disposal (right column) options for water management in the oil and gas industry. (Reclamation 2013).

Water Management Costs

Costs for water management in the oil and gas industry are highly variable. Cost calculations for water sourcing, transportation, storage, treatment, and disposal are not commonly presented on a whole-cost basis. Comparison between management costs is thus difficult to quantify. General ranges of costs are presented as a basis for understanding the relative cost of water management. Costs included in this section represent ranges of costs documented in the Government Accountability Office report (2012).

Transportation

Water transportation is required to move water on-site for well development and off-site for treatment or disposal. Trucking costs may range from \$0.50 to \$8.00 per barrel (bbl) depending on the state and transportation distance.

Water Sourcing

Water required for well development may be purchased for use from local landowners or municipalities for \$0.25 to \$1.75 per bbl (Boschee, 2012).

Disposal

Disposal is commonly managed through injection wells with costs for underground injection ranging from \$0.07 to \$1.60 per bbl of produced water. Options such as impoundments or evaporation ponds are not always available due to permitting restrictions.

Treatment

Treatment costs both on-site and off-site vary considerably based on technology, water quality, and end use. Estimates depend on the site location and type of project and range from \$0.20 to \$8.50 per bbl.

Produced Water Quality and Constituents

Generally, produced water requires treatment to make it suitable for recycling or beneficial use due to the naturally occurring constituents and chemical additives in the water. Water quality varies widely in quantity and quality—depending on the method of extraction, type of oil and gas reservoir, geographical location, and the geochemistry of the producing formation (see Guerra et al., 2011). These are some constituents that commonly occur in produced water:

Salinity

Salinity in flowback and produced water originates from water associated with the producing formation. Salinity in produced water commonly consists of sodium and chloride. Calcium, magnesium, potassium, and sulfate may also exist due to mineral ion exchange. Salinity levels vary greatly nationally and even in one location over a well's lifetime. Produced water ranges from fresh (< 700 milligrams per liter [mg/L]) to highly saline (> 200,000 mg/L), depending on the location and type of hydrocarbon produced. Produced water with lower levels of salinity is generally diluted by fresh groundwater

recharge and exhibits meteoric water compositions. Ionic mineral exchange and residual high salinity water from paleogeologic attributes influence both the concentration and composition of high salinity waters.

Suspended Solids

Suspended solids accumulate in flowback and produced water as residual particles from the fracturing process, naturally occurring granular material from the formation, and aggregate biological or chemical compounds. Concentrations are highly variable, based on the hydrocarbon produced and well location.

Oil and Grease, Hydrocarbons, and Natural Organic Matter

Organic contaminants exist naturally in the formation and are expected to be present in flowback and produced water. Oil and gas water separators are not 100 percent efficient at separating these compounds from produced water. Furthermore, these constituents may be difficult to remove in gravity processes as they are suspended and generally lighter than water. The concentration and type of organic contaminant will vary by well type and location.

Dissolved Gas and Volatile Compounds

Naturally occurring dissolved gases and volatile compounds exist in flowback and produced water. Dissolved gas may be present due to the hydrocarbons produced (e.g., methane) or due to other saturated gases in the formation, such as carbon dioxide or hydrogen sulfide. Additionally, volatile compounds, such as benzene, toluene, ethylbenzene, and xylene may also exist in produced water. Care should be taken when dealing with certain volatile constituents as they may be hazardous to human health.

Iron and Manganese

Concentrations and occurrence of iron and manganese vary by location, but these compounds are generally present in flowback and produced water, as they are naturally present in the surrounding geology. Water existing naturally in the formation is generally anoxic; therefore, iron and manganese occur in their reduced forms. When iron and manganese are exposed to oxygen, they form oxides that precipitate on equipment and in pipelines. Furthermore, iron sulfides are detrimental to the hydraulic fracturing process and must be removed if water is to be recycled.

Barium and Strontium

Barium and strontium exist naturally in subsurface geology. Dissolution and weathering of these minerals may result in their presence in groundwater. These compounds are of particular concern as they form sparingly soluble salts that precipitate in certain treatment processes and cause decreased efficiency or damage. These constituents occur at much higher concentrations in produced water than in groundwater resources.

Boron and Bromide

Both boron and bromide are present in seawater and may occur in flowback and produced water. Both these compounds are mentioned as they may be difficult to remove or detrimental to downstream users. Boron may not be readily removed in reverse osmosis, for instance, without raising the pH or adding ion-exchange treatment to polish the reverse osmosis permeate. Bromate is not always measured, and trace amounts may cause formation of disinfection byproducts when combined with ozone as a disinfectant.

Trace Metals

Mineral dissolution leads to the presence of various trace metals in flowback and produced water. Certain constituents, such as arsenic and chromium are detrimental to certain end uses. Care should be taken, as these constituents may be harmful—even at trace levels. Trace metals are not commonly measured in produced water, so subsequent analyses may be necessary to identify occurrence and concentration.

Radionuclides

Radionuclides occur naturally in subsurface formation and generally depend on subsurface geology. Therefore, certain areas nationally are predisposed to high concentrations of radioactive compounds. Care must be taken in areas with high concentrations as process equipment and solids bound for landfills may accumulate radioactive material, making them hazardous.

Well Additives and Fracturing Chemicals

Chemicals are added during well development and well production to maintain well operations or to improve fracturing conditions. A wide range of chemicals can reduce scaling, improve crosslinking, or act as biocides to removal microbial growth. Chemical disclosure is generally an industry practice, and databases with chemical registries may be used to identify compounds used by the industry.

The U.S. Geological Survey (USGS) Produced Water Database has a comprehensive national dataset for oil and gas produced water. The USGS has updated the National Produced Waters Geochemical Database and Map Viewer to include trace elements, isotopes, and time-series data. Although water quality data may be highly variable (depending on formation, depth, location, and well type), the USGS database includes a variety of datasets and offers a unique asset to understanding produced water quality. See <http://energy.usgs.gov/EnvironmentalAspects/EnvironmentalAspectsOfEnergyProductionandUse/ProducedWaters.aspx>.

Technology Selection References

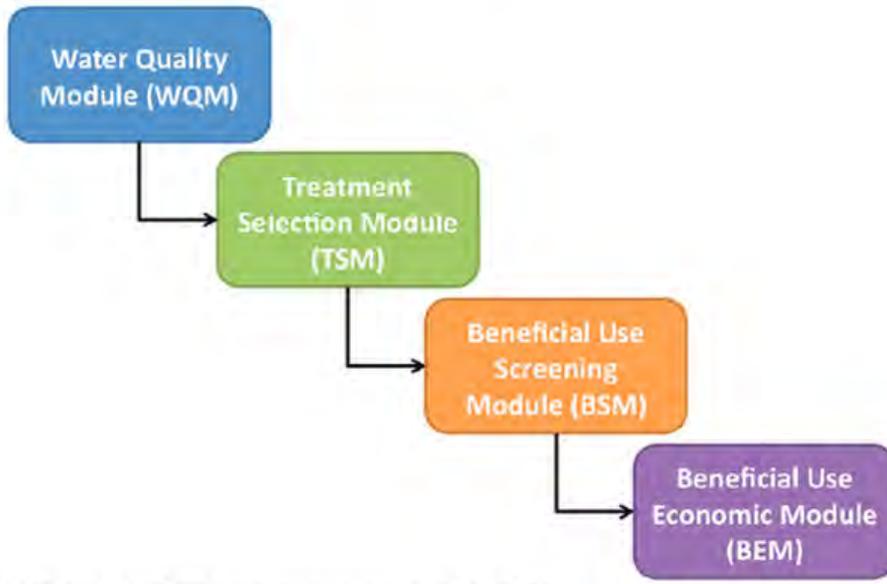
Evaluations for determining the best technology for a particular site must consider the types of constituents removed by each technology and the degree of removal required for end use. This document serves as an introduction for types of treatment technology, and readers should consult the library of literature on this topic, including a number of selection tools and guidance documents. The following list provides some example reference documents and additional Reclamation studies:

Produced Water Treatment and Beneficial Use Screening Tool

http://aqwaterc.mines.edu/produced_water/tools/:

Colorado School of Mines, Kennedy/Jenks Consultants, and Argonne National Laboratory. Also see Plumlee et al., 2014.

The CBM Produced Water Management Tool is a macro-enabled Excel workbook that contains four modules: Water Quality Module (WQM), Treatment Selection Module (TSM), Beneficial Use Screening Module (BSM), and Beneficial Use Economic Module (BEM).



CBM Produced Water Management Tool Modules

Flowchart for modules. (Colorado School of Mines, used by permission).

Water Treatment Technology Catalog and Decision Tool

www.all-llc.com/projects/produced_water_tool/

ALL Consulting, LLC, nd.

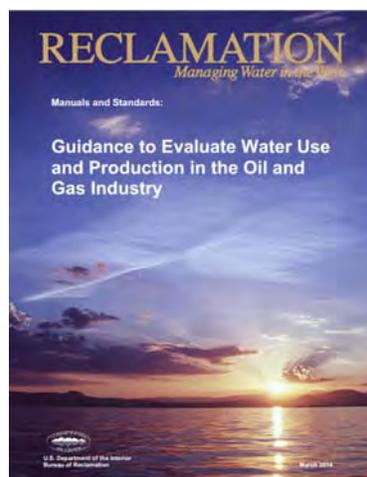
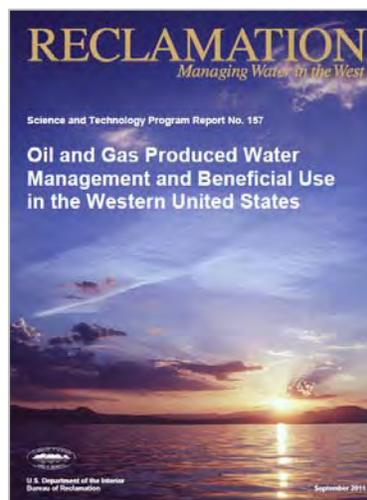


Screenshot of Decision Tool (ALL Consulting, used by permission).

Reclamation Reports:

Oil and Gas Produced Water Management and Beneficial Use in the Western United States. This report was created in 2011 as a comprehensive background document on the treatment and management of produced water from beneficial use in the Western U.S. The report includes information on produced water quality, water treatment technologies, and suitability for beneficial use opportunities (Guerra, 2011). www.usbr.gov/research/AWT/reportpdfs/report157.pdf.

Guidance for the Evaluation of Water Management Strategies to Provide Regional Water Supplies for the Oil and Gas Industry. This document offers an assessment technique for basin water demands and supplies generated by the oil and gas industry. A number of tradeoffs are highlighted in the decision structure, including using alternative water sources for oil and gas development, recycling water, and using produced water from the oil and gas industry as beneficial product. (Dahm, 2014) www.usbr.gov/research/projects/detail.cfm?id=1617.



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Summary of Treatment Technologies

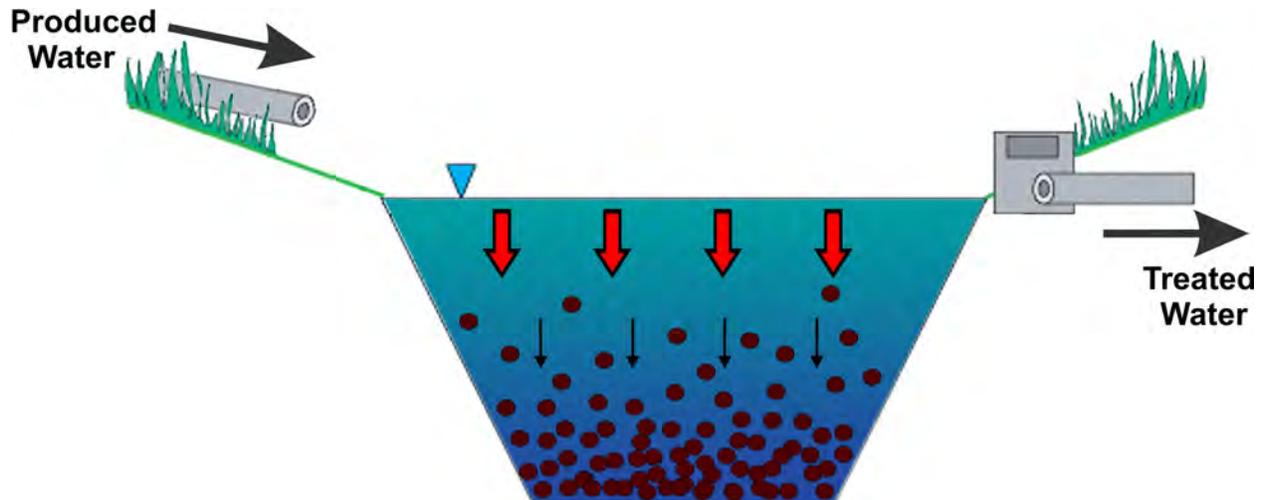
This section introduces treatment technologies currently used in the oil and gas industry. Information provided for each technology category includes a brief description of the technology, applicable contaminants removed, application with removal mechanisms, and a qualitative summary of benefits and limitations. For additional information on these technologies, additional emerging technologies, and a comprehensive list of specific industry technology combinations see Guerra et al., 2011.

Pretreatment Technologies

Pretreatment technologies are categorized as technologies that remove constituents such as suspended solids, oil and grease, and organic matter. Pretreatment technologies generally precede desalination technologies to protect downstream processes from clogging and damage. Technologies referenced in this section pertain to case studies in this document and are not inclusive of every technology used by the industry. Additional technologies not listed include:

- Air stripping
- Centrifuge
- Oxidation
- Chemical precipitation
- Zeolites
- Granular activated carbon
- Biologically aerated filters
- Adsorptive or organic filters
- Disinfection
- Electrodialysis
- Electrodialysis reversal
- Electrodeionization

Settling Pond



Application:

Why: Initial separation of suspended solids before piping or trucking for off-site treatment or disposal as well as off-site facility use for separation after biological processes and conventional coagulation/flocculation.

Where: Commonly used in **on-site facilities** for storage and initial removal (where permitted) and as an integrated process at **off-site facilities**.

Target Contaminants:

Suspended solids

Iron and manganese (via oxidation from dissolved oxygen equalization with atmospheric conditions)

Organic chemicals naturally occurring or present in fracturing chemical (partially degraded through photolysis)

Higher removal efficiencies are possible by adding chemical addition (pH adjustment, coagulants, biocides, etc.)

Settling ponds use gravity to separate and remove suspended solids. Water flows across the settling pond with sufficient time for large particles to settle out. Particles that accumulate on the pond bottom are periodically removed and sent to landfills for disposal.

Settling ponds are open to the atmosphere and also provide some limited oxygen diffusion and photolysis (i.e., degrading chemicals via light and photons). However, complete degradation for organic compounds in a settling pond is unlikely. If photolysis occurs, it will likely only promote byproduct compound formations and subsequent organic compounds derivatives that will also need to be removed.

Benefits:

- Low chemical demand
- Low energy demand
- Minimal maintenance, periodic removal of sediment is required
- Minimal periodic operator oversight
- Capital costs in most producing area are generally low for land acquisition

Limitations:

- Large footprint
- Lack of mobility
- Poor removal of oil and grease
- Requires regulatory permitting (environmental protection)



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Plate Settler

Application:

Why: To provide initial separation of suspended solids as a part of a high rate clarification. Use after conventional coagulation/flocculation in both mobilized container units for on-site recycling or in centralized facilities at off-site locations.

Where: On-site facilities and off-site locations.

Target Contaminants:

Suspended solids

Aggregated compounds including iron, manganese, zinc, naturally occurring organic matter, and radionuclides targeted by coagulation chemicals (in combination with conventional coagulation and flocculation)

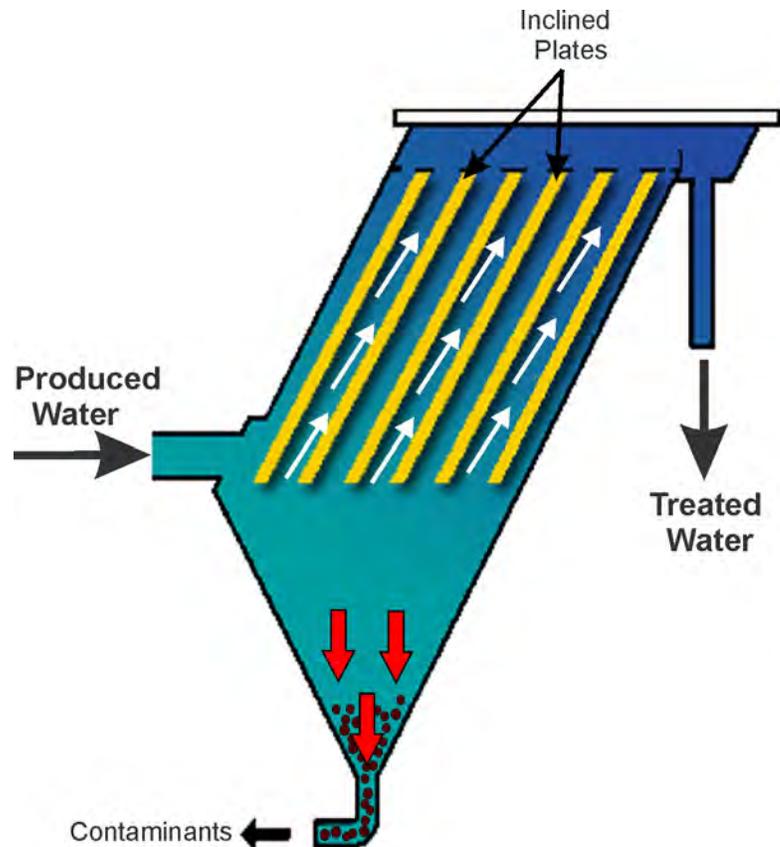
Benefits:

- Low chemical demand
- Easy to operate
- Mobile units

Limitations:

- Moderate maintenance
- Long hydraulic retention time
- Poor removal of oil and grease

Plate settlers use gravity to separate and remove suspended solids. Water usually flows from the coagulation/flocculation unit directly to the plate settler. In the settler, water flows upward along inclined plates to separate suspended particles from the main water stream. Plate settlers decrease the time required for settling by operating in the reverse direction of the separation mechanism, gravity, to promote removal. Plate settlers are designed to funnel or collect particles that accumulate for easy thickening or removal to landfills for disposal.



Inclined plate settler (Parkson Corp., used by permission).



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RECLAMATION
Managing Water in the West

Hydrocyclone

Application:

Why: Density driven pretreatment to separate low density hydrocarbons from higher density water and particulates.

Where: **On-site** at the well head or **off-site** as pre-treatment at large facilities.

Target Contaminants:

Oil and suspended solids.

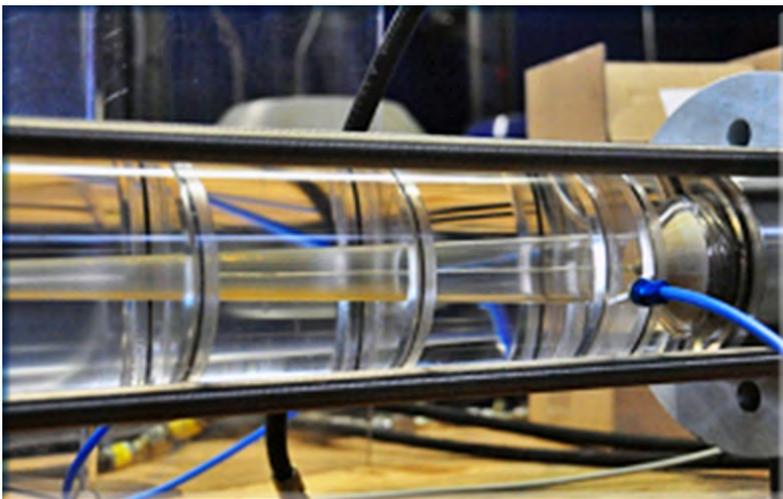
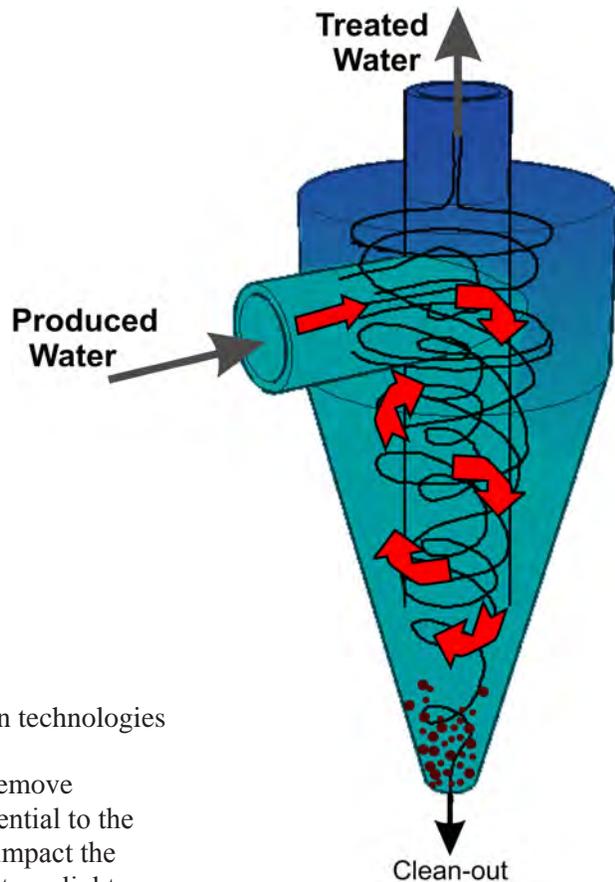
Benefits:

- No pretreatment
- Mobile units
- Smaller footprint

Limitations:

- High velocity abrasion
- Higher relative cost compared to gravity separation technologies

Hydrocyclones use centripetal force to separate and remove suspended solids. Water is pumped into the inlet tangential to the wall. The water's spiral flow path causes particles to impact the walls of the separator. Heavier particles fall to the bottom; lighter particles may form a cake layer on the entrance wall and fall to the bottom in clumps. If oil is present, it is carried to the overflow exit. Water and sand or other heavy particles exit through the underflow. If the system is just for solids, then they are washed out through the underflow while treated water exits through the overflow. Depending on the design, both particulates and oil particles may be removed due to differing density from the main water stream.



InLine HydroCyclone Separator (FMC Technologies, used by permission).



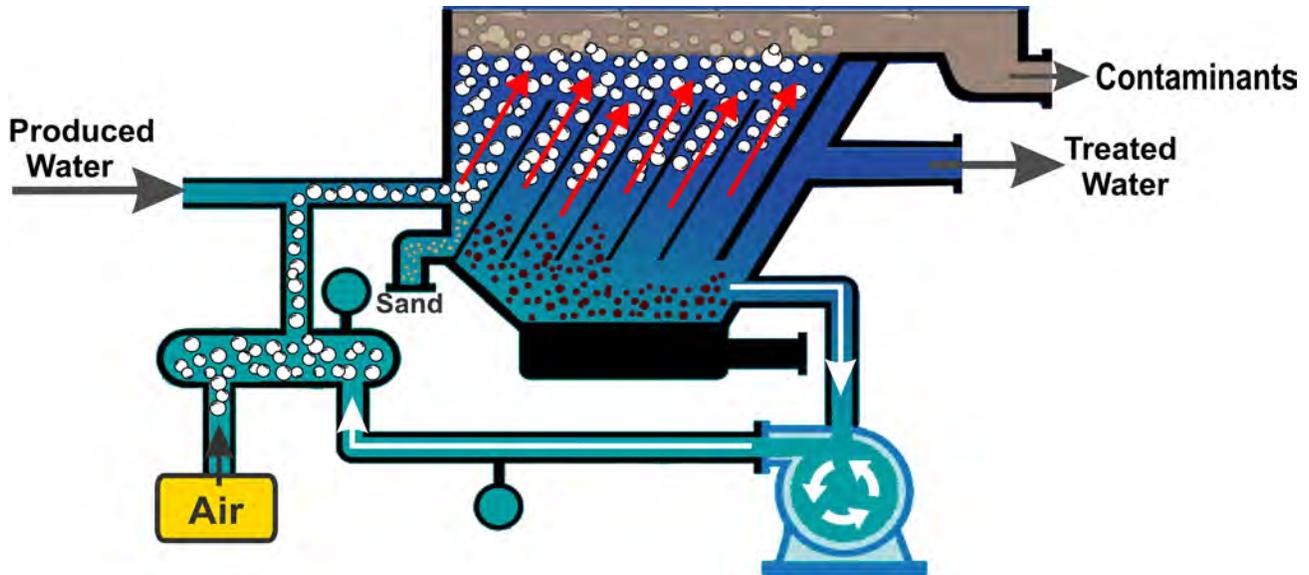
Hydrocyclone Separator (CDE Global Inc., used by permission).



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RECLAMATION
Managing Water in the West

Dissolved Air Flotation



Application:

Why: Separate particles and other organic materials that are lighter than (or close to) the density of water.

Where: On-site treatment and recycling in containerized systems.

Off-site large-scale facilities use dissolved air flotation in a treatment process after coagulation and flocculation and before bioreactors and membrane filtration.

Target Contaminants:

- Oil
- Grease
- Lightweight suspended particles (e.g., transparent exopolymers)
- Organic matter
- Dissolved gases
- Volatile compounds

Benefits:

- No pretreatment requirements
- Mobile units available for pretreatment
- Smaller footprint than sedimentation ponds
- Effective removal of low density

Limitations:

- Operations at higher temperatures could be more difficult because the viscosity of water is less and oils and greases could become dissolved
- Higher operation and maintenance costs than sedimentation ponds, due to system complexity and aeration requirements

Dissolved air flotation uses gas bubbles to lift lighter suspended particles to the surface of a tank for removal. The dissolved air comes out of solution: micro-bubbles rise and capture small, light particles (e.g., grease, oils, and organic material), bringing them to the surface as foam to effectively filter out lightweight particles. This is similar to foam generated by wave action and falling water. (Degrémont, 1991, pages 171 – 176.) The foam is scraped off the surface. Heavier solids are collected from the bottom of the tank.

Note that dissolved air generally provides significant aeration, so oxidizable compounds may form complexes that will also be readily removed. If volatile compounds are dangerous to human health (e.g., hydrogen sulfide), care should be taken to vent gasses.



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RECLAMATION
Managing Water in the West

Electrocoagulation/Electrofloatation

Application:

Why: Target compounds that need to be removed for water reuse.

These systems, in combination with filtration, may meet requirements to directly reuse flowback or produced water for hydraulic fracturing.

Where: **On-site** recycling systems and **off-site** treatment facilities.

Target Contaminants:

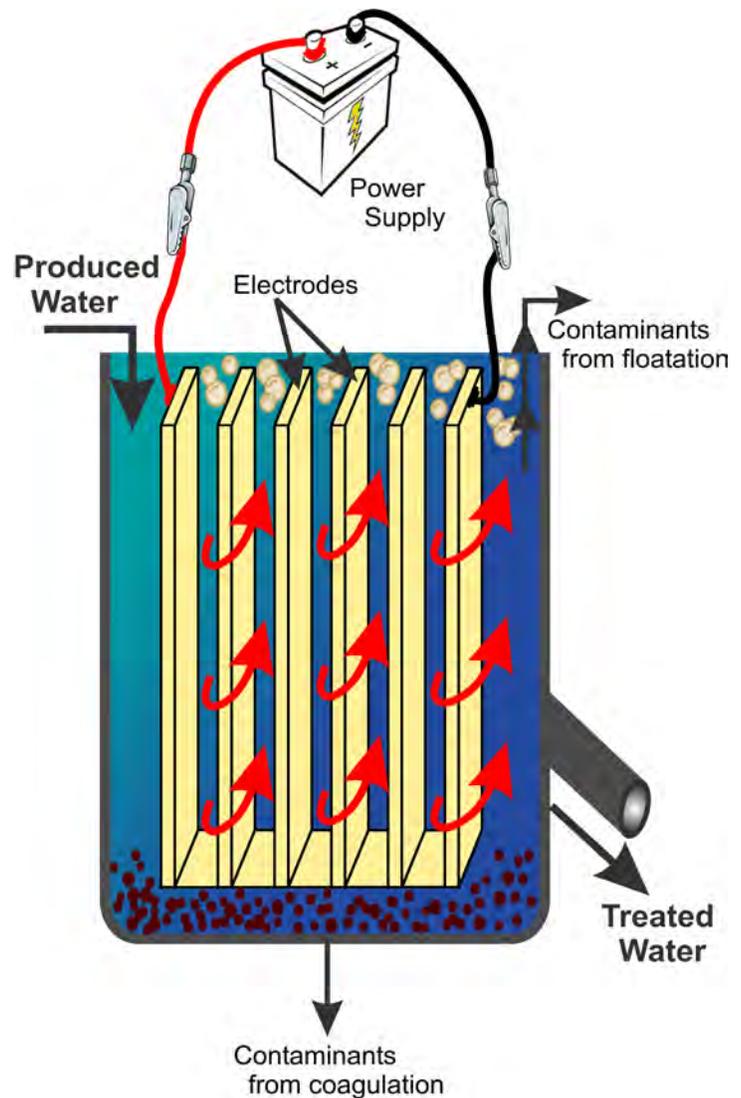
- Emulsions (which are difficult to remove with chemical or filtration treatment processes)
- Suspended solids
- Heavy metals
- Natural organic matter
- Biological contaminants
- Fracturing chemicals

Benefits:

- Lower chemical demand than conventional coagulation and flocculation
- Targeted treatment for water recycling
- Relatively small footprint

Limitations:

- High energy requirements
- Higher relative cost
- Maintenance required for anode and cathode plates



Electrocoagulation uses electricity to gather particles, heavy metals, oils, and grease suspended in water into a sludge that can be removed. Sacrificial electrodes of iron or aluminum are connected in parallel to a DC current. When an electric potential is applied across the electrodes, it drives off metal ions from the electrode. These ions neutralize charged particles and form metal hydroxide precipitates that rise to the top in a foam or settle to the bottom, depending on their density.

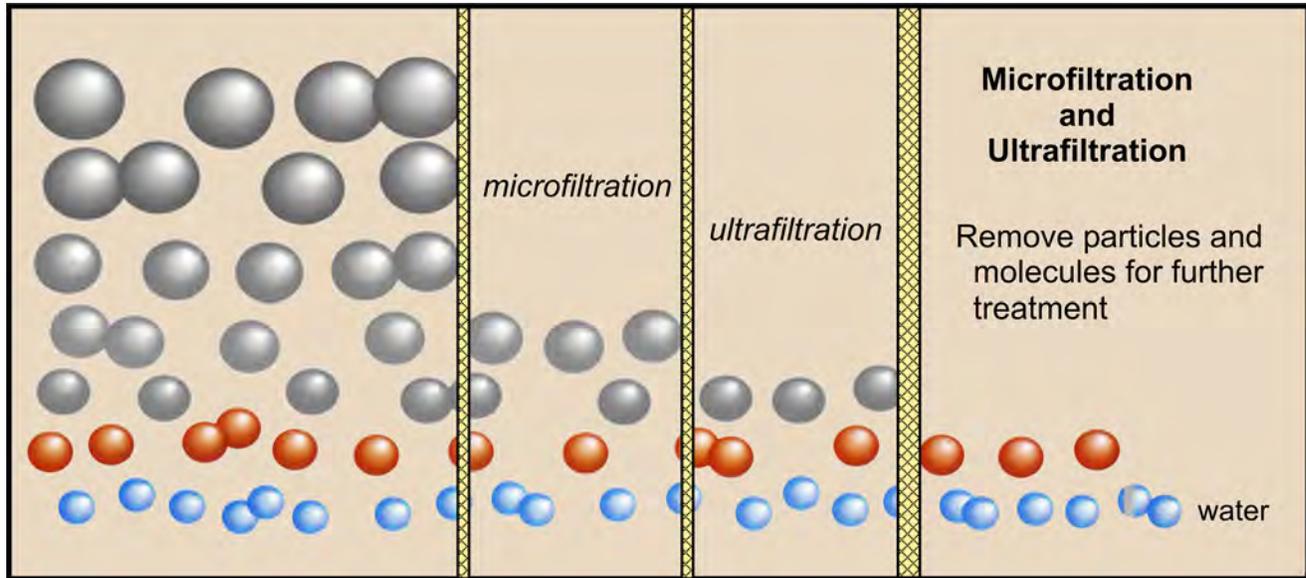
Electrofloatation occurs when the electrical current creates dissolved gas (hydrogen or oxygen) from the water that lifts particulates out of solution. Like dissolved air floatation, this captures oils, grease, and light particles, and carries them to the surface. Foam is skimmed off the surface, solids are scraped from the bottom, and clarified water is discharged from the center of the reactor.



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RECLAMATION
Managing Water in the West

Microfiltration/Ultrafiltration



Application:

Why: Pretreatment technology to remove particles and colloidal material before further membrane treatment.

Where: Both mobile **on-site** systems for water recycling and **off-site** facilities.

Target Contaminants:

- Trace particulates
- Oil and grease
- Biological and organic constituents
- Large molecular weight organic compounds.

Benefits:

- Small footprint
- Modular and mobile systems
- Consistent constituent removal

Limitations:

- Moderate energy demand
- Material susceptible to damage
- Require chemicals for cleaning

Membranes are classified by the size of the particles that they exclude. Microfiltration and ultrafiltration filter larger particles and are thus only used for pretreatment or removing particulates. These membranes use pressure or suction to filter water through a porous membrane. Membranes can be made from either polymeric or ceramic materials. Ceramic materials have a longer lifetime and can be cleaned with more aggressive chemicals, but they generally cost more than polymeric materials.

As the required footprint per volume of water treated is relatively smaller than traditional media filtration, microfiltration and ultrafiltration modules are commonly combined with other treatment processes in containerized trailers for on-site produced water recycling treatment, such as hydrocyclones for sand and oil separation, followed by microfiltration or ultrafiltration for smaller particles and colloidal material, before a desalting process.



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RECLAMATION
Managing Water in the West

Bioreactors

Application:

Why: Pretreat water and remove organic matter before ultra or microfiltration and reverse osmosis treatments.

Where: Off-site treatment facilities (due to sensitivities in transporting cultures and stabilizing inflow water qualities).

Target Contaminants:

- Oil, grease, and hydrocarbons
- Fracturing chemicals
- Naturally occurring organic matter
- Iron and manganese (from oxidation during aeration)

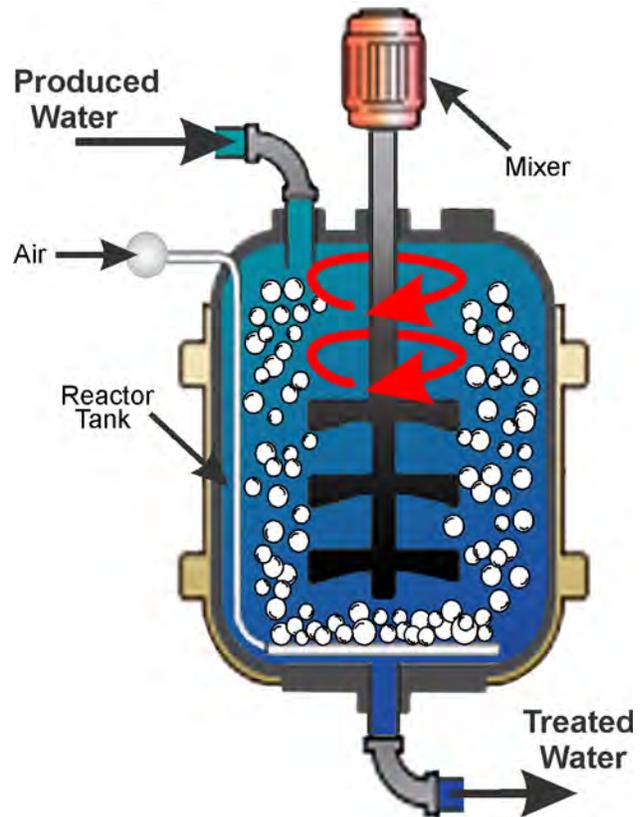
Benefits:

- Lower chemical demand than conventional coagulation and flocculation
- Modular systems

Limitations:

- Moderate energy demand
- Requires a stable and robust microbial culture
- Post treatment required

Bioreactors use naturally occurring microbial processes to removal biodegradable compounds. Reactors seeded with active microbial cultures treat incoming produced water. Biological reactors generally include diffusers to add oxygen to promote aerobic reactions and degradation. Oil, grease, and hydrocarbons, fracturing chemicals, and naturally occurring organic matter may all be readily biodegradable.



Kruger Neosep membrane bioreactor system at San Diego Pt. Loma WWTP (Reclamation photograph).



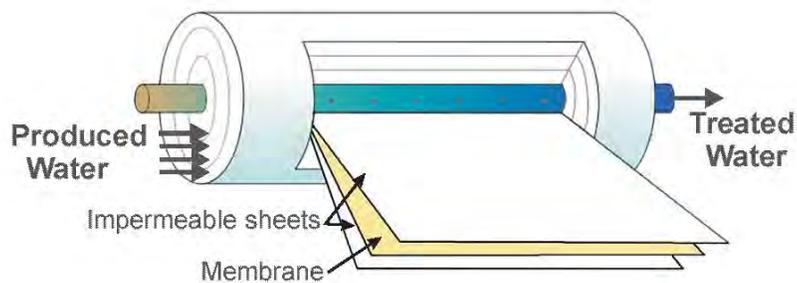
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RECLAMATION
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Membrane Treatment Technologies

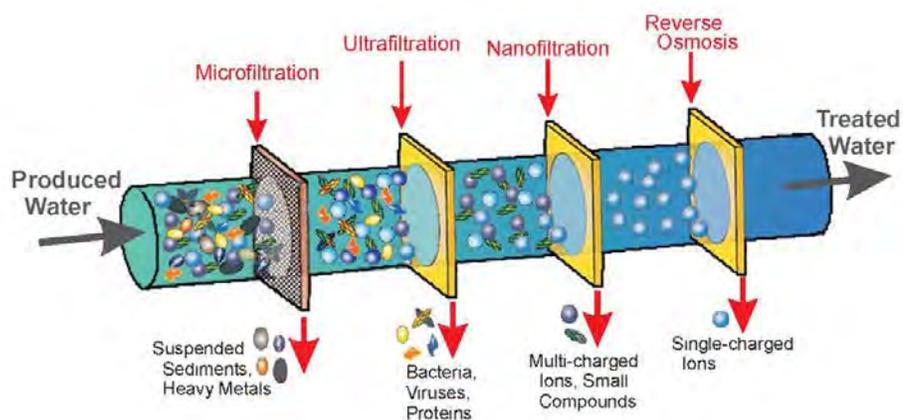
A variety of membrane technologies can remove dissolved contaminants. Both ultrafiltration and microfiltration membranes were listed under the pretreatment category, this section focuses mainly on common desalination membrane processes. Additional technologies not listed include: electrodialysis, electrodialysis reversal, and electrodeionization. Additional information on these technologies and the technologies included is available in Guerra et al., 2011.

Membranes are flat sheets, which are then wound in a tight spiral for the most surface area in the smallest space.



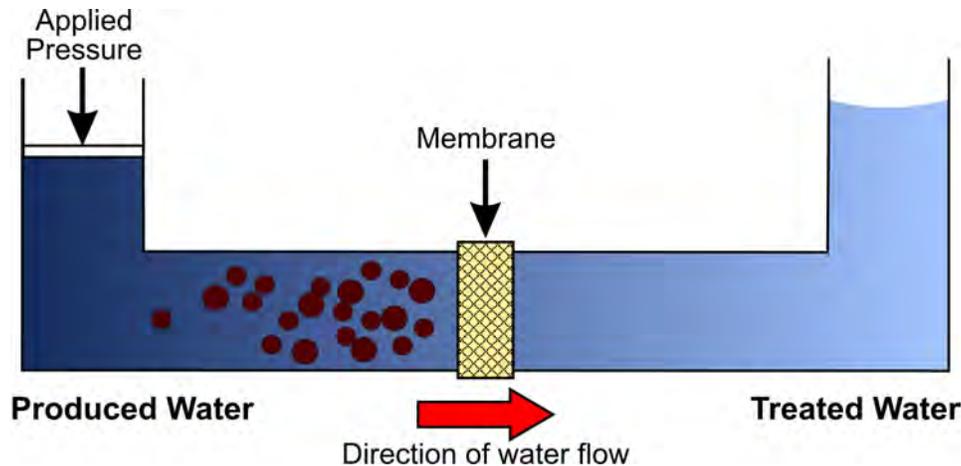
A diagram of a basic spiral membrane.

Water filters through these membranes, which capture various contaminants, depending on the filter size.



A diagram of the membrane filtration spectrum.

Nanofiltration and Reverse Osmosis



Application:

Why: Water recycling and brackish groundwater treatment.

Where: Containerized systems **on-site**, maybe near **well heads** and **off-site facilities** where technologies are preceded by significant pretreatment processes.

Target Contaminants:

Divalent salts (e.g., calcium sulfate, calcium carbonate) (nanofiltration may be used in tandem with reverse osmosis or a second stage of nanofiltration membranes to increase constituent rejection)

Ions, including sodium, nitrate, and chloride.

Nanofiltration and reverse osmosis are cross-flow membrane filtration processes. Nanofiltration membranes have a higher rate of salt transport and preferentially retain higher charged ions such as calcium and sulfate than reverse osmosis membranes. Depending on the specific membrane properties, the rejection of monovalent ions, such as nitrate, sodium, and chloride will be as low as 45 percent. Reverse osmosis membranes, by definition, have a very low salt transport rate, and will reject as much 99.5 percent of all dissolved ions. Both types of membrane act on charged ions or molecules. Uncharged molecules will pass through the membrane, depending on the size. Some molecules may be too large to pass through the membrane and are retained in the concentrate.

Both processes are harmed by particulates, biological material, and high concentrations of slightly soluble salts, so pretreatment is necessary to provide an acceptable feed water.

Benefits:

- Produces high quality water for reuse
- Modular and mobile systems
- Consistent constituent removal

Limitations:

- High energy demand
- Susceptible to scaling and biofouling
- Require chemicals for operation and cleaning



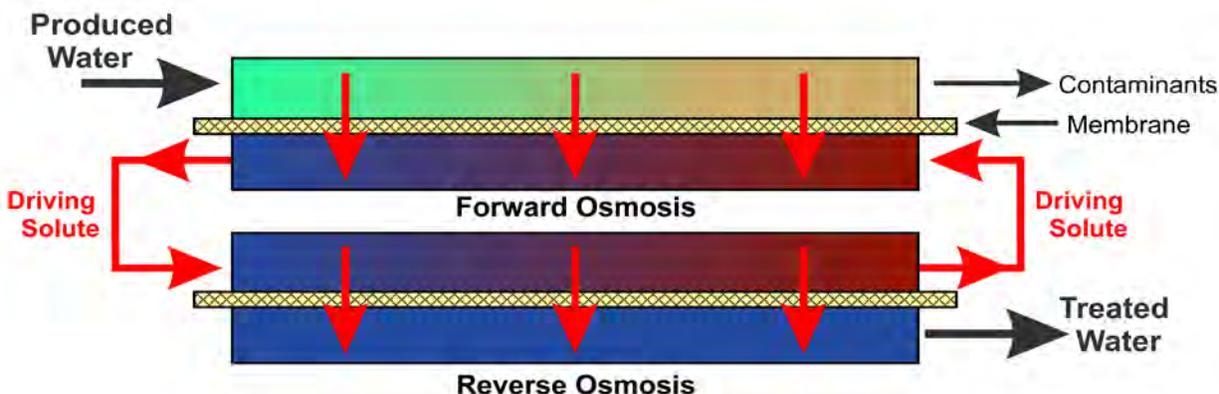
Long Beach Nanofiltration Prototype
(Reclamation photograph).



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Forward Osmosis



Application:

Why: Reduce volume of produced water for injection or disposal. May be energetically preferred over reverse osmosis or distillation if there is a high salinity water available to use as the draw solution.

Since forward osmosis does not operate under pressure, membranes are less susceptible to irreversible fouling due to colloidal or biological contamination.

Coupled with reverse osmosis or distillation systems to recover the draw solution.

Where: On-site water recycling

Centralized facilities

Well head and off-site facilities

Forward osmosis is an osmotic process that uses a semi-permeable membrane and a draw solution as a driving force to separate water from dissolved solutes. Draw solutions must have higher osmotic potential due to higher concentration of solute than the feedwater; otherwise, movement would flow from the driving solution to the feed water.

As feed water flows along the semi-permeable membrane surface, product water moves through the membrane, diluting the driving solution. The driving solution is thus continually diluted along the flow path, increasing in volume and the feed solution is continually concentrated along the flow path, decreasing in volume.

The second critical step in forward osmosis is recovering the driving solution, which can be done by distillation or membrane distillation and reverse osmosis.

Target Contaminants:

Same type of applications as nanofiltration and reverse osmosis membranes.

Dissolved minerals.

A saline source of water with organic or biological contamination can be concentrated using another available source of water that is excessively saline but does may be easier to pretreat to a level that can be used as feed to reverse osmosis.

Benefits:

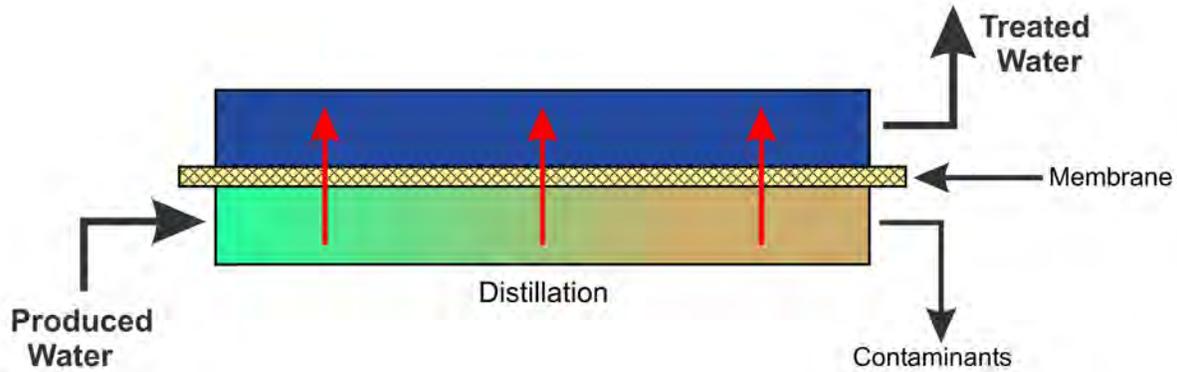
- Low energy requirements
- Modular and mobile systems
- Consistent constituent removal

Limitations:

- Requires a draw solution
- Larger footprint than reverse osmosis
- Relatively new technology



Membrane Distillation



Application:

Why: Membrane distillation could be used for brackish groundwater desalination to generate hydraulic source water

Where: **On-site** or may be coupled with renewable energy sources at centralized off grid locations.

Membrane distillation systems can use latent heat from produced water, or heat from burning off natural gas in certain areas to reduce energy requirements

Target Contaminants:

Dissolved salts.

Membrane distillation is a thermally driven membrane separation process where constituents are separated as the heated feed solution passes through the membrane as vapor and condenses into the chilled product water. The rate of production depends on the difference in temperature between the feed and product sides of the membrane (Singh and Sirkar, 2011). A source of clean chilled water is required to start the process

Membrane distillation can be used in the same applications as reverse osmosis or nanofiltration when there are sources of economical heat and cooling available. Membrane distillation is can also be used to strip volatile compounds from a source of water, dissolving them into the cool water source or into air.

Benefits:

- Potential for off-grid systems
- Modular and mobile systems
- Consistent constituent removal

Limitations:

- Requires energy for heat and a source of cold water.
- Volatile compounds are not removed and may be preferentially transferred across the membrane.
- Relatively new technology



*Membrane Development,
(Reclamation photograph).*



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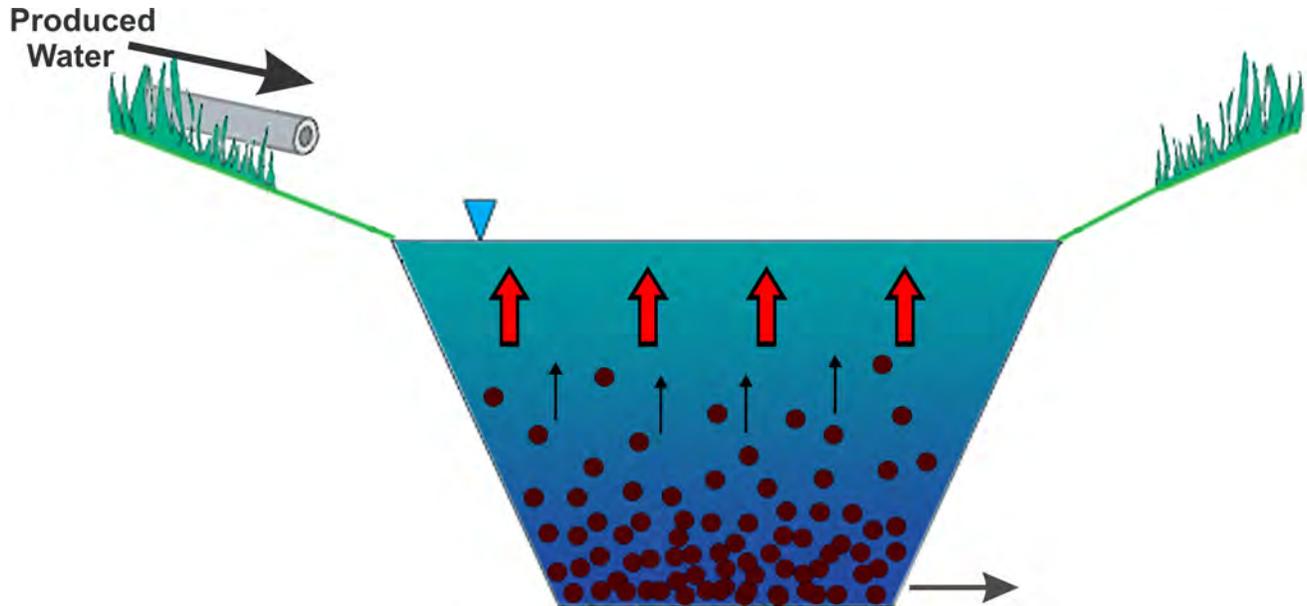
Hybrid and Thermal Technologies

As an alternative to membrane technologies, a variety of thermal and hybrid technologies can remove dissolved contaminants. Thermal processes generally require higher amounts of energy to change the phase of water from liquid to gas. Technologies highlighted in this section range from simple natural processes to mechanically enhanced processes. Additional technologies not listed include:

- Multi-effect distillation
- Multi-stage flash
- Vapor compression
- Vertical tube evaporation
- Carrier gas (pervaporation)
- Capacitive deionization

Additional information on these technologies and the technologies included is available in Guerra et al., 2011.

Evaporation



Application:

Why: Reduce produced water volumes.

Where: On-site or off-site at a centralized location.

Generally, near the well head, but in some areas, centralized ponds are used for many wells.

Target Contaminants:

Contaminants that can be addressed in concentrated volumes. If evaporation ponds can be reduced to dry solids suitable for landfills, then solids may be transported or ponds may be covered and converted to disposal pits.

Benefits:

- Relatively low cost
- Low energy and chemical requirements
- Minimal maintenance

Limitations:

- No beneficial products
- Large footprint
- Lack of mobility
- Long retention time to complete evaporation
- Permitting and protection issues

Evaporation ponds can use the latent heat of evaporation to reduce produced water volumes for disposal. Evaporation, without a condensation system to recapture treated water, is a concentrate minimization technique, and thus evaporation alone will not recover water for beneficial use. Evaporation ponds leave all ions as residuals. Evaporation is most effective in areas with high solar radiation.

Environmental concerns to wildlife, particularly migratory birds, require permitting and protection of certain open water ponds. Furthermore, protection for wildlife, such as cattle, may also be required to prevent livestock from consuming produced water.

Similar to settling ponds, evaporation ponds are open to the atmosphere and also allow some limited oxygen diffusion and photolysis to occur.



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Crystallizer

Application:

Why: Reduce produced water volumes on-site to reduce transportation costs off-site for disposal.

Where: Due to power requirements, crystallizers are often used in **centralized facilities** to treat water before transporting to more distant disposal facilities or **on-site** at locations with power connections.

Target Contaminants:

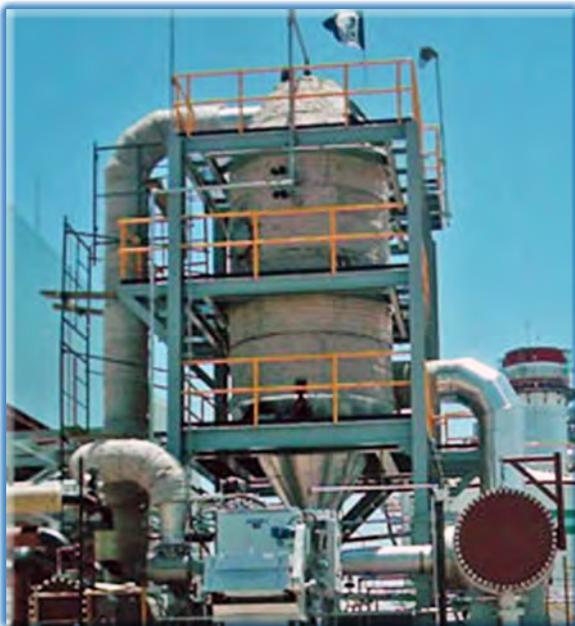
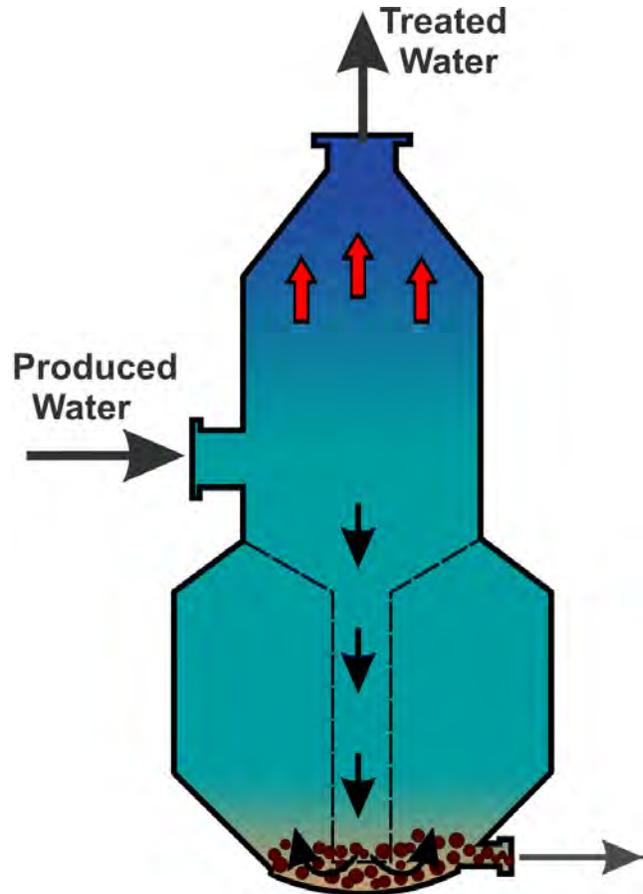
Liquid concentrated wastes are reduced to solids or slurries of greatly reduced volume.

Benefits:

- Volume reduction
- Solid disposable product
- Smaller footprint than evaporation ponds

Limitations:

- High energy requirements
- Relatively expensive
- Lack of significant beneficial product



Evaporative Crystallizer (Dedert Corp., used by permission).



Forced Circulation Crystallizer (Dedert Corp., used by permission).

Previously described desalination processes produce a concentrate waste product that may still have significant volume. In these situations, crystallization will reduce the concentrated produced water to a crystalline solid by distilling off the remaining water.



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Ion Exchange

Application:

Why: Exchange problematic ions for less obtrusive ions as a polishing step for treated water.

Where: Ion exchange is used with low total dissolved solids water to remove hardness, or other hazardous contaminants that remain in the treated water in low concentrations.

Target Contaminants:

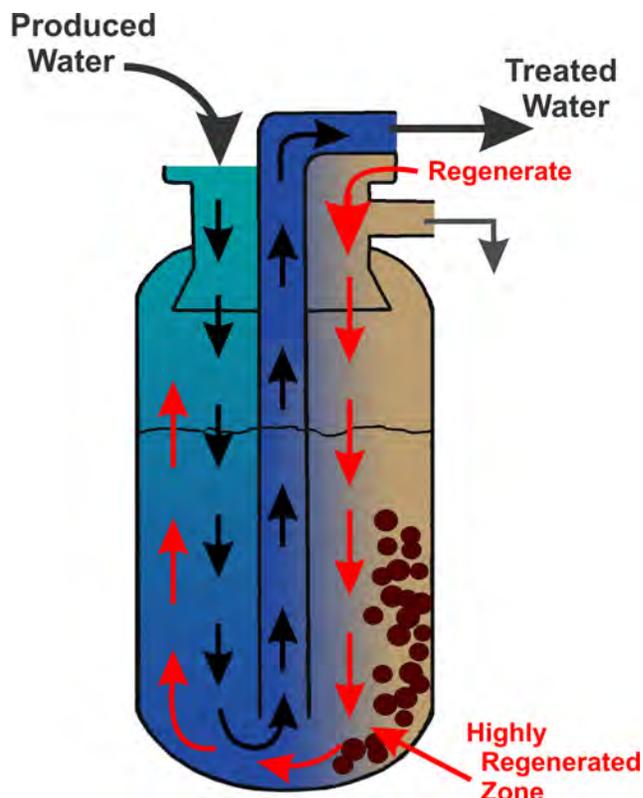
Fluoride, nitrate, arsenate, selenate, chromate, or anionic uranium complexes.

Benefits:

- Low energy
- Small footprint
- Modular and mobile systems

Limitations:

- High chemical demand for regeneration
- Limited TDS concentrations



Ion exchange processes are reversible chemical reactions to remove dissolved ions from solution, replacing them with less troublesome ions of the same charge. For example, each calcium ion is exchanged for two sodium ions in a salt form cation exchange resin, or two hydrogens in the acid form. Ion exchange resin beads have surface charges (i.e., negative for cation exchange resin beads and positive for anion exchange resin beads) and affinities for certain ions over others depending on concentration and pH. Strong base anion exchange resins have the following relative affinity order (DeSilva, 2005): *uranium/perchlorate* >> *sulfate/chromium* > *selenium/arsenate nitrate* > *chloride* > *bicarbonate* > *fluoride*.

The resin must be re-charged periodically when the target ions begin to pass through the system. Concentrated (20 percent by weight) sodium chloride solution is used to recharge anion or cation resin in the salt phase. In the acid-base phase, hydrochloric acid can be used to recharge the cation resin and sodium hydroxide to recharge the anion resin. The is greater with acid and base regeneration because of the higher materials cost of equipment for corrosion resistance, more expensive chemical cost, and disposal cost of the spent regeneration solution, however the resin is more completely regenerated with acid and base solutions.

Packed Bed technology ion exchange filter
(Ecodyne, used by permission).



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Case Studies of Treatment Applications

Links are provided to case studies and applications of water treatment applications in the oil and gas industry under a variety of broad treatment technology categories. Links to additional information are organized with examples for treatment applications in alternative water sourcing, on-site mobile treatment, and off-site centralized facilities.

Alternative Water Sourcing

Bakken, Montana

This study piloted the use of desalination technology on brackish groundwater to create an alternative water supply for hydraulic fracturing operations in the Bakken shale play in Montana. Alternative water sources are needed in the Bakken as production has increased significantly and additional fresh water availability in the area is not available.

Reference Information: Kurz, B. 2010. “Bakken Water Opportunities Assessment”. University of North Dakota’s Energy and Environmental Research Center (EERC)



Process of mixing water with fracking fluids to be injected into the ground (Wikimedia commons).

Barnhart, Texas

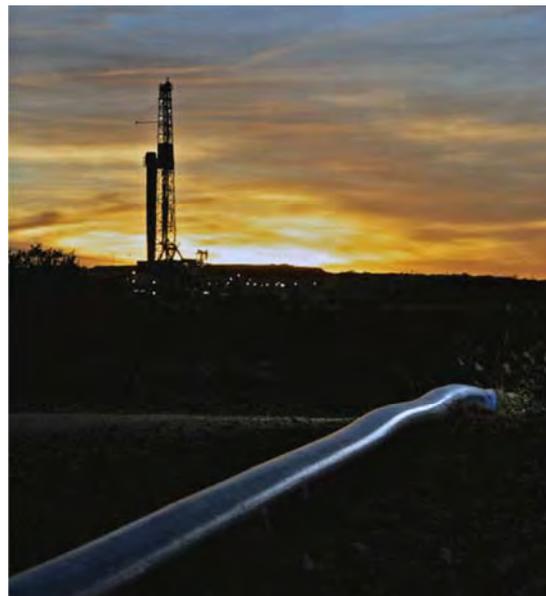
Background: Water scarcity in west Texas has promoted the use of a blended fracturing supply of brackish and recycled flowback water. The company has a closed-loop system that uses only brackish and recycled water in hydraulic fracturing operations at its 35,000 acre Barnhart project area in Irion County west of San Angelo. Nonpotable brackish water from the Santa Rosa aquifer is moved to large, lined retention ponds and then treated to remove bacteria before it is used. Produced water is treated to remove sulfates, magnesium, iron, bacteria, and large solids that can damage pipelines and pumping equipment and then pumped to the company's numerous pad drilling sites in the area.

Reference: Apache Corporation. Recycling Water for Drilling Operations. www.apachecorp.com/Sustainability/Environment/Water/Recycling_water_for_drilling_operations/index.aspx.

www.ogj.com/articles/uogr/print/volume-2/issue-1/wolfcamp/apache-fracs-wolfcamp-wells-without-fresh-water-in-dry-barnhart-project-area.html. Site date: 9/4/2013. Accessed 11/14/13.



Apache uses above ground modified grain bins with double-layer plastic liners to hold and treat produced water that is recycled for use in Wolfcamp shale wells in Irion County, Texas (Apache Corp., used by permission).



Apache transports brackish and recycled water from a central facility to well sites for use in hydraulic fracturing completion operations in the Barnhart area, in Irion County, Texas (Apache Corp. used by permission).



Apache Corporation uses non-potable brackish water from the Santa Rosa aquifer and recycles produced water to supply all of the water needed for well completions in the Barnhart area. The re-engineered grain bins are used to treat produced water before it is reused (Apache Corp., used by permission).



Apache Corporation pumps water from the brackish Santa Rosa aquifer into large, lined detention ponds for use in its well completion operations at the Barnhart project area in Irion County, Texas, west of San Angelo (Apache Corp., used by permission).

Stiles Ranch Water Recycling Plant, Wheeler County

Background: Apache is expanding its use of alternative water sources in an effort to minimize freshwater used in hydraulic fracturing operations. The company has dramatically increased its use of produced water and brackish water for drilling in the Anadarko and Permian basins of Oklahoma and Texas.

Reference: Apache Corporation. Recycling Water for Drilling Operations. www.apachecorp.com/Sustainability/Environment/Water/Recycling_water_for_drilling_operations/index.aspx. Site date: 9/4/2013. Accessed 11/14/13.



Apache runs fracture-stimulation operations at Stiles Ranch in the Texas Panhandle (Apache Corp., used by permission).

Onsite Water Reuse

Alberta, Canada

Background: Evaporative and crystallizer water treatment technologies are commonly employed to produced reuse in remote locations, such as Albert's Oil Sand deposits. GE Power and Water, Water and Process Technologies provides a number of technologies for industrial water reuse including zero-liquid-discharge systems, membrane bioreactors, and mobile units.

Reference: GE Power and Water, Water and Process Technologies, Managing Water Resources in the Oil Sands Industry, nd.



Top photo: Membrane bioreactor



Right photo: Evaporative system

Bottom photo: GE Mobile evaporator unit (GE Power & Water, used by permission).



Eagle Ford Shale, Texas

Background: This basin commonly uses onsite water reuse to treat flowback water for reuse hydraulic fracturing operations. Purestream Services will deploy its vapor recompression commercial water treatment system in Gonzalez County, Texas. On-site treatment technology allows producers to integrate water management options into existing operations.

Reference: For more information, visit www.purestreamtechnology.com.
www.wateronline.com/doc/purestream-operations-treat-eagle-water-gonzalez-county-texas-0001.



Purestream Services commercial operations deployment March 2014 to treat Eagle Ford Shale produced and flow-back water In Gonzalez County, Texas (Avara, used by permission).



Purestream deploys AVARA vapor recompression systems to Eagle Ford to treat 2,500 barrels per day for reuse (Avara, used by permission).

Permian Basin, Texas

Background: The Permian Basin produced water quality varies across the basin and hydrocarbons can be produced from conventional oil to shale gas. The Halliburton CleanWave® Water Treatment Service is an electrocoagulation process that cleans produced water with TDS up to 285,000 mg/L and removes hydrocarbons, heavy metals and suspended solids. The technology is employed in a number of basins generally as a containerized system for on-site reuse.

Reference: Halliburton 2014. A Case Study: Effective fracturing with recycled water. Halliburton.

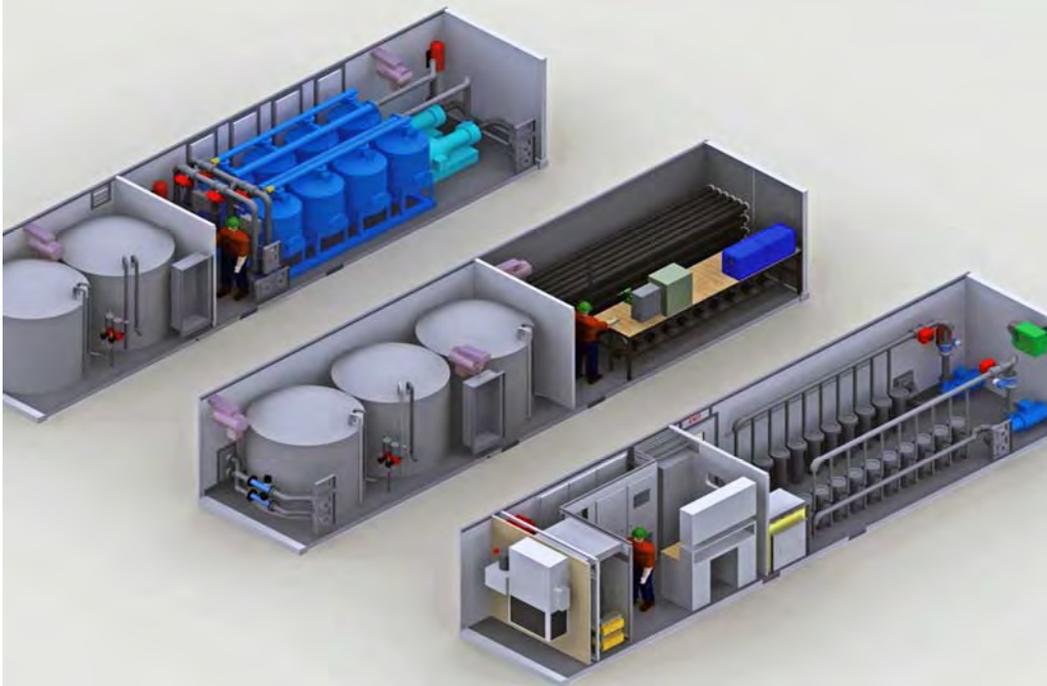
www.halliburton.com/public/pe/contents/Case_Histories/web/A_through_R/H09855.pdf



Inside of Truck: Inside view of the electrocoagulation unit used in the CleanWave® Water Treatment Service (Halliburton, used by permission).



IGF Plus technology can treat anywhere from 2,500 to 80,000 barrels per day. It is commonly used in offshore platforms and removes suspended solids and oil and grease to 1 micron, but does not remove chlorides. Producers are able to re-use the treated water to frack with; typically it can treat water for under \$.75 per barrel (Purestream, Inc., used by permission).



3D CAD: Equipment trailers used in the CleanWave® Water Treatment Service (Halliburton, used by permission).



Cutaway: Onsite CleanWave® Water Treatment Service (Halliburton, used by permission).

Centralized Treatment Beneficial Use

Clarion and McKean County, Pennsylvania

Background: Clarion Altela Environmental Services (CAES) produced water treatment plant and CARES McKean Facility treat flowback and produced water from the Marcellus Shale. Both facilities use the AltelaRain® distillation process to treat and reuse flowback water.

Reference: www.CAESwater.com, www.caresforwater.com, www.altelainc.com.



Trucks delivering produced water to CAES for treatment (Altela Inc., used by permission).



Top and middle photos: AltelaRain® Towers and additional equipment inside the CARES Treatment Facility

Bottom photo: Produced Water Holding Pond at CARES Treatment Facility (Altela, Inc., used by permission).



Wellington, Colorado

Background: Wellington Water Works treats oilfield produced water which is injected and stored through aquifer storage for use as a non-tributary water supply for energy development. The town of Wellington is located in the north area of Larimer County, Colorado

Reference: Stewart Environmental Consultants, Inc.
www.stewartenv.com/php_uploads/stewart_lg_20100604154748.pdf.



Inside the Wellington Waterworks, consultants Randy Evans, left, and David Stewart, center, work with project partner Richard Seaworth in the heart of the processing system. (Stewart Environmental Consultants, Inc., used by permission).



Ceramic Microfilter Skid for treatment (Stewart Environmental Consultants, Inc., used by permission).



*Treatment building at the Wellington Operating Company Site.
(Stewart Environmental Consultants, Inc., used by permission).*



*Oil/water separator at the Wellington Operating Site.
(Stewart Environmental Consultants, Inc., used by permission).*

Pinedale Anticline, Wyoming

Background: Anticline Disposal treats flowback and produced water for hydraulic fracturing and discharge at the Pinedale Anticline facility in southwestern Wyoming. Limitations on disposal prompted this facility to treat water from a collection of producers where 75 percent of received water is treated and redelivered and 25 percent of water is further treated and discharged to the river.

Reference: High Sierra Energy, LP, www.highsierrawater.com, www.highsierrawater.com/water-disposal/.



Reverse osmosis process (NGL Water Solutions, used by permission).



Last treatment step before environmental discharge into New Fork River (NGL Water Solutions, used by permission).



Exterior facility shot focusing on one of the two large dissolved air flotation units (NGL Water Solutions, used by permission).



External facility shot, focusing on the Main Process Building (NGL Water Solutions, used by permission).

San Ardo, California

Background: San Ardo treats produced water for the purposes of discharge to recharge basins and production of Once Through Steam Generator make-up water. This was the first membrane - based produced water desalination facility in the US and is operated by Veolia Water for Chevron U.S.A.

Reference: Veolia and Chevron USA,
www.vwsoilandgas.com/resourcecenter/case-studies/27696.htm.



San Ardo (Veolia, used by permission).

Shell Pearl GTL Plant, Qatar

Background: Shell's plant in Qatar is a zero liquid discharge facility that disposes of 100% of the influent produced water with a capacity of up to 280,000 barrels per day. The plant, operated by Shell and Veolia, produces more water than gas-to-liquid product.

Reference: For more information see Shell (www.shell.com/global/aboutshell/major-projects-2/pearl/water-treatment.html) and Veolia (www.vwsoilandgas.com/)



Shell's gas-to-liquids plant in Ras Laffan, Qatar (Veolia, used by permission).