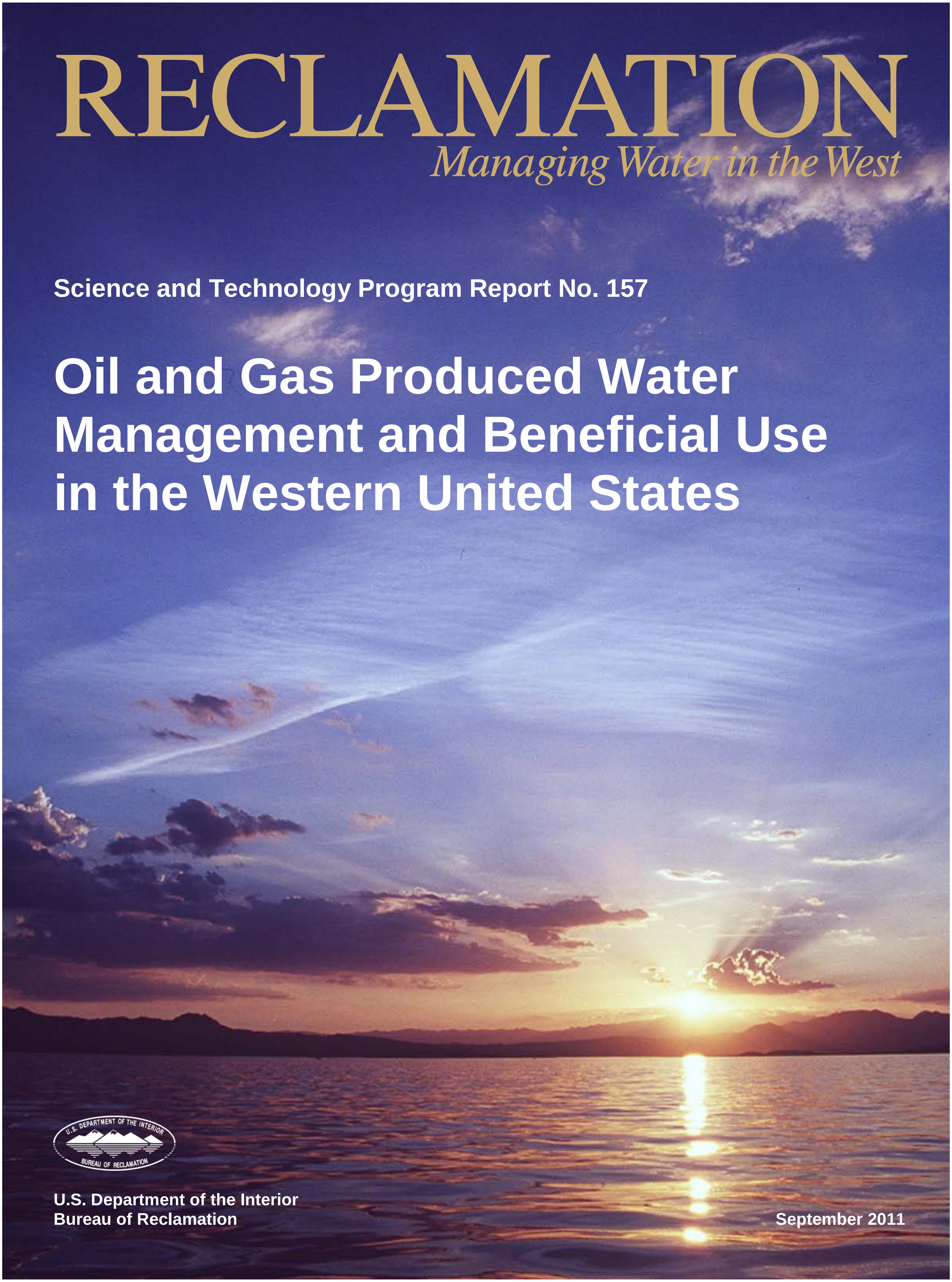


RECLAMATION

Managing Water in the West

Science and Technology Program Report No. 157

Oil and Gas Produced Water Management and Beneficial Use in the Western United States

U.S. Department of the Interior
Bureau of Reclamation

September 2011

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
September 2011

2. REPORT TYPE
Final

3. DATES COVERED *(From - To)*
10/2006 to 9/2010

4. TITLE AND SUBTITLE
Oil and Gas Produced Water Management and Beneficial Use in the Western United States

5a. PROJECT NUMBER
3180

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Katie Guerra, Katharine Dahm, Steve Dundorf

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Department of the Interior
Bureau of Reclamation
Denver Federal Center
PO Box 25007
Denver CO 80225-0007

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Department of the Interior
Bureau of Reclamation,
Denver Federal Center
PO Box 25007, Denver CO 80225-0007

10. SPONSOR/MONITOR'S ACRONYM(S)
Reclamation

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
S&T Report No. 157

12. DISTRIBUTION / AVAILABILITY STATEMENT
Available from the National Technical Information Service
Operations Division, 5285 Port Royal Road, Springfield VA 22161

13. SUPPLEMENTARY NOTES
Report can be downloaded from Reclamation Web site:
www.usbr.gov/pmts/water/publications/reports.html

14. ABSTRACT ***(Maximum 200 words)***
Produced water from oil and gas operations is currently handled as a waste product. The quality of produced water varies significantly based on the geochemistry of the producing formation, the type of hydrocarbon produced, and the characteristics of the producing well. If produced water meets appropriate water quality criteria, it may be used beneficially for purposes such as irrigation, livestock watering, aquifer storage, streamflow augmentation, and municipal and industrial uses. Treatment may be required to improve the quality of produced water so that it can be put to beneficial use.

15. SUBJECT TERMS
Water reuse, wastewater treatment, ultrasound, disinfection, sonochemical process

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
			SAR	113	Katie Guerra
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*
UL	UL	UL			303-445-2013

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. 239-18

Oil and Gas Produced Water Management and Beneficial Use in the Western United States

Prepared for Reclamation Under Agreement No. A10-1541-8053-381-01-0-1

by

Katie Guerra
Katharine Dahm
Steve Dundorf

U.S. Department of the Interior
Bureau of Reclamation
Technical Service Center
Water and Environmental Resources Division
Water Treatment Engineering Research Group
Denver, Colorado

September 2011

MISSION STATEMENTS

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.

Acronyms

acre/lb	acres per pound
AFY	acre-feet per year
AOC	assimilable organic carbon
AWWA	American Water Works Associations
BAF	biological aerated filter
bbl/MCF	barrels per million cubic feet
bpd	barrels per day
BAC	biologically active carbon
BOD	biological oxygen demand
BOE	barrels of energy
BTEX	benzene, toluene, ethylbenzene, and xylene
CBM	coal bed methane, also coal bed natural gas
CIP	clean in place
COD	chemical oxygen demand
COGCC	Colorado Oil and Gas Conservation Commission
DBP	disinfection byproduct
DGF	dissolved gas flotation
EC_w	electrical conductivity
EOR	enhanced oil recovery
DAF	dissolved air flotation
DO	dissolved oxygen
DOE	U.S. Department of Energy
dS/m	decisiemens per meter
ED	electrodialysis
EDI	electrodeionization
GAC	granular activated carbon
gpd	gallons per day
IGF	induced gas flotation
kgal	kilogallon
kWh/day	kilowatthours per day

Acronyms (continued)

m^2/gram	square meters per gram
MCF	million cubic feet
meq/L	milliequivalent per liter
MF	microfiltration
mrem/yr	millirem per year
MFL	magnetic flux leakage
mg/L	milligrams per liter
NOM	natural organic matter
NORM	naturally occurring radioactive materials
O&M	operation and maintenance
OPUS	optimized pretreatment and unique separation
pCi/L	picocuries per liter
ppm	parts per million
psi	pounds per square inch
Reclamation	Bureau of Reclamation
SAR	sodium absorption ratio
S/cm	siemens per centimeter
TDS	total dissolved solids
THMs	trihalomethanes
TN	total nitrogen
TOC	total organic carbon
TSS	total suspended solids
UF	ultrafiltration
USEIA	U.S. Energy Information Administration
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UV	ultraviolet
VOC	volatile organic chemicals
WAC	weak acid cation
ZLD	zero liquid discharge
°F	degree Fahrenheit
µg/L	microgram per liter

Acronyms (continued)

µm	micrometers
>	greater than
<	less than
%	percent

Contents

	Page
Acronyms	iii
1. Executive Summary	1
2. Background	3
2.1 Petroleum Resource Formation and Production	3
2.1.1 Conventional Oil and Gas	3
2.1.2 Unconventional Petroleum Resources	3
2.2 Produced Water Generation and Production	5
2.2.1 Conventional Oil and Gas	5
2.2.2 Unconventional Resources	6
2.3 Current Produced Water Management Practices	7
2.4 Environmental Impacts Caused by Produced Water	8
2.5 Study Objectives	9
3. Conclusions and Recommendations	11
4. Geographical Occurrence of Produced Water	13
4.1 Conventional Oil and Gas Resources	13
4.2 Unconventional Oil and Gas Resources	17
4.2.1 Oil Shale	17
4.2.2 Gas Shale	17
4.2.3 Tight Sands Gas	17
4.2.4 Coalbed Methane	17
4.3 Geographic Distribution of Produced Water Generation	20
5. Beneficial Uses of Produced Water	23
5.1 Produced Water Use	24
5.2 Produced Water Volumes Compared to Use Demands	24
5.3 Beneficial Uses of Produced Water	26
5.3.2 Livestock Watering	27
5.3.3 Irrigation	29
5.3.4 Stream Flow Augmentation	31
5.3.5 Rangeland Restoration	33
5.3.6 Industrial Uses	33
5.3.10 Domestic	37
6. Produced Water Quality Characterization	41
6.1 Salt Concentration and Composition	42
6.2 Inorganic Constituents	49
6.2.1 Major Ions	49
6.2.2 Minor Ions	53
6.3 Organic Constituents	56
6.3 Organic Constituents	56
6.4 Naturally Occurring Radioactive Materials	58
6.5 Chemical Additives	60
6.6 Beneficial Use Potential	60

Contents (continued)

Page

7. Assessment of Technologies for Treatment of Produced Water 69
   7.1 Organic, Particulate, and Microbial Inactivation/ Removal Technologies 70
      7.1.1 Biological Aerated Filters 70
      7.1.2 Hydrocyclone 72
      7.1.3 Flotation 73
      7.1.4 Adsorption 74
      7.1.5 Media Filtration 75
      7.1.6 Oxidation 75
      7.1.7 Settling 76
      7.1.8 Air Stripping 76
      7.1.9 Surfactant Modified Zeolite Vapor Phase Bioreactor 77
      7.1.10 Constructed Wetlands 78
      7.1.11 Granular Activated Carbon 78
      7.1.12 Ultraviolet Disinfection 80
      7.1.13 Microfiltration/Ultrafiltration 81
   7.2 Desalination Technologies 84
      7.2.1 Reverse Osmosis and Nanofiltration 85
      7.2.2 Electrodialysis/Electrodialysis Reversal 85
      7.2.3 Forward Osmosis 86
      7.2.4 Hybrid Membrane Processes 86
      7.2.5 Thermal Processes 87
      7.2.6 Alternative Desalination Processes 88
   7.3 Commercial Processes 89
      7.3.2 CDM Produced Water Technology 89
      7.3.3 Veolia OPUS™ 91
      7.3.4 Altela Rain℠ (Dewvaporation) 91
      7.3.5 212Resources 91
   7.4 Implications of Water Quality for Treatment Technologies 92
8. GIS-Based Approach to Produced Water Management 93
   8.1 Produced Water GIS Database 93
      8.1.1 Base Map and Reference Data 93
      8.1.2 Oil and Gas Distribution, Well and Basin Data 93
   8.2 Examples of GIS-Based Approach 97
      8.2.1 Denver Basin Example 98
      8.2.2 Powder River Basin Example 101
      8.2.3 Uinta-Piceance Basin Example 102
9. References 107

Tables

Page

Table 1	CBM recoverable gas reserves and water quality	5
Table 2	Geographic location of conventional oil and gas resources in the Western United States	16
Table 3	Geographic location of unconventional oil and gas resources in the Western United States	18
Table 4	Water use and produced water generation in the Western United States	26
Table 5	Water intake volumes for livestock	27
Table 6	National Science Foundation recommended levels of specific constituents for livestock drinking water	28
Table 7	TDS categories for livestock water	29
Table 8	Crop tolerance to boron in irrigation water	31
Table 9	Constituent limits for irrigation water	32
Table 10	Acute and chronic concentration levels by hardness	34
Table 11	USEPA drinking water standards	38
Table 12	Conventional basins TDS and SAR statistics	51
Table 13	Common inorganic constituents in conventional produced water	52
Table 14	Ranges of inorganic constituents in produced water	55
Table 15	Organic material in produced water from oil operations	58
Table 16	Volatile organics in produced water from gas operations	58
Table 17	Chemicals added for treatment of produced water	61
Table 18	Suitability statistics for produced water for agricultural uses	64
Table 19	Constituents with the potential to be detected above requirements	67
Table 20	Comparison of organic contaminant and particulate removal technologies for treatment of produced water .... follows page	70
Table 21	Comparison of desalination technologies for treatment of produced water .... follows page	84

Figures

Page

Figure 1	Typical water and gas production for CBM	6
Figure 2	Geographic location of major oil and gas producing wells and basins in the United States	14
Figure 3	Geographic distribution of oil wells in the Western United States	15

Figures (continued)

		Page
Figure 4	Geographic distribution of conventional gas wells in the Western United States	15
Figure 5	Conventional and unconventional well distribution by State	21
Figure 6	Produced water quantities by State in the Western United States	22
Figure 7	Overlay of oil and gas producing basins and areas with a potential for water conflict	23
Figure 8	Fresh water usage in the Western United States	25
Figure 9	Suitability of water for irrigation (adapted from Ayers and Westcot 1994)	30
Figure 10	Distribution of TDS for conventional basins	43
Figure 11	Distribution of TDS concentration for conventional oil and gas	45
Figure 12	Distribution of TDS concentration for unconventional CBM basins	45
Figure 13	Major cations and anions for produced water	47
Figure 14	Dominant salt types of produced water	48
Figure 15	Western United States oil and gas basins: dominant salt type distribution	48
Figure 16	Geochemical fingerprints of conventional and unconventional basins	52
Figure 17	Western United States oil and gas basins: water geochemistry	54
Figure 18	Radioactive oilfield equipment (USGS Fact Sheet 0142-99)	59
Figure 19	Conventional versus unconventional well distribution in the TDS requirement categories for each beneficial use	62
Figure 20	Western United States oil and gas basins: percentage of wells in various beneficial use categories	63
Figure 21	Conventional versus unconventional well distribution in the irrigation requirement categories for SAR	65
Figure 22	Western United States oil and gas basins: percentage of wells in SAR irrigation categories	66
Figure 23	Dead-end versus cross flow filtration	81
Figure 24	Schematic diagram of CDM produced water treatment process	91
Figure 25	Base map with reference data and sources	94
Figure 26	Location of oil and gas producing basins and the top 100 producing oil and gas wells in the Western United States	95

Figures (continued)

		Page
Figure 27	Geographic relationship between hydrologic units and petroleum basins	95
Figure 28	Potential water conflict and produced water generation	96
Figure 29	Areas of irrigated agriculture compared to produced water generation	97
Figure 30	Selection of top 100 producing well in the Denver basin	98
Figure 31	Agricultural data within the study area	99
Figure 32	Oil and gas well location data within the study area	100
Figure 33	Irrigated land within the study area	100
Figure 34	Powder River basin example area	101
Figure 35	Location of oil and gas wells within 5-mile radius of top producing well in the Powder River basin	102
Figure 36	Irrigated and nonirrigated agriculture within the study area	103
Figure 37	Uinta-Piceance basin example study area	103
Figure 38	Five-mile study radius for Piceance basin example	104
Figure 39	Surface discharge beneficial use option for Uinta-Piceance study area	104

1. Executive Summary

Due to increasing demand on fresh water sources, there is a need to develop new water supplies in the Western United States. Large volumes of water produced during oil and gas extraction, called produced water, are generated in drought prone locations that are also experiencing an increase in population. Produced water is a waste byproduct of the oil and gas industry; however, with appropriate treatment and application to beneficial use, produced water can serve as a new water supply in the Western United States.

The Bureau of Reclamation (Reclamation) Technical Service Center gathered data from publically available sources to describe the water quality characteristics of produced water, performed an assessment of water quality in terms of geographic location and water quality criteria of potential beneficial uses, identified appropriate treatment technologies for produced water, and described practical beneficial uses of produced water.

Produced water quality varies significantly based on geographical location, type of hydrocarbon produced, and the geochemistry of the producing formation. In general, the total dissolved solids concentration can range from 100 milligrams per liter (mg/L) to over 400,000 mg/L. Silt and particulates, sodium, bicarbonate, and chloride are the most commonly occurring inorganic constituents in produced water. Benzene, toluene, ethylbenzene, and xylene (BTEX) compounds are the most commonly occurring organic contaminants in produced water. The types of contaminants found in produced water and their concentrations have a large impact on the most appropriate type of beneficial use and the degree and cost of treatment required.

Many different types of technologies can be used to treat produced water; however, the types of constituents removed by each technology and the degree of removal must be considered to identify potential treatment technologies for a given application. For some types of produced water, more than one type of treatment technology may be capable of meeting the contaminant removal target; and a set of selection criteria must be applied to narrow down multiple treatment options.

Beneficial uses of produced water include crop irrigation, livestock watering, streamflow augmentation, and municipal and industrial uses. Produced water also can be placed in aquifer storage for future use. The type of beneficial use most appropriate for a produced water application depends on the geographical location of the produced water generation, the location of the beneficial use, and the constituent concentrations in the produced water.

Given the large volumes of produced water generated in the Western United States and the growing need for new water supplies, produced water has the potential to augment conventional water supplies. Produced water, if managed as a resource rather than a waste for disposal, has the potential to be used beneficially.

2. Background

Produced water is defined as the water that exists in subsurface formations and is brought to the surface during oil and gas production. Water is generated from conventional oil and gas production, as well as the production of unconventional sources such as coal bed methane, tight sands, and gas shale. The concentration of constituents and the volume of produced water differ dramatically depending on the type and location of the petroleum product. Produced water accounts for the largest waste stream volume associated with oil and gas production.

2.1 Petroleum Resource Formation and Production

2.1.1 Conventional Oil and Gas

Oil is formed from plant and animal material that accumulates at the bottom of a water supply such as an ocean, river, lake, or coral reef. Over time, this material is buried by accumulating sediment and is pushed deeper into the earth's surface where the pressure increases from the weight of the overlying sediment and the temperature increases due to heat from the earth's core. Oil and gas reservoirs are created when hydrocarbon pyrolysis occurs in a confined layer of porous reservoir material. The confined material restrains the fossil fuel in the subsurface, while the permeable and porous reservoir material allows for accumulation. Oil exists underground as small droplets trapped inside the small void spaces in rock. When a well is drilled into an oil reservoir, the high pressure that exists in the reservoir pushes oil out of the small voids and to the surface.

2.1.2 Unconventional Petroleum Resources

Oil shale, gas shale, tight sands, and coal bed methane are considered unconventional petroleum resources. Oil shale reservoirs are confined in sedimentary formations. Oil shale formations do not convert hydrocarbons into crude oil. Oil shale commonly is refined to produce a cleaner energy product for high grade fuel use. Tight sedimentary formations retain the hydrocarbons requiring energy and water intensive well development. Fracturing polymers in combination with water are injected at high pressures into the reservoir formation. Fracturing is necessary to produce sufficient effective aquifer conductivity to allow the production of economical quantities of oil and gas. The United States has the largest oil shale deposits. The Green River formation in Wyoming, Colorado, and Utah contains the largest oil shale deposit in the United States. Seventy percent of the commercially attractive resource in the Green River formation resides on land managed by the United States Federal Government.

Gas shale also is produced naturally from the shale formation. Gas is stored in fractures, pore space, and adsorbed to the organic reservoir material. Gas shale was first developed by producing it from large fractures in the formations that provided sufficient gas flow for economic development. Recent advances in well completion technology and artificial fracturing have increased the exploration of this resource. Shale gas has been produced for extend periods in the United States in the Illinois and the Appalachian basins. Due to recent advances in technology, the Barnett Shale in Texas also has been highly economical.

Tight sands gas are an unconventional natural gas resource produced from low permeability compacted sediments. Similar to gas shale, advancements in technology have increased the development of tight sands into an economic resource. Gas is tightly contained in the low permeability reservoir formation, and wells must be stimulated to produce from the reservoir formation. Tight sands basins in the United States overlap certain gas shales basins, but there is no coincidence of tight sands in shale gas basins. Tight sands production occurs in the Great Plains, Rocky Mountains, the Four Corners region, onshore gulf coast, and in Arkansas/Oklahoma.

Coal bed methane or coal bed natural gas is an unconventional natural gas resource extracted from coal beds. Methane (CH_4) is formed in the coal seam as a result of both the bacterial processes (biogenic) and the chemical reactions that occur with high temperature and pressure during the bituminization phase (thermogenic). Methane from higher ranking coals is formed by thermogenic production, and lower rank coals produce methane by biogenic production. Additionally, the volume of gas increases with coal rank, depth, and reservoir pressure. Coal has a large surface area per volume, so that coal seams can contain large volumes of gas. Coal seams are capable of containing six to seven times more gas than conventional gas reservoirs of comparable size (Taulis 2007).

Because of the way in which coal is formed, large amounts of coal bed methane exist at shallow depths. The shallow depths make drilling wells for coal bed methane production relatively inexpensive. At greater depths, higher pressure causes fractures in the coal seam to close, making the formations less permeable and more difficult for gas to move through the coal. Many of the coal bed methane basins in the Rocky Mountain region, including the Powder River and the San Juan basins contain subbituminous coals. Subbituminous coal is soft enough that conventional well bores can be used, and the well is drilled to the top of the target coal seam.

The Energy Information Administration publishes estimates of the proved reserves of coal bed methane. The proved reserves represent estimated quantities of coal bed methane (CBM)[1] that analysis of geological and engineering data demonstrate, with reasonable certainty, to be recoverable in future years from known reservoirs under existing economic and operating conditions (United States Energy Information Administration 2007). Actual coal bed methane production data, formation testing, coal core analyses, and other data are used to

[1] Also known as coal bed natural gas.

determine the economic production capacity of the coal formations. It is not necessary that production, gathering, or transportation facilities be installed or operative for a reservoir to be considered proved. Table 1 contains estimates of total and proved reserves for the major coal bed methane producing basins in the Western United States. In general, as more data becomes available and technology advances, the estimated recoverable reserves of CBM increase. Between 2002–2007, the estimated total United States reserves increased by 18 percent (%) based on historical data provided by the U.S. Energy Information Administration (USEIA).

Table 1. CBM recoverable gas reserves and water quality

Basin	Cumulative Production (BCF)[1]	Proved CBM Reserves (BCF)[1]	2008 Average Water Production (million barrels)[2]	Water to Gas Ratio (bbl/MCF)[2]
Powder River	2,314	2,418	718	2.75
Raton	625	2,486	131	1.34
San Juan	13,147	8,446	46	0.031
Uinta	758	1,995	31	0.42
Piceance	41	NA	0.30	1.2

NA – information not available

[1] United States Energy Information Administration 2007; BCF = billion cubic feet.

[2] National Research Council (NRC) Committee on Management and Effects of Coalbed Methane Development and Produced Water in the Western United States 2010; bbl/MCF = barrels per million cubic feet.

2.2 Produced Water Generation and Production

2.2.1 Conventional Oil and Gas

On average, about 7 to 10 barrels, or 280 to 400 gallons, of water are produced for every barrel of crude oil. Formation water (or connate water) exists naturally in the porous aquifer with the hydrocarbons. Formation water generally reflects the water quality associated with the depositional environment for the reservoir—marine, brackish, or continental fresh water. Oil reservoirs commonly contain larger volumes of water then gas reservoirs. This is due to the higher compressibility and sorption capacity of gas. Gas is stored and produced from less porous reservoirs that contain source rock with a lower water capacity. Produced water generation commonly increases over time in conventional reservoirs as the oil and gas is depleted during hydrocarbon production.

2.2.2 Unconventional Resources

Produced water from most unconventional resources is minimal due to tighter reservoir formations, such as in tight sands, oil shale, and gas shale reservoirs. Producers commonly import water to these operations for onsite use in drilling, fracturing, and production. Fresh water used in drilling applications and reservoir fracturing is contaminated by the saline terrestrial water associated with the reservoir depositional environment. Fresh water brought onsite for use in operations, such as flow back or frac water returning from fracturing applications, also is managed as a waste stream. This waste stream commonly is associated with the initial phase of well development and production. In most unconventional oil and gas operations, frac water is considered the largest waste stream of production.

Alternatively, coal bed methane produces the largest volumes of water during gas production as compared to other unconventional hydrocarbon production. The water in coal beds contributes to the pressure in the reservoir that keeps methane gas adsorbed to the surface of the coal. The water must be removed by pumping to lower the pressure in the reservoir and stimulate desorption of methane from the coal. Generally, as the gas production increases, the water production decreases; therefore, the volume of CBM-produced water generated decreases over time. Figure 1 shows the typical water and gas production profile for CBM producing gas wells.

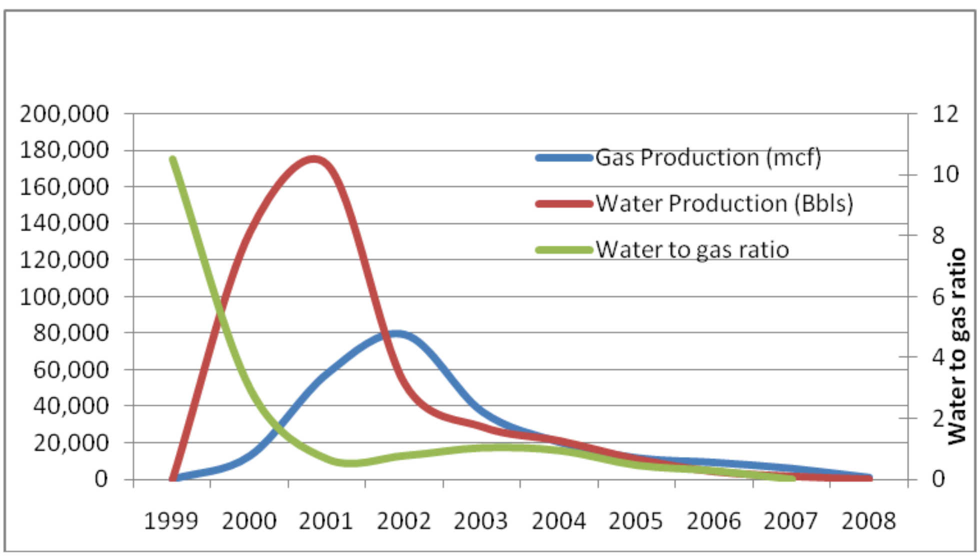


Figure 1. Typical water and gas production for CBM.

Coal beds contain fractures and pores that can transmit large volumes of water. In some areas, coal beds may function as local or regional aquifers and are important sources for ground water (Rice and Nuccio 2000). The volume of water varies significantly from basin to basin. These variations can occur for many different reasons depending on the part the CBM development cycle plays, the rank of the coal, the depth of the coal, and the hydrologic connectivity to other water bearing aquifers. Generally, deeper coal seams will contain less water, but the salinity of the water will be higher. Water to gas ratios are used to describe the volume of water produced per million cubic feet of natural gas. Water to gas ratios are used, along with the estimated recoverable reserves of natural gas, to predict the volume of water that will be generated in each producing basin.

2.3 Current Produced Water Management Practices

Water is considered a byproduct of oil and gas production and generally is treated by the oil and gas industry as a waste for disposal. Produced water management practices are driven by the cost of the hydrocarbon resource. Produced water is the largest volume waste stream associated with oil and gas production. Because produced water is viewed as a waste byproduct to the oil and gas industry, historically, the most commonly practiced management strategies are aimed at disposal rather than beneficial use. The most common practices for produced water disposal include land application or discharge, subsurface injection, and offsite trucking.

- Land application or discharge is a relatively inexpensive method of disposal for produced water. However, this is only an option for relatively high quality produced waters. If the water is of poor quality, contamination of the surrounding soil, water, and vegetation can occur. Regulatory guidelines also must permit land applications.

- Subsurface injection is the industry preferred alternative to produced water disposal. In some cases, re-injection of produce waters is not feasible because the subsurface formation does not have the capacity to receive the water.

- In the event that land application or re-injection is not feasible, the water may be trucked to offsite, re-injection facilities. Re-injection facilities commonly are located around a feasible accepting geologic formation for injection. These facilities sometimes include minor treatment applications aimed at lowering the scaling potential of the reinjection water or modify the chemistry of the water to aid in disposal.

Typically, producers have limited water treatment experience and are hesitant to employ produced water treatment technologies given their negative past experiences. From an oil and gas producer’s perspective, the primary concern of beneficial use of produced water as a management strategy is liability; therefore, re-injecting the water into the subsurface formation is the preferred disposal/ management method. However, in some areas, disposal is not possible because the geology of the subsurface formation cannot accommodate the water, or re-injection may cause contamination of other subsurface water supplies. Offsite trucking is another water management strategy preferred by producers from a liability standpoint; however, it is very costly.

2.4 Environmental Impacts Caused by Produced Water

Environmental impacts caused by the disposal of produced water have been reported since the mid-1800s when the first oil and gas wells were drilled and operated. The most commonly reported environmental concerns are as follows: degradation of soils, ground water, surface water, and ecosystems they support (Otton 2006). Because many produced waters contain elevated levels of dissolved ions (salts), hydrocarbons, and trace elements, untreated produced water discharges may be harmful to the surrounding environment.

Large water volumes also can cause environmental impacts through erosion, large land area disposal basins, and pipeline and road infrastructure. Water hauling spills and unplanned discharges are all risks when managing produced water. The volume of the receiving body is critical in determining environmental impacts as ocean discharge offers substantive dilution, while small streams offer low dilution capacity. Physical water properties of concern include temperature, effervescence, low dissolved oxygen concentrations, as well as high and low pH depending on the well type.

Sodium is the most commonly occurring dominant cation in produced water. High sodium levels compete with calcium, magnesium, and potassium for uptake by plant roots; therefore, excess sodium can prompt deficiencies of other cations. Elevated levels of sodium also can cause poor soil structure and inhibit water infiltration in soils (Davis, Waskom et al. 2007). Infiltration into shallow ground water sources is also a concern when water is applied for irrigation use. Mineral accumulation due to subsurface ion exchange can change the water quality of shallow, underlying aquifers.

Trace elements, including boron, lithium, bromine, fluorine, and radium, also occur in elevated concentrations in some produced waters. Many trace elements are phytotoxic and are adsorbed in the soil. These elements may even remain in soils after the saline water has been flushed away. Radium-bearing scale and sludge found in oilfield equipment and discarded on soils pose additional hazards to human health and ecosystems. Meteoric water applied to contaminated soils has the potential to solubilize metals and transport them through the subsurface. Precipitation of metals and metal solubility are important considerations in applying these constituents to soils.

2.5 Study Objectives

The objectives of this project are as follows:

(1) Describe the characteristics of produced water: constituent concentration and volumes produced.

(2) Identify potential beneficial uses of produced water and the geographical relationship between produced water generation and potential beneficial uses. Three case studies are presented.

(3) Identify constituents in produced water that exceed water quality requirements of beneficial uses and constituents that will be problematic for treatment of produced water

(4) Evaluate produced water treatment technologies (organic/particulate removal technologies, desalination, brine management technologies, and post-treatment or stabilization technologies) and describe benefits and limitations of each technology based on produced water specific design requirements.

3. Conclusions and Recommendations

Produced water is generated in large volumes across the Western United States from both conventional and unconventional petroleum production with the majority of the water produced in Texas, Oklahoma, Kansas, California, and the Rocky Mountain region including Montana, Wyoming, Utah, Colorado, and New Mexico. Given the large volume of water generated during operations, produced water could be considered an alternative water resource in locations experiencing water shortage.

Produced water could be used to augment conventional water supplies for use in irrigation and livestock watering, streamflow augmentation, and industrial applications. Water quality issues may need to be addressed for produced water to be used for these beneficial uses. For agricultural purposes, most produced water sources contain elevated levels of sodium and high conductivity that require treatment to eliminate the possibility of damage to crops and livestock. In some states, produced water volumes are large enough to make a significant contribution to the water demand for irrigation and livestock.

Numerous treatment technologies have been suggested for produced water. This document provides a qualitative comparison of the different technologies and provides guidance on the benefits and limitations of each technology. Water quality constraints and site-specific design criteria should be used to select the most appropriate treatment technology for a given produced water source and desired beneficial use.

Three case studies were presented, which illustrate the large potential for beneficial use in the Western United States for different types of applications: agriculture, stream low augmentation, and industrial use. Appropriate management techniques will allow produced water to be used as a resource rather than treated as a waste to meet the growing water demand in the Western United States.

This work, along with research conducted by others (through the Department of Energy, National Energy Technology Laboratory, and the Research Partnership to Secure Energy for America), has thoroughly evaluated produced water occurrence, quality, quantity, beneficial uses of produced water, and produced water treatment technologies. Future work should focus on simultaneously considering all of this information to develop site-specific produced water management strategies that are both environmentally and economically efficient.

4. Geographical Occurrence of Produced Water

4.1 Conventional Oil and Gas Resources

Conventional oil and gas resources are explored across the United States. In 2008, the U.S. Energy Information Administration estimated that 363,107 oil wells and 460,261 gas wells were producing in the United States. Of the wells in operation, 78% of the oil wells and 65% of the gas wells produced 10 barrels of energy (BOE) per day or less. Conventional resources are not commonly produced by a few wells with excellent production numbers. Instead, since a majority of wells produce less energy per day, production is compensated by drilling dense well populations to increase production in a field. The large quantity of wells also contributes to a large volume of produced water generated. The geographic location of oil and gas wells within the United States is shown in the context of the major producing basins and the top producing oil and gas wells; see figure 2.

Conventional oil and gas wells in the Western United States represented 86% of the total oil and 72% of the total gas wells nationwide in 2008. States in the Western United States containing more than 25,000 oil wells include California, Kansas, Oklahoma, and Texas, while States containing more than 25,000 gas wells include Colorado, Kansas, New Mexico, Oklahoma, Texas and Wyoming. Conventional oil and gas wells in the Western States are presented in figures 3 and 4. As mentioned previously, oil reservoirs commonly contain larger volumes of water then gas reservoirs. For conventional wells, States with the largest volumes of produced water quantities should include California, Kansas, Oklahoma, and Texas.

Conventional well fields across this Western United States are tabulated in table 2. The 22 basins recognized are included based on the number of wells associated with each basin. This table is not comprehensive to all oil and gas basins, which exist in this region. Idaho, Nevada, Oregon, and Washington are not included in the State distribution in table 2, due to the absence or small number of oil and gas wells in these locations. The USEIA does report that 20 gas wells exist in the State of Oregon and 73 oil wells in the State of Nevada. It also should be noted that oil and gas operations also exist off shore in the Gulf of Mexico, off of Texas-Louisiana, and the Pacific Ocean off the coast of California. These wells and basins are not included in this assessment of Western State resources; however, information on these coastal basins and wells is available through the USEIA.

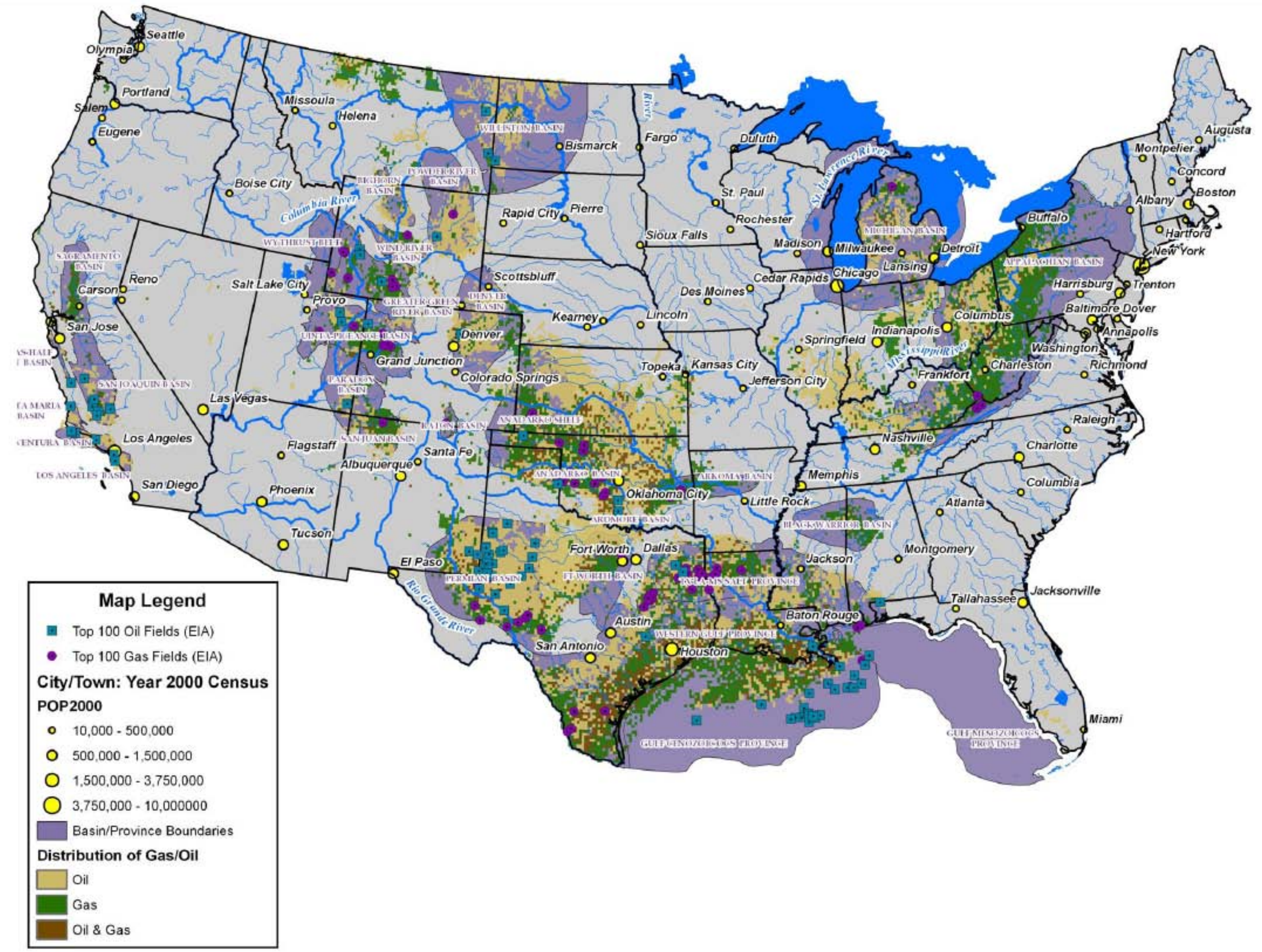


Figure 2. Geographic location of major oil and gas producing wells and basins in the United States.

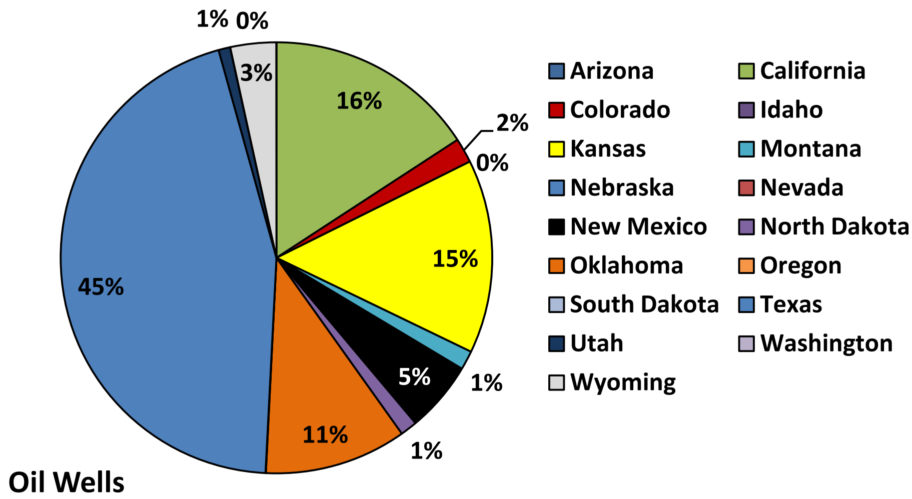


Figure 3. Geographic distribution of oil wells in the Western United States.

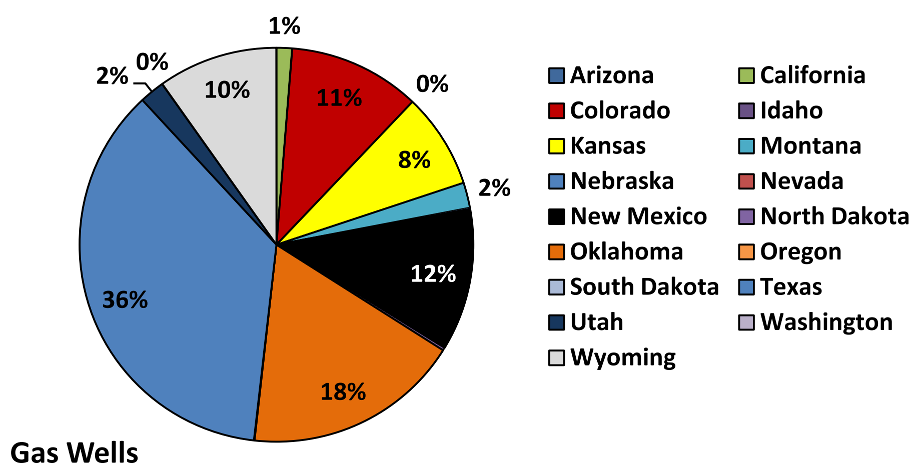


Figure 4. Geographic distribution of conventional gas wells in the Western United States.

Table 2. Geographic location of conventional oil and gas resources in the Western United States

Basins	AZ	CA	CO	KS	MT	NE	NM	ND	OK	SD	TX	UT	WY
Anadarko			X	X					X		X		
Ardmore									X				
Bighorn					X								X
Denver			X			X			X			X	
Forest City-Cherokee-Arkoma						X			X				
Greater Green River			X									X	X
Los Angeles		X											
Montana Thrust Belt					X								
Palo Duro											X		
Paradox			X									X	
Permian							X				X		
Piceance			X										
Powder River					X								X
Raton			X				X						
Sacramento		X											
San Juan	X		X				X					X	
Uinta												X	
Ventura		X											
Western Gulf											X		
Williston					X			X		X		X	
Wind River													X
Wyoming Thrust Belt												X	X

4.2 Unconventional Oil and Gas Resources

Unconventional oil and gas resources are produced nationwide. The unconventional resources focused upon in this report include oil shale, gas shale, tight sands gas, and coalbed methane. Table 3 summarizes the locations of 5 oil shale, 16 gas shale, 8 tight sands gas, and 6 coalbed methane basins in the Western United States. Again, Idaho, Nevada, Oregon, and Washington are not included in the State distribution in table 3, due to the absence or small number of wells in these locations. General summaries of the geographic distribution of unconventional wells are provided by unconventional resource in the following text.

4.2.1 Oil Shale

Oil shale basins in the Western United States are limited to Colorado, Utah, and Wyoming. The large water volumes associated with oil shale production originate from fracture watering. Fracturing water is primarily used during well development. This water represents a large volume over a small period of time, which is often difficult to manage.

4.2.2 Gas Shale

Basins occur in the Western United States in 10 states. Texas, New Mexico, Oklahoma, Montana, and Utah contain the largest number of individual basins. Gas shale basins commonly overlap other unconventional resources such as coalbed methane. Gas shale layers commonly act as aquitards and confining layers to coal seams. The Raton, San Juan, Uinta, and Piceance all contain both resources. Specific gas plays are recognized in table 3 to differentiate these unconventional resources.

4.2.3 Tight Sands Gas

Basins are located in eight Western States and do not extend north of Wyoming or west of Utah. Colorado and Texas include the greatest number of basins. Specific gas plays are recognized in table 3 for tight sands gas as well. Similar to oil shale and gas shale, water production during gas production in this resource is low. Water is primarily associated with well development during artificial reservoir fracturing.

4.2.4 Coalbed Methane

Western basins are located along the Rocky Mountain regions of the United States in Colorado, New Mexico, Utah, Wyoming, and Montana. The coal formations are commonly associated with conventional oil and gas as well as unconventional

Table 3. Geographic location of unconventional oil and gas resources in the Western United States

Oil Shale

Basin	AZ	CA	CO	KS	MT	NE	NM	ND	OK	SD	TX	UT	WY
Great Divide													X
Green River			X									X	X
Piceance			X										
Uinta			X									X	
Washakie			X										X

Gas Shale

Basin	Specific Gas Plays	AZ	CA	CO	KS	MT	NE	NM	ND	OK	SD	TX	UT	WY
Anadarko	**Woodford**									X				
Arkoma	**Woodford-Caney, Fayetteville**									X				
Big Horn	**Mowry**					X								X
East Texas Salt	**Haynesville**											X		
Forest City-Cherokee-Arkoma	**Excello-Mulky**				X					X				
Ft. Worth	**Barnett**											X		
Greater Green River	**Hillard-Baxter-Mancos**			X									X	X
Maverick-Rio Grande Embayment	**Pearsall-Eagle Ford**											X		
Montana Thrust Belt	**Cody**					X								
Palo Duro	**Bend**											X		
Paradox	**Hermosa**												X	
Permian-Marfa	**Barnett-Woodford**							X				X		
Raton	**Pierre**			X				X						
San Juan	**Lewis**							X						
Uinta-Piceance	**Mancos**												X	
Williston	**Gammon**					X			X		X			

Table 3. Geographic location of unconventional oil and gas resources in the Western United States (continued)

Tight Sands Gas

Basin	Specific Gas Plays	AZ	CA	CO	KS	MT	NE	NM	ND	OK	SD	TX	UT	WY
Anadarko	**Cleveland, Red Fork, Granite Wash**									X		X		
Denver	**Muddy J, Niobrara Chalk**			X	X		X							X
Ft. Worth	**Davis**											X		
Permian	**Abo, Penn-Perm Carbonate, Morrow, Thirty-one, Ozona Canyon**							X				X		
Piceance	**Mesaverde, Mancos-Dakota**			X									X	
San Juan	**Mesaverde, Pictured Cliffs, Dakota**			X				X						
Uinta	**Wasatch-Mesaverde, Mancos-Dakota**			X									X	
W. Gulf Coast	**Wilcox Lobo, Olmos, Stuart City-Edwards, Vicksburg**											X		
W. Gulf Coast-Texas-Louisiana-Mississippi Salt	**Austin Chalk, Travis Peak, Bossier, Cotton Valley, Gilmer Lime**											X		

Coalbed Methane

Basin	Coal Formations	AZ	CA	CO	KS	MT	NE	NM	ND	OK	SD	TX	UT	WY
Piceance	**Mesaverde Group**			X										
Powder River	**Wasatch, Fort Union**					X								X
Raton	**Vermejo, Raton**			X				X						
San Juan	**Fruitland**			X				X						
Sand Wash	**Iles, Williams Fork, Fort Union, Wasatch**			X										X
Uinta	**Mancos Shale, Mesaverde Group**			X									X	

resources such as gas shale. Coal formations specific to coalbed methane production are provided in table 3. Coalbed methane represents the largest water contributor over a well lifetime of all the unconventional resources. Produced water volumes from unconventional resources are primarily from coalbed methane well production. In further sections, produced water from unconventional resources will be limited to coalbed methane.

4.3 Geographic Distribution of Produced Water Generation

Over 80% of the produced water generated nationwide is produced in the Western United States. Conventional and unconventional resources contribute to produced water volumes. Figure 5 relates conventional and unconventional well numbers to one another by State locations. The geographic distribution of water volumes should follow a similar trend the well population of each State. It is expected that conventional oil wells will have a larger impact than conventional gas wells on produced water volumes. Therefore, it is expected that California, Kansas, Oklahoma, and Texas will produce large amounts of produced water due to the number of conventional wells present in these States.

Coalbed methane wells in Wyoming, Montana, New Mexico, and Colorado also contribute to the produced water volumes generated by each State.

Figure 6 summarizes the produced water quantities by State. Wyoming is associated with the second highest volumes for produced water in the Western United States. Wyoming generates substantial quantities of water due to the large number of coalbed methane wells in the Powder River basin. Conventional oil and gas wells supplement this volume; however, the unconventional wells represent a significant contribution. Texas dominates total well numbers in conventional resources with 45% of the gas and 36% of the oil wells in the Western United States. Texas also dominates the produced water generation at 44% or 236,914 thousand acre-feet per year. This is a significant water volume for the State. If produced water is managed as a water resource instead of a waste product, the volumes generated annually in each State could supplement the water supply required.

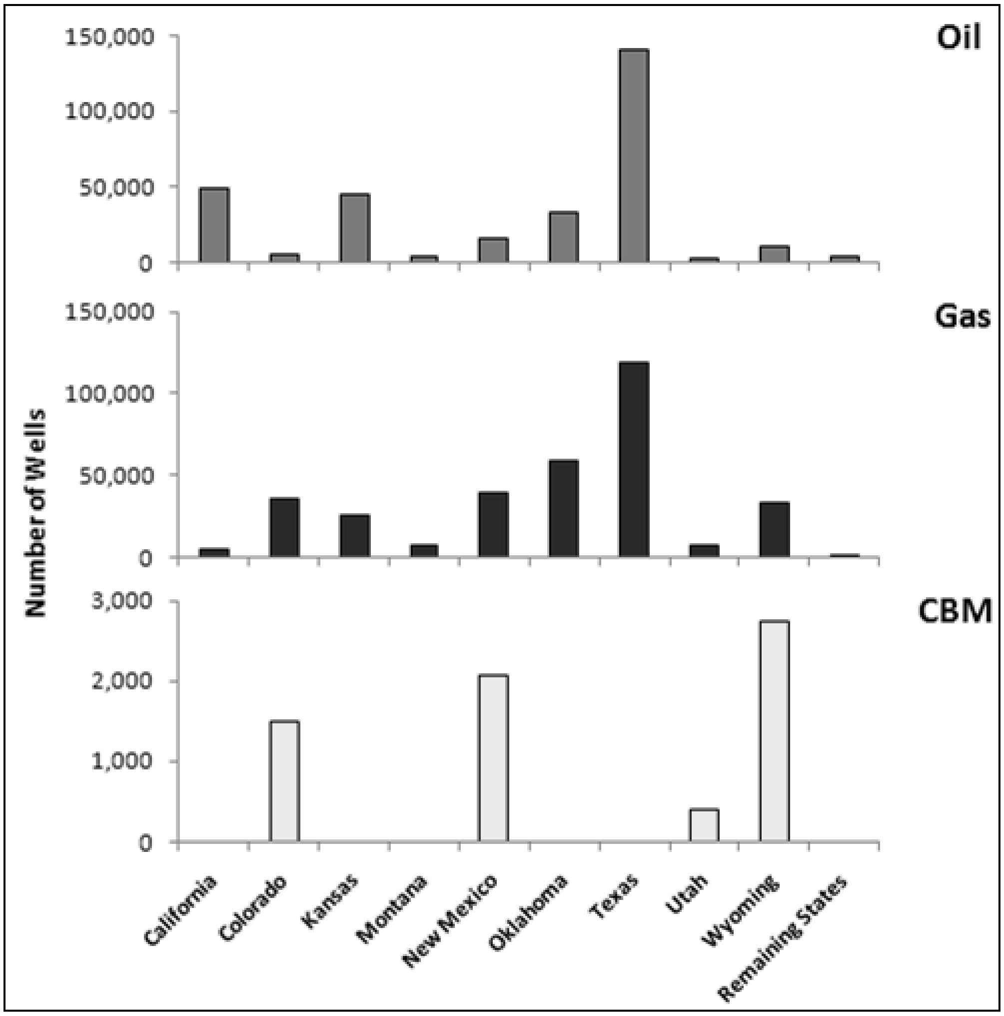


Figure 5. Conventional and unconventional well distribution by State.

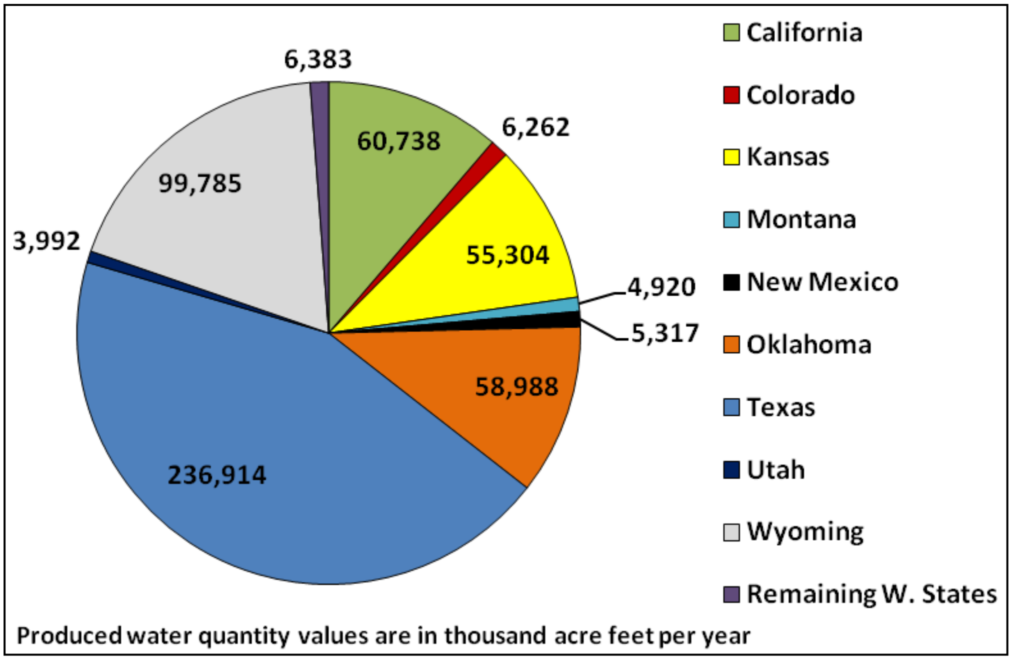


Figure 6. Produced water quantities by State in the Western United States.

5. Beneficial Uses of Produced Water

The Nation faces an increasing set of water resource challenges: aging infrastructure, rapid population growth, depletion of ground water resources, impaired water quality associated with particular land uses and land covers, water needed for human and environmental uses, and climate variability and change. All play a role in determining the amount of fresh water available at any given place and time (WaterSMART). Figure 7 shows the areas of the Western United States that have the potential for conflict over water. With appropriate treatment and management strategies, produced water has the potential to augment conventional water supplies.

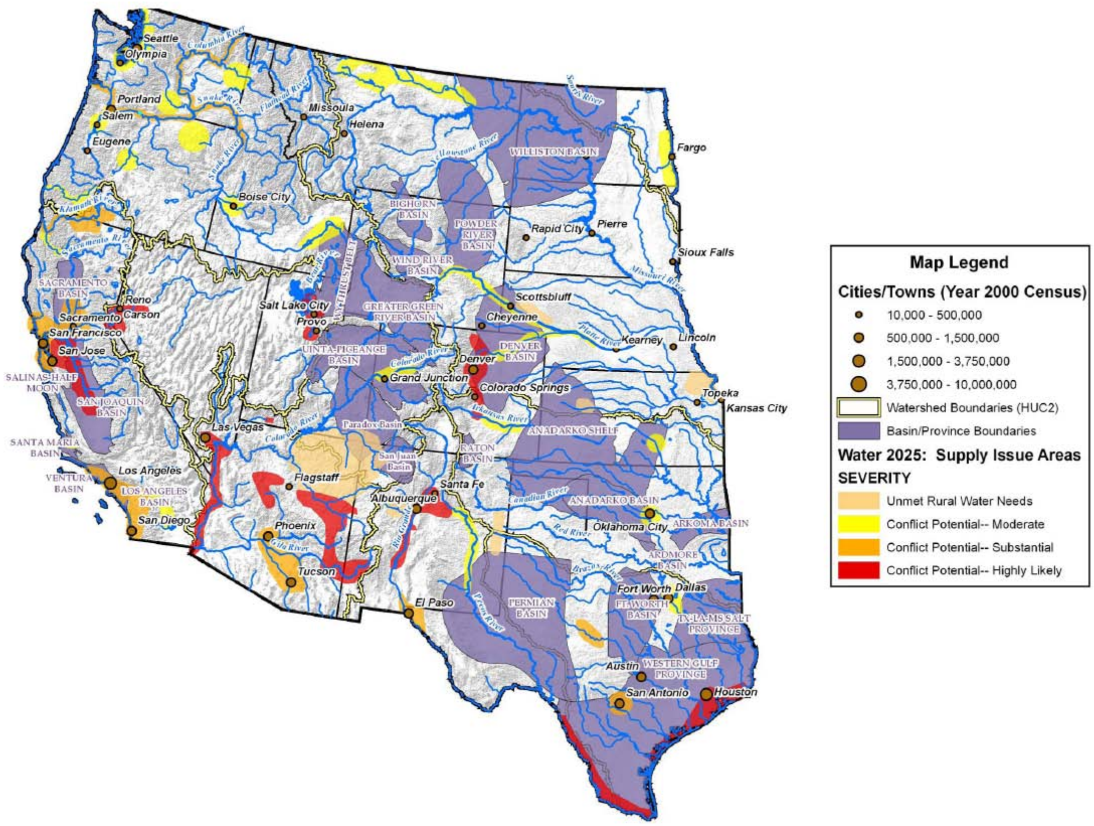


Figure 7. Overlay of oil and gas producing basins and areas with a potential for water conflict.

5.1 Produced Water Use

Although produced water from oil and gas wells commonly is considered a high volume, high salinity waste stream, produced water has the potential to be used to offset water demands and over allocation of water supplies. Waste stream management is necessary to continue hydrocarbon production from oil and gas wells. Therefore, for use of produced water for beneficial purposes to be effective, the value of produced water must be assessed in each use scenario. The value of treating and managing produced water to be used for beneficial purposes will, therefore, depend on the specific situation including the water volume, water characteristics, and proposed use.

Produced water operators include extensive costs in the handling and management of produced water. Costs include bringing the water to the surface, re-injecting the water into the formation for disposal, and transporting the large amounts of water to injection wells. Often, transportation of large water volumes is so expensive that produced water may be treated onsite, including desalination, for less cost. Treatment onsite, even with the creation of a brine or concentrate waste stream, minimizes the total waste volume that requires injection. Furthermore, treatment creates a product of sufficient quality to alleviate dependences on local fresh water sources for many applications. Water volumes available from oil and gas production and potential beneficial uses of produced water are outlined in this chapter.

5.2 Produced Water Volumes Compared to Use Demands

To determine how produced water volumes compare relative to water use in the United States, information from two studies was used. The first study provided comprehensive information on produced water in a report from the U.S Department of Energy (DOE), entitled "A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane." This publication estimated the annual onshore U.S. produced water volumes for 1985, 1995, and 2002. The U.S. Geological Survey (USGS) also has done comprehensive studies on water use in the United States for 2000 and 2005. Combining the data provided in those studies, the following information was extracted for the Western United States.

Volumes of fresh water used annually in the Western States range from an estimated 600 thousand acre-feet per year (AFY) in South Dakota to 43,000 thousand AFY in California. Water supply uses are presented by State in figure 8. Water usage in the Western United States is dominated by irrigation in most States. State specific trends in water use include elevated water consumption for thermoelectric power generation in Kansas, Nebraska, and

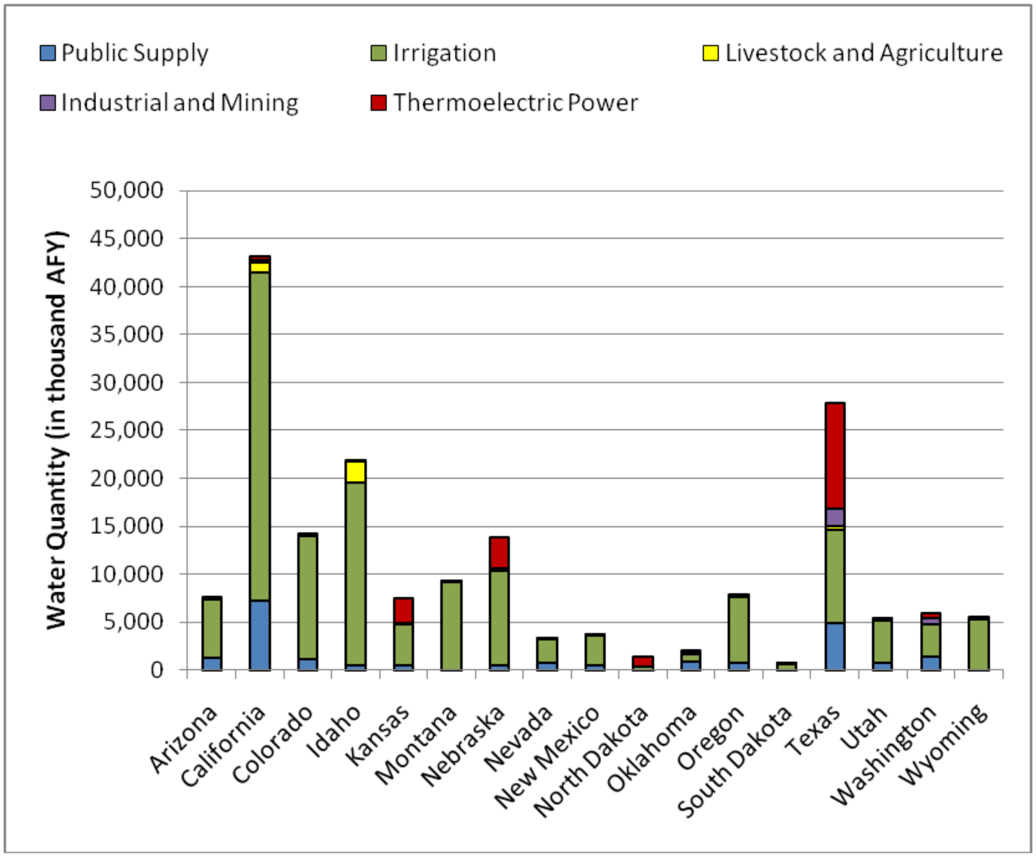


Figure 8. Fresh water usage in the Western United States.

Texas. Texas also uses significant water quantities for mining applications. California and Texas, meanwhile, use more water for public supply and consumption than Western States such as Nevada, New Mexico, North Dakota, Oklahoma, and South Dakota, use annually.

Significant oil and gas production takes place in the arid regions of the Western United States, consequently, producing large annual quantities of produced water. In the Western United States, produced water volumes have the potential to contribute to the overall water supplies utilized by each State. Produced water production was estimated in 2002, to be 1,487 AFY in the Western United States. The largest produced water production, in Texas, is almost double the quantity used in the state for livestock and agriculture (table 4). Due to arid to semi arid climates in these regions, there is an increased value for new water sources.

Although a potential value exists for treated water sources, in the United States, more than 98% of produced water from onshore wells is re-injected (Clark and Veil 2009). A number of options are available locally as potential uses of this water. The following section outlines potential beneficial uses of produced water and includes information on water quantities and quality requirements.

Table 4. Water use and produced water generation in the Western United States

State	Public Supply	Irrigation	Livestock and Agriculture	Industrial, Mining, Thermo-electric	Total Water Use	Produced Water Generated
Arizona	1,242	6,060		230	7,533	0.01
California	7,180	34,200	1,061	632	43,073	168
Colorado	1,085	12,800		290	14,174	17
Idaho	370	19,100	2,249	62	21,781	0
Kansas	490	4,160	130	2,628	7,409	153
Montana	188	8,920		192	9,300	14
Nebraska	424	9,860	105	3,347	13,737	7
Nevada	730	2,360		53	3,143	0.4
New Mexico	367	3,210		75	3,652	15
North Dakota	85	163		1,031	1,278	10
Oklahoma	786	804	187	196	1,972	163
Oregon	720	6,810		236	7,765	0
South Dakota	116	418	47.1	12	592	0.4
Texas	4,887	9,680	346	12,880	27,793	654
Utah	733	4,330	130	147	5,340	11
Washington	1,280	3,400		1,229	5,909	0
Wyoming	126	5,050		368	5,544	276
TOTAL	20,808	131,325	4,256	23,608	179,996	1,487

Note: Water volumes are in 1,000 AFY.

5.3 Beneficial Uses of Produced Water

The following outlined beneficial uses of produced water do not represent a comprehensive list but are provided as examples of application scenarios for produced water. These examples were chosen due to the variable nature of the consumer, water quantity requirements, and water quality criteria. Although not discussed in detail within this report, ownership of produced water first must be assessed, and proper permitting must be acquired to execute a beneficial use of produced water. Information on regulatory guidelines and permitting is available through the DOE's National Energy Technology Laboratory online Web site

"Produced Water Management Information System" created by Argonne National Laboratories as a resource for technical and regulatory information for managing produced water, including current practices, State and Federal regulations, and guidelines for optimal management practices (Veil).

5.3.2 Livestock Watering

In 2000, it was estimated that livestock water use represented for livestock watering, feedlots, dairy operations, and other on-farm needs such as cooling of facilities for the animals and products, dairy sanitation and wash down of facilities, animal waste-disposal systems, and incidental water losses constituted 1,760 million gallons per day of fresh water (USGS 2005). This represented less than 1% of the total water use in the United States in 2000; however, 50% of that consumption was used by California, Texas, and Oklahoma (USGS 2005). These states represented 53% of the produced water production in 2002 nationally (Clark and Veil 2009).

Livestock water requirements depend on the animal and are influenced by several factors such as activity, feed intake and environmental temperature (Lardy, Stoltenow et al. 2008). Table 5 is a summary of water volumes required for different species. Water requirements vary throughout the year; and the gender and size of an animal also impacts the estimated water consumption. To encompass these variations, table 5 provides an estimated range of daily water consumption for each livestock species. For grazing species, such as cows and horses, water sources throughout grazing land are important in ranching regions.

Table 5. Water intake volumes for livestock

Livestock	Water Intake	Units
Cattle	3.5 to 23.0	Gallons per day
Sheep	1.5 to 3.0	Gallons per day
Swine	0.5 to 5.5	Gallons per day
Horses	6.0 to 18.0	Gallons per day

While livestock can tolerate water of a lesser quality than humans, some important considerations must be made evaluating a potential water source. High levels of specific ions and salinity can harm the animals. The National Academy of Sciences offers upper limits for toxic substances in water (see table 6). Additional constituent concentrations and maximum levels that should be noted include sulfate and alkalinity not to exceed 2,000 mg/L and pH ranging between 5.5–8.5 for livestock watering.

Table 6. National Science Foundation recommended levels of specific constituents for livestock drinking water

Constituent	Upper Limit (mg/L)
Aluminium	5
Arsenic	0.2
Beryllium	No data available.
Boron	5.0
Cadmium	0.05
Chromium	1.0
Cobalt	1.0
Copper	10.5
Fluorine	2.0
Iron	No data available
Lead	0.1
Manganese	No data available
Mercury	0.01
Molybdenum	No data available
Nitrate + nitrite	100
Nitrite	10
Selenium	0.05
Vanadium	0.10
Zinc	24
Total dissolved solids	10,000

The total dissolved solid (TDS) cutoff concentration listed in table 6 of 10,000 mg/L is the maximum concentration in water above which it is not recommended for livestock watering use. Table 7 includes additional information on TDS levels for livestock (Lardy, Stoltenow et al. 2008). Specific TDS categories are outlined in table 7 because TDS requirements vary between species, with certain species being more susceptible to the impacts of saline water consumption than others. Also, table 7 notes the relative time periods water of certain quality may be utilized. It is important to consider not only the water quality but also the duration of consumption when predicting adverse effects.

Table 7. TDS categories for livestock water

TDS Category	TDS Range[1]	Description
Level 1	< 1,000	Satisfactory
Level 2	1,000 to 2,999	Satisfactory, slight temporary illness
Level 3	3,000 to 4,999	Satisfactory for livestock, increased poultry mortality
Level 4	5,000 to 6,999	Reasonable for livestock, unsafe for poultry
Level 5	7,000 to 10,000	Unfit for poultry and swine, acceptable short term for livestock
Level 6	> 10,000	Not recommended

[1] < = less than; > = greater than.

Water quality is an important consideration for livestock watering. Meeting limits for specific constituents is necessary to provide protection of livestock consuming produced water, and treatment is often necessary to meet requirements. Although water requirements for livestock watering are relatively low, oil and gas wells drilled on property leased from farmers and ranchers represent a local source of water available for use. The use of produced water for livestock watering is convenient, given large ranching areas in areas producing large volumes of produced water. These overlapping areas include States such as Oklahoma, Wyoming, Texas, and California.

5.3.3 Irrigation

In most States, irrigation represents the majority of fresh water use. In estimates for the Western United States in 2000, irrigation represented over 70% of total state water usage (USGS 2005). Water used for irrigation is less easily recovered than water used for public consumption. Water loss occurs through transpiration from plants and through evaporation, while irrigating or during transport. Nationally, 59% of irrigation water is supplied from surface water sources; while in the Western United States, 64% is supplied from surface water resources. Almost a quarter of the 5% discrepancy between the Western United States and the Nation reliance on surface water sources could be supplied by produced water resources discharged into streams and channels to be used downstream for uses such as irrigation.

Irrigation not only requires large water volumes, but also has stringent water quality criteria. Specifically for produced water, parameters such as the sodium adsorption ratio are important criteria for ensuring that the water quality is sufficient to not damage crops. The sodium absorption ratio (SAR) is a calculation of the suitability for a water source for irrigation. The equation for the calculation is:

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{+2}]+[Mg^{+2}]]}{2}}} \qquad (1)$$

The concentrations of sodium (Na^+), calcium (Ca^{+2}), and magnesium (Mg^{+2}) are in milliequivalents per liter. When irrigation water has high SAR values, above three, then much more control of salt accumulation is needed. Water with high SAR can be used if enough water is applied to wash the salts down below the root zone of the crops.

The SAR and electrical conductivity (EC_w) of the water must be considered together to determine the probable affect of using the water for irrigation (Ayers and Westcot 1994) (see figure 9). When the source water has a higher conductivity, then there is a greater potential for salt damage at lower SAR levels. EC_w normally is expressed as decisiements per meter (dS/m), which is the same as siemens per centimeter (S/cm). Given the saline nature of produced water with high sodium content the SAR and EC_w are both important parameters to consider before use.

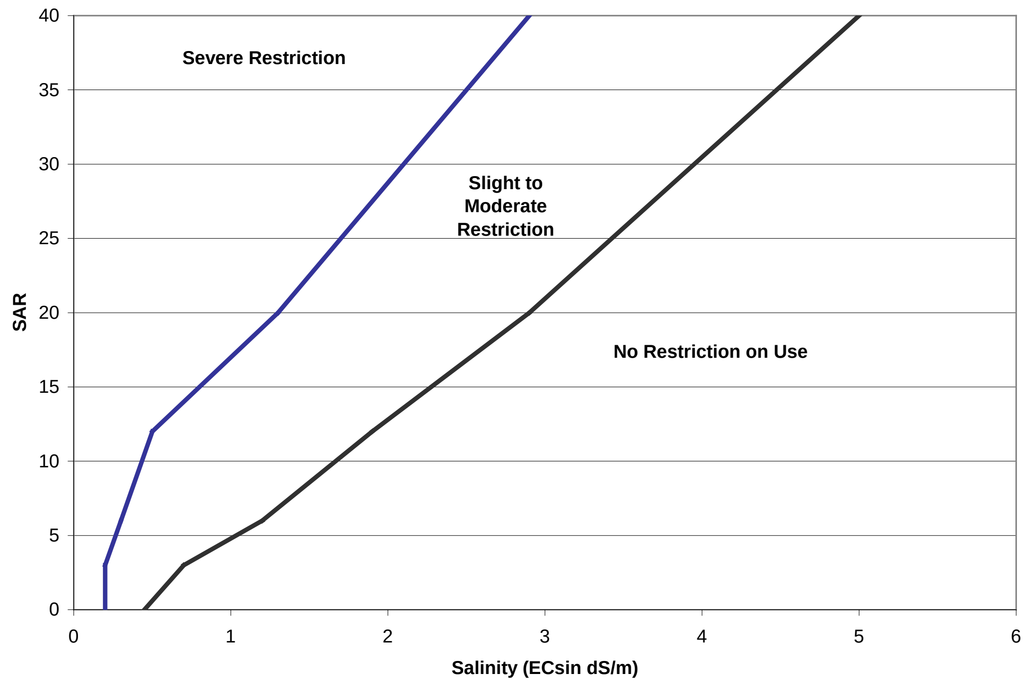


Figure 9. Suitability of water for irrigation (adapted from Ayers and Westcot 1994).

Boron is also important to consider when identifying the healthy range for most plants. The Food and Agriculture Organization publication, Water Quality for Agriculture, outlines boron concentration considerations for various types of crops (Ayers and Westcot 1994). Boron concentration limits are summarized in table 8.

Table 8. Crop tolerance to boron in irrigation water

Tolerance Level	Range of Boron Concentration	Crops
Very Sensitive	< 0.5 mg/L	Lemon, blackberry
Sensitive	0.5–0.75 mg/L	Avocado, grapefruit, orange, apricot, peach, cherry, plum, persimmon, fig, grape, walnut, pecan, cowpea, onion
Sensitive	0.75–1.0 mg/L	Garlic, sweet potato, wheat barley, sunflower, mung bean, sesame, lupine, strawberry, jerusalem artichoke, kidney bean, lima bean, peanut
Sensitive	1.0–2.0 mg/L	Red pepper, pea, carrot, radish, potato, cucumber
Moderately tolerant	2.0–4.0 mg/L	Lettuce, cabbage, celery, turnip, kentucky bluegrass, oats, maize, artichoke, tobacco, mustard, sweet clover, squash, muskmelon
Tolerant	4.0–6.0 mg/L	Sorghum, tomato, alfalfa, purple vetch, parsley, red beet, sugarbeet
Very tolerant	60–15.0 mg/L	Cotton, asparagus

Specific constituent criteria for irrigation waters are outlined in table 9. The table outlines minor constituents that may be prohibitive to plant growth used at concentrations above those listed for short- and long-term applications. In addition to these constituents, the following constituents and parameters also are identified as potentially detrimental at high concentrations to crops (Texas Coorperative Extension 2003):

- pH normal range 6.5–8.4
- Chloride < 70 parts per million (ppm) generally safe for all plants
- Nitrate < 10 ppm nitrate nitrogen (NO_3-N), 45 ppm nitrate (NO_3)

5.3.4 Stream Flow Augmentation

Although previously discussed in the context of irrigation, the discharge of produced water into streams provides more benefits than just the use of a surface water body as a conduit. Streamflow augmentation is the addition of waters to surface bodies to supplement low flows, thereby sustaining the surface body ecosystem. When not provided by precipitation or runoff, surface bodies are primarily derived from ground water. Urbanization has lead to changes in the ground water gradient, which may result in streams shifting from perennial, biologically rich streams to ephemeral streams (Shaver, Horner et al. 2007). Additionally, climate variations also affect surface water flows. Produced water may be used to sustain stream flow levels during low flow periods.

Table 9. Constituent limits for irrigation water (adapted from Rowe and Abdel-Magid, 1995)

Constituent	Long-term Use (mg/L)	Short-term Use (mg/L)
Aluminum (Al)	5	20
Arsenic (As)	0.1	2
Beryllium (Be)	0.1	0.5
Boron (B)	0.75	2
Cadmium (Cd)	0.01	0.05
Chromium (Cr)	0.1	1
Cobalt (Co)	0.05	5
Copper (Cu)	0.2	5
Fluoride (F)	1	15
Iron (Fe)	5	20
Lead (Pb)	5	10
Lithium (Li)	2.5	2.5
Manganese (Mn)	0.2	10
Molybdenum (Mo)	0.01	0.05
Nickel (Ni)	0.2	2
Selenium (Se)	0.02	0.02
Vanadium (V)	0.1	1
Zinc (Zn)	2	10

The quantity of water required to augment low stream flows is specific to the water body of application and the natural variations in water flow. For instance, creation of a perennial stream from a historically ephemeral stream using produced water flows may create an unsustainable ecosystem, because, as wells are abandoned, water sources will no longer be available. Over allocated water resources, where water taken from a surface body exceeds the flow or water sources where downstream users are in need of additional flow when available, are ideal situations for produced water augmentation. Produced water could be used to offset water use in surface bodies downstream from production, resulting in cheap transport of the water along a watershed and further dilution of the water through mixing with existing flow.

Important parameters to consider for this water management technique include impacts of elevated flows, which may include adverse affects such as erosion, total quantity losses due to evaporation, and impacts on the ecosystem based on water quality and physicochemical characteristics. Physical characteristics of the water that have potential to impact the ecosystem and aquatic life in a surface water body include temperature and dissolved oxygen (DO) levels resulting in high biological and chemical oxygen demand (BOD and COD). Depending on the species and application, water is expected to have DO levels from 3.0 to above 7.0 mg/L prior to discharge (Shaver 2007, #88). Additionally, salinity and specific constituents also must be managed to protect the ecosystem. Table 10 outlines constituents for aquatic life requirements and includes values for both chronic and acute toxicity, which are commonly dictated by the water hardness (Colorado Department of Public Health and Environment 2010).

5.3.5 Rangeland Restoration

Rangelands consist of shrubs and grasses and covers approximately 50% of the land surface in the United States. The most common use for rangelands is livestock grazing. Overstocking and drought are two of the causes of rangeland degradation. Degradation of rangeland also is caused by improper use of vehicles and other industrial activity and changing weather patterns resulting in drought.

Produced water can be applied to rangeland to help the natural biotic community to reestablish vegetation and to increase the response of the native species (Fox and Burnett 2002) . SAR is an important criterion for using produced water for rangeland restoration. Similarly to irrigation water, high SAR values can further damage soils; therefore, treatment may be required for some produced water sources to be used for rangeland restoration.

5.3.6 Industrial Uses

5.3.6.1 Reuse in Oil and Gas Operations

Reuse of produced water on site at oil and gas operation includes multiple applications, such as well drilling, hydraulic fracturing, secondary oil recovery, and sustaining aquifer pressure, which require large water volumes. Use of fresh water supplies in these practices may be minimized by treating and recycling produced water resources. Well head generation makes the resource available on site lowering transportation and trucking costs. Therefore, the market for treating produced water on site to meet water quality standards for use becomes economical as costs are compared to the cost of trucking fresh water on site at the volumes required for these operations. Water treated at a produced water collection point in a well field represents a local source of water commonly in closer proximity to most wells than fresh water sources. Although many onsite uses exist, two uses, well development through hydraulic fracturing and secondary recovery through enhanced oil recovery techniques, are described here in more detail.

Fracturing Water.—Unconventional resources commonly exist in subsurface formations with low permeability. Stimulation, in the form of hydraulic fracturing, is required to enhance permeability and allow for commercial production of the hydrocarbon resource. Hydraulic fracturing is the creation or extension of natural fractures in the formation material. Fractures increase the formation permeability as gas may flow unabated through these conduits to the wellhead. To create or extend naturally occurring fractures, pressurized hydraulic

Table 10. Acute and chronic concentration levels by hardness

	Mean Hardness in mg/L Calcium Carbonate									
	25	**50**	**75**	**100**	**150**	**200**	**250**	**300**	**350**	**400**
Aluminum										
Acute	512	1,324	2,307	3,421	5,960	8,838	10,071	10,071	10,071	10,071
Chronic	73	189	329	488	851	1,262	1,438	1,438	1,438	1,438
Cadmium										5.7
Acute	0.8	1.5	2.1	2.7	3.9	5	6.1	7.1	8.1	9.2
Chronic	0.15	0.25	0.34	0.42	0.58	0.72	0.85	0.97	1.1	1.2
Chromium										
Acute	183	323	450	570	794	1,005	1,207	1,401	1,590	1,773
Chronic	24	42	59	74	103	131	157	182	207	231
Copper										
Acute	3.6	7	10	13	20	26	32	38	44	50
Chronic	2.7	5	7	9	13	16	20	23	26	29
Lead										
Acute	14	30	47	65	100	136	172	209	245	281
Chronic	0.5	1.2	1.8	2.5	3.9	5.3	6.7	8.1	9.5	11
Manganese										
Acute	1,881	2,370	2,713	2,986	3,417	3,761	4,051	4,305	4,532	4,738
Chronic	1,040	1,310	1,499	1,650	1,888	2,078	2,238	2,379	2,504	2,618

Table 10. Acute and chronic concentration levels by hardness (continued)

	Mean Hardness in mg/L Calcium Carbonate									
	25	**50**	**75**	**100**	**150**	**200**	**250**	**300**	**350**	**400**
Nickel										
Acute	145	260	367	468	660	842	1,017	1,186	1,351	1,513
Chronic	16	29	41	52	72	94	113	132	150	168
Silver										
Acute	0.19	0.62	1.2	2	4.1	6.7	9.8	13	18	22
Chronic	0.03	0.1	0.2	0.32	0.64	1	1.6	2.1	2.8	3.5
Uranium										
Acute	521	1,119	1,750	2,402	3,756	5,157	6,595	8,062	9,555	11,070
Chronic	326	699	1,093	1,501	2,346	3,221	4,119	5,036	5,968	6,915
Zinc										
Acute	45	85	123	160	231	301	368	435	500	565
Chronic	34	65	93	121	175	228	279	329	379	428

Source: Colorado Department of Public Health and Environment 2010.

fluid is pumped into the geologic formation through the well bore into the target formation. When the pressure exceeds the rock strength, the fluids open or enlarge fractures that can extend several hundred feet away from the well. Current fracturing processes use “Slick Water” or “Light Sand” fracturing, which uses larger volumes of water than historically used to complete the process (R.W. Harden & Associates 2007).

This hydraulic fluid is composed mainly of water and a proppant material, such as sand or ceramic beads, and is used to maintain openings after fracturing has concluded (R.W. Harden & Associates 2007, #8). Fracturing fluids can be up to 99% water (USEPA 2010). Water used for fracturing (frac water) is usually fresh water containing low salt concentrations and low concentrations of sparingly soluble salt products such as barium and silica. Lower soluble salts are important considerations because precipitation of these salts in the formation would block fractures and lower formation permeability. Numerous chemical additives also are present in the hydraulic fluid mixture at low volume percentages as compared to the water/proppant mixture. Specific chemical additives can include friction reducers, biocides, and scale inhibitors.

Frac water is usually trucked onsite to the well head. Limited fresh water reservoirs are available onsite that provide sufficient quality and volume for the frac water mixture. Deep horizontal wells can require anywhere from 2–10 million gallons of frac water to complete the well hydraulic fracturing (ProchemTech, 2008 #3). In the Barnett Shale in Texas, wells require 1.2 to 3.5 million gallons of water for hydraulically fracturing, usually spanning an interval of about one month per gas well (R.W. Harden & Associates 2007). After frac water is injected, the internal pressure of the geologic formation causes the injected fracturing fluids to rise to the surface and recovered fracturing fluid is referred to as flowback water (USEPA 2010). Not all fracturing fluids injected during hydraulic fracturing are recovered. Estimates of the fluids recovered range from 15–80% of the volume injected depending on the site (USEPA 2010).

Hydraulic fracturing can occur repeatedly throughout the well lifetime. Some companies reuse flowback to hydraulically fracture more than one well as a way of conserving water and recycling the fluids (USEPA 2010). Flowback water represents only a portion of the water injected into the formation, making this option sustainable only as long as the water quantity is sufficient for continued fracturing. Unlike the intermittent production of flowback water from fracturing operations, produced water is generated continuously as long as gas production is occurring. Treated produced water used to supplement water quantities for hydraulic fracturing lowers the use of fresh water sources for well development and creates a more sustainable water use cycle within the well drilling operation.

Enhanced Oil Recovery.—Enhanced oil recovery (EOR) is used to extract additional oil in place in a reservoir, since only 20–40% of the total amount of oil in place can be recovered by standard extraction methods (Petroleum Technology Transfer Council). A number of EOR techniques exist as secondary recovery mechanisms. Water injection into an aquifer will displace oil towards the production well. EOR involving the injection of water and carbon dioxide into depleted oil fields can extract up to 10% of the remaining oil. Meanwhile, chemical EOR uses a fluid injection consisting of chemicals that promote the hydrocarbon movement through the formation to aid in recovering more products from a well (Petroleum Technology Transfer Council). Volumes of water used depend on the reservoir, while water quality concerns for injection include lowering divalent cation and silica levels to minimize scaling. Ten barrels of water are produced for each barrel of crude oil during EOR, which can be treated and re-used for further EOR (Petroleum Technology Transfer Council). Produced water generated at alternative well sites during well production may be used and treated for EOR applications.

5.3.6.2 Dust Suppression

Produced water is often generated in arid regions that are dust-prone. Produced water can be used for dust suppression on unpaved lease roads in oil and gas fields. Typically, the spray of produced water for dust suppression is well controlled so that the water is not applied beyond the road boundaries or within buffer zones around stream crossings and near buildings (Veil). Produced water has also been used for dust suppression in surface coal mining operations.

5.3.6.3 Fire Protection

Produced water could potentially be used for wild-land firefighting or municipal fire hydrants and sprinkler systems. Often drinking water is used for fire fighting, however, water quality requirements for water used in fire fighting are not stringent, and the use of alternative water sources does not adversely affect drinking water supplies.

In order to use produced water for fire protection, the water supply needs to be easily accessible and contain a sufficient volume. In 2002, CBM produced water stored in impoundments from the San Juan Basin was used effectively to fight a wildfire near Durango, Colorado (ALLConsulting 2003).

5.3.6.4 Cooling Towers

Cooling towers for powerplants required large volumes of water. As water demands increase, alternative water sources are sought for use in cooling towers. In some cases, it may be possible to use produced water for a portion of the cooling water demand at powerplants located near produced water generation (Veil).

5.3.10 Domestic

In some cases, produced water is of sufficiently high quality that it could be considered for municipal drinking water (table 11).

Table 11. USEPA drinking water standards

Inorganic Constituent (µg/L)	Maximum Contaminant Levels (MCLs)				
	California Department of Health Services		Environmental Protection Agency Limits		
	Primary MCL	Secondary MCL	USEPA Primary MCL	USEPA Secondary MCL	Regional Water Quality Board Limits
Aluminum	1,000	200		50 to 200	200
Antimony	6		6		6
Arsenic	50		50		50
Asbestos	7 MFL		7 MFL		7 MFL
Barium	1,000		2,000		1,000
Beryllium	4		4		4
Cadmium	5		5		5
Chloride		250 mg/L		250 mg/L	10
Chromium (total)	50		100		50
Color		15 units		15 units	15 units
Copper	1,300	1,000	1,300	1,000	1,000
Corrosivity		Noncorrosive		Noncorrosive	Noncorrosive
Cyanide	150		150		150
Fluoride	2,000		2,000		2,100
Iron		300		300	300
Lead	15		15		50
Manganese		50		50	50
Mercury, inorganic	2		2		2
Nickel	100				45
Odor		3 threshold units		3 threshold units	3 threshold units
pH				6.5 to 8.5	6.0 to 9.0
Radioactivity, Gross Alpha	15 pCi/L		15 pCi/L		15 pCi/L
Radioactivity, Gross Beta	50 pCi/L		4 mrem/yr		Zero
Radium-226 + Radium-228	5 pCi/L		5 pCi/L		5 pCi/L
Selenium	50		50		5
Silver		100		100	50
Specific Conductance (EC)		900 umhos/cm			
Strontium-90	8 pCi/L				8 pCi/L
Sulfate		250 mg/L	500 mg/L	250 mg/L	20 mg/L
Thallium	2		2		2

Table 11. USEPA drinking water standards (continued)

Inorganic Constituent (µg/L)	Maximum Contaminant Levels (MCLs)				
	California Department of Health Services		Environmental Protection Agency Limits		
	Primary MCL	Secondary MCL	USEPA Primary MCL	USEPA Secondary MCL	Regional Water Quality Board Limits
Total Dissolved Solids		500 mg/L		500 mg/L	300 mg/L
Total Hardness as $CaCO_3$					225 mg/L
Total Nitrogen (TN)	5,000				
	10,000				
Tritium	20,000 pCi/L				20,000 pCi/L
Turbidity		5 NTU	1.0/0.5/0.1 NTU		5 NTU
Uranium	20 pCi/L		20 pCi/L	Zero	20 pCi/L
Zinc		5,000		5,000	5,000

[1] MFL = million fibers per liter; µg/L = microgram per liter; pCi/L = picocuries per liter; mrem/yr = millirem per year; $CaCO_3$ = calcium carbonate.

6. Produced Water Quality Characterization

Produced water is in contact with the hydrocarbon-bearing formation for centuries before it is produced and contains some of the chemical characteristics of the formation and the hydrocarbon (Veil et al. 2004). Additionally, naturally present water in the pore structure also reflects characteristics of the hydrocarbon depositional environment. Conventional and unconventional resources vary in depositional environment from continental fresh water deposits to brackish or marine water deposits. Resulting water quality of the produced formation water is a blend of the fresh to marine source environment origin and dissolved mineral species characteristic to source formation dissolution. To generalize the characteristics of produced water quality, information has been gathered from public resources on salt concentrations and composition, major and minor inorganic constituents, organic constituents, naturally occurring radioactive material, and chemical additives used during well development and well production.

The USGS has published an extensive online database of produced water quality for producing basins across the United States. This database contains major ion analysis and TDS concentrations for over 27,500 oil and gas wells nationwide. The database is limited in certain areas because it does not explicitly state which wells produce oil or natural gas, the age of the wells, the flow rate of water from the well at the time of the sampling, the sampling technique used or the analytical method. The database is best used to draw general conclusions about produced water generated by the petroleum industry as a whole. For the purpose of this report, data collected and analyzed from this source is considered to reflect conventional produced water quality. To supplement this database general water quality summary, studies on conventional oil and gas water quality such as Fakhru'l-Razi et al. (2009), Fillo and Evans (1990), Shepard et al. (1992) and Tibbetts et al. (1992) are used to provide general information on minor ions, organics, and radionuclides.

State governing entities on oil and gas production also keep produced water quality records for conventional and unconventional resources. The Colorado Oil and Gas Conservation Commission (COGCC) keeps public records of both major and minor ions associated with conventional and unconventional oil and gas resources. Due to the extent of coal bed natural gas production in the Rocky Mountain region, the COGCC keeps categorized water quality information on CBM. Major CBM basins in Colorado include the San Juan and Raton basins of southern Colorado and the Piceance basin in western Colorado. Data varies in completeness by well log; but major ions, total dissolved solids data, and certain minor ions are available for 1,455 unconventional well in Colorado. This well data in combination with case studies in the Powder River and other national basins is used to draw general conclusions for unconventional gas produced water quality.

For the purpose of this report, unconventional water quality data is categorized as CBM produced water. Information on CBM produced water quality is more easily found in the public domain than information on flowback water; however, an effort was made to distinguish water quality from initial production of flowback water during hydraulic fracturing operations in various unconventional resources from produced water quality information. The following sections describe the characteristics of both conventional and unconventional produced water quality. Information presented represents a general summary of water compositions reported in produced water quality databases and previous studies. A list of relevant resources, for specific wellhead database data or case studies on produced water, is provided at the end of this section.

6.1 Salt Concentration and Composition

Produced water is a mixture of inorganic and organic compounds (Fakhru'l-Razi et al. 2009). Salinity is a general attribute of produced water. The properties of produced water vary depending on the geographic location of the field, the geological host formation, and the type of hydrocarbon product being produced (Veil et al. 2004). Salinity or salt concentration, described as TDS, can vary in conventional oil and gas well produced waters from 1,000–400,000 mg/L (United States Geological Survey 2002). Variations in TDS are related to geologic variations between basins, well location in a well field, and the resource produced. The USGS and COGCC databases are used to describe distinctions in TDS between wells producing conventional or unconventional resources.

The large range of TDS observed in the USGS database for conventional wells is broken down into basin entries in figure 10 (USGS 2005). Figure 10 demonstrates the variations of TDS in Western United States basins through using of a box and whisker plot. The top and bottom of the box represent the 75th and 25th percentiles, respectively. The midline through the box represents the 50th percentile. The up and down bars, or whiskers, represent the minimum and maximum concentrations observed in the basins. The basins in figure 10 have been arranged to depict basin locations from north (left side of graph) to south (right side of graph).

The range of TDS, from minimum to maximum concentrations, in entries for the Western United States basins are extensive, spanning more than 150,000 mg/L in all basins and over 300,000 mg/L in more than half. The statistical percentiles, however, confine the expected span of water quality to more specific regions. For example, the Sweetgrass, Powder River, Big Horn, Wind River, Green River,

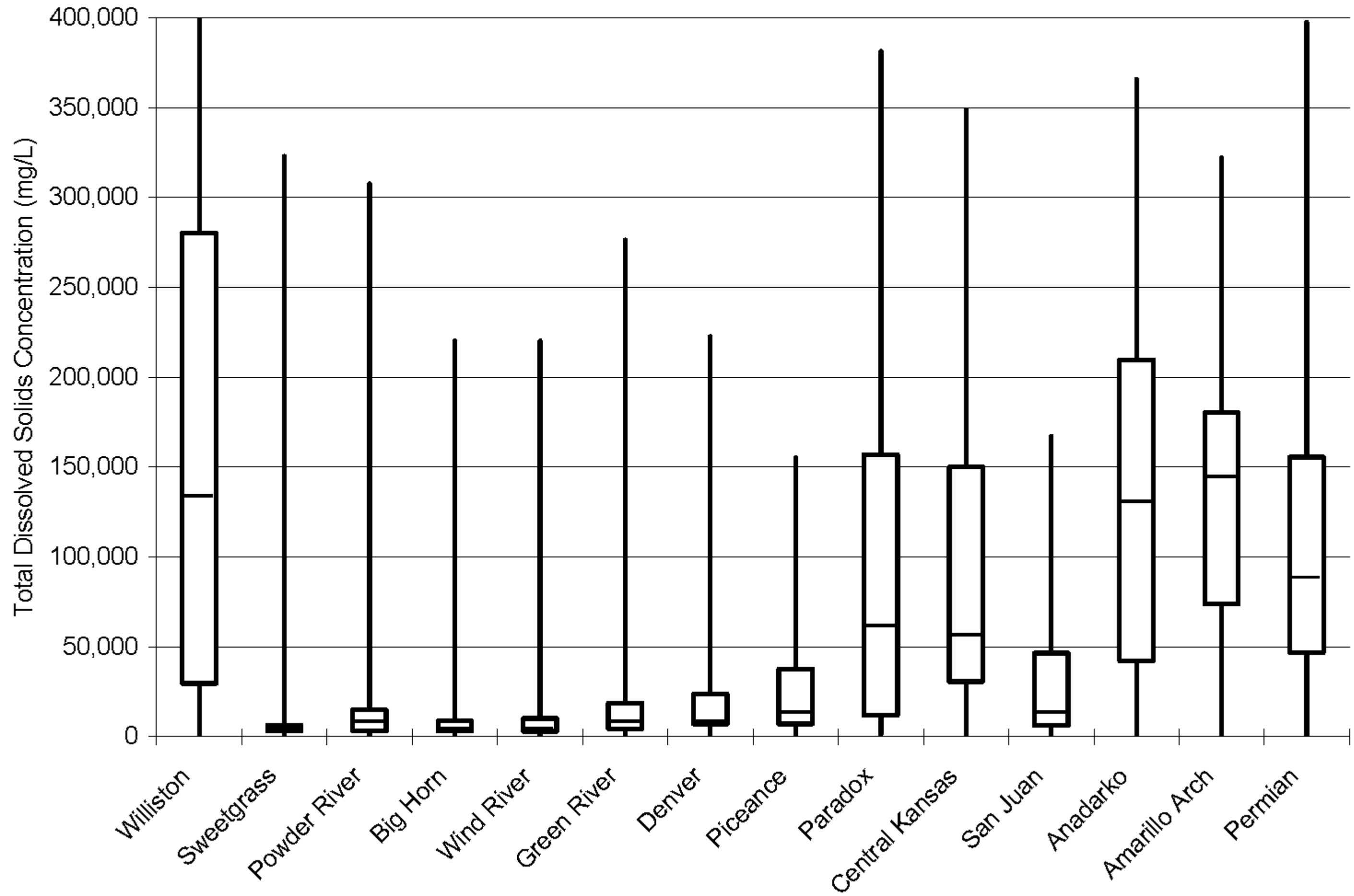


Figure 10. Distribution of TDS for conventional basins.

Denver, Piceance, and San Juan are all comprised of 75th percentile TDS values below 50,000 mg/L; and a majority of these wells have a TDS of 35,000 ppm or less. Trends in TDS can be observed as the basins are located more southerly. Basin TDS concentrations in the southern basins—with the exception of the Williston basin in Montana, North Dakota, and South Dakota that also have higher TDS–contain a majority of entries above 50,000–100,000 mg/L. The formation environments as well as the formation material contribute to the overall salinity of the produced water in both conventional and unconventional wells. Increased salinity in the southern basins could be attributed to marine type depositional environments during the late cretaceous period. Reservoirs in these regions were formed in brackish to marine environments, while continental reservoirs such as the Powder River basin were formed in fresh water environments (Van Voast 2003).

Comparing conventional wells to unconventional wells, a large distinction can be made in well type based on the observed range of TDS concentrations. While conventional wells can approach TDS concentrations of 400,000 mg/L, CBM wells are generally less than 50,000 mg/L (Benko and Drewes, 2008). Figure 11 depicts the distribution of TDS in conventional wells, and figure 12 shows the distribution in unconventional wells. The histogram charts use TDS bins to differentiate wells of different concentrations. The percentage of wells in each bin dictates the height of each bar. Note the difference in scale of the TDS concentrations for conventional versus unconventional well water qualities.

Distinct differences in the histogram shapes exist between conventional and unconventional wells in the distribution of TDS. Conventional wells consistently span the TDS range between 5,000–200,000 mg/L, but the percentage of wells in higher TDS ranges tends to decrease as TDS concentrations increase beyond 200,000 mg/L. The distribution of wells above 200,000 mg/L is 18%, while 53%, or the majority of wells, range from 50,000–200,000 mg/L; and 29% exhibit TDS concentrations below 50,000 mg/L. Conversely, 99% of the unconventional wells in the COGCC database exhibit TDS concentrations below 50,000 mg/L. Furthermore, 86% of unconventional wells exhibit a TDS of 5,000 mg/L or less. Close to three times as many unconventional wells (86%) display TDS concentrations less than 5,000 mg/L as compared to conventional wells (29%) with TDS values less than 50,000 mg/L. Salt concentration, signified by TDS, represents a clear distinction in composition between waters produced from conventional wells versus CBM wells.

In addition to salt concentration, salt composition or makeup is equally important in distinguishing between produced water types. The dominant cations observed for both conventional and unconventional produced water types include sodium, calcium, magnesium, and potassium. The dominant anions are most commonly bicarbonate, chloride, and sulfate. Significant differences exist in the dominant ions of conventional and unconventional

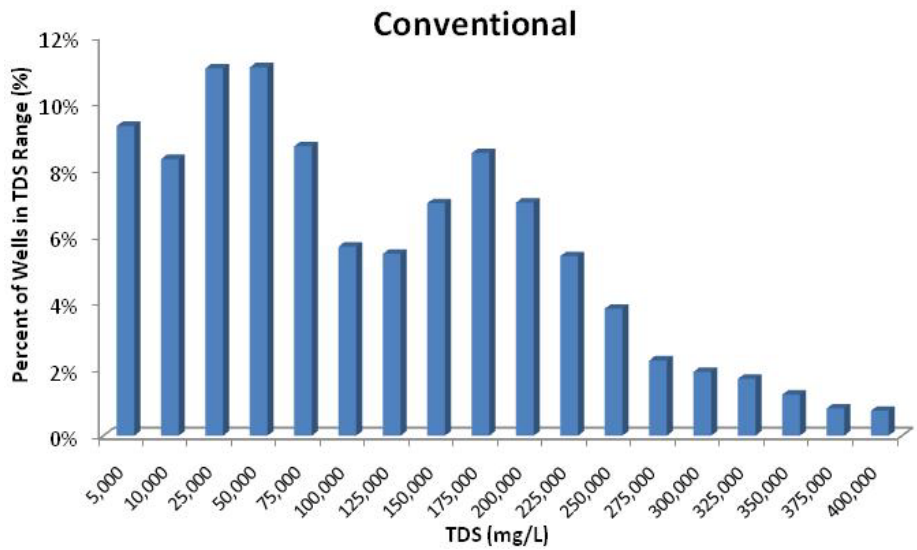


Figure 11. Distribution of TDS concentration for conventional oil and gas.

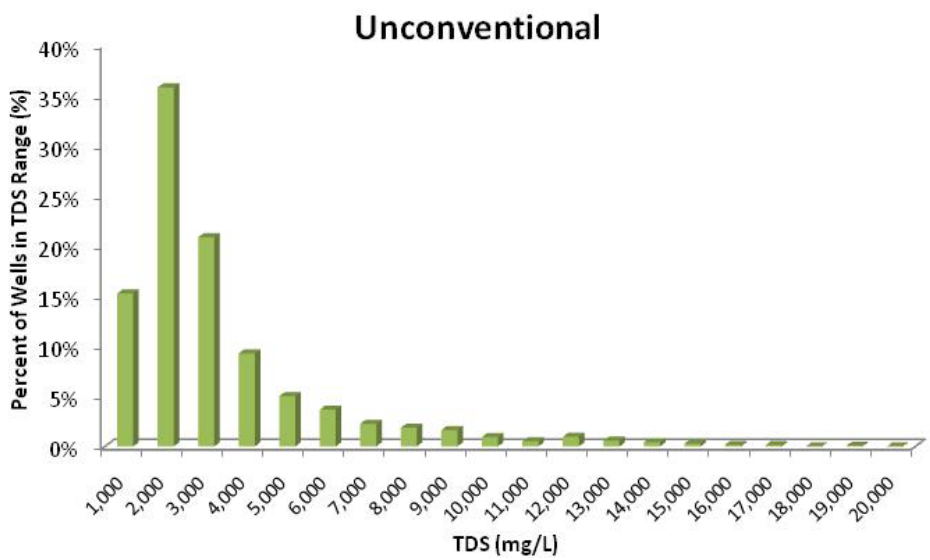


Figure 12. Distribution of TDS concentration for unconventional CBM basins.

produced water. Salinity in conventional resources is due mainly to dissolved sodium and chloride, with fewer contributions from calcium, magnesium, and potassium (Fakhru'l-Razi et al. 2009). Meanwhile, Rice and Nuccio (2000) reported that TDS concentrations at CBM wellheads ranged from 370 to 1,940 mg/L, generally a result of increased sodium and bicarbonate.

To verify the existence of significant cation and anion variations, the USGS and COGCC databases were used to create cation and anion makeup compositions for comparison of conventional and unconventional resources. These cations (calcium, magnesium, potassium, sodium) and anions (bicarbonate, chloride, and sulfate) were present for most wells in both the USGS and COGCC databases. In figure 13, conventional and unconventional produced water compositions are compared through pie charts relating the percentage concentrations of major cations and anions. These charts are separated for comparison purposes with conventional well compositions on the top and unconventional compositions on the bottom. The values plotted in these charts represent average cation and anion values for all basins in each database category.

Sodium is the dominant cation for water produced from both conventional and unconventional wells. For conventional wells, sodium makes up 81% of the cations, but calcium also represents 14% of the cation makeup, while magnesium and potassium account for 5%. The unconventional wells are almost completely sodium dominated with calcium, magnesium, and potassium representing 5% of the cations. Distinict differences can be observed between the anion makeup in conventional and unconventional wells. Conventional wells are mainly chloride anions, which represent 97% of the total anions present. In unconventional wells, bicarbonate makes up 66% of the anions, while chloride makes up 32%.

Dominance of chloride in conventional wells may be attributed to marine influence in the hydrocarbon depositional environment as aforementioned during the discussion of salt concentration. Bicarbonate concentrations, however, are likely attributes of subsurface anaerobic methanogensis or the creation of biogenic methane, which result in increased bicarbonate concentrations in CBM wells resulting in the precipitation of calcium and magnesium from solution (Van Voast 2003). Low concentrations of sulfates also indicate that the coal reservoir has undergone, or is undergoing, methanogenesis (Rice, Flores et al. 2008). This subsurface process dictates anion dominance in the unconventional CBM water quality.

Although cations and anions makeups provide insight into the relative makeup of well water quality, the dominant salt is also an important descriptive factor. This descriptive factor differs from the cation and anion contributions previously presented. For example, although the average chloride concentrations may indicate chloride as 32% of the anion makeup in unconventional wells, dominant salt type of a well may not directly reflect these values. The dominant salt type represents the salt formed by the dominant anion and cation for each individual

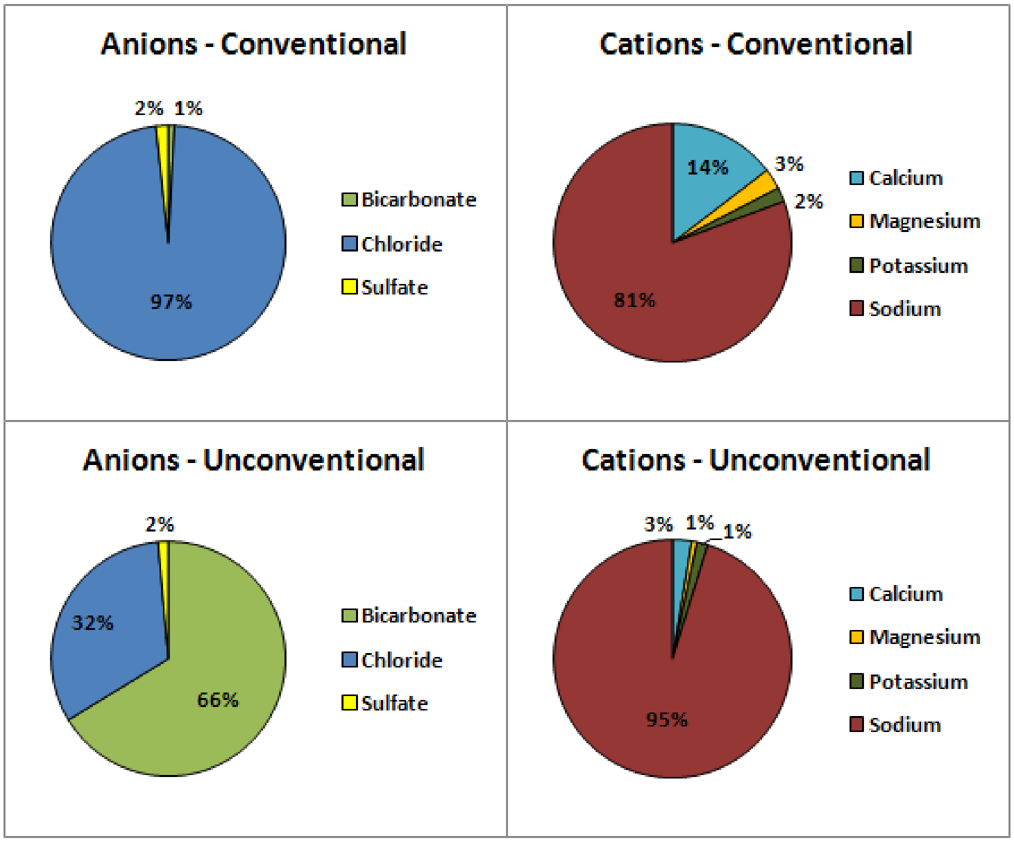


Figure 13. Major cations and anions for produced water.

well. Using the databases, figure 14 was created to compare the salt makeup of individual conventional and unconventional wells. The salt types include sodium chloride and sodium bicarbonate type, while sodium sulfate, calcium sulfate, calcium chloride, and others are included in the category, "Other."

The salt type can reflect the formation environment as well as the system processes, such as the impacts of methanogenesis in CBM reservoirs. The dominant salt makeup of conventional produced water is mainly sodium chloride type. Sodium bicarbonate type exists for 4% of the conventional wells, but sodium bicarbonate type waters do not exceed the combined occurance of other salt types of which sodium sulfate and calcium chloride occur at 4 and 6%, respectively. The uncnventional CBM wells, alternatively, are made up primarily of sodium bicarbonate type waters at 82% and sodium chloride type waters at 17%. The occurance of produced water from unconventional CBM wells falling under the "Other" category is only 1%.

Dominant salt types also are variable based on their geographic location. Dominant salt type charts are included for the Western United States basins in figure 15. Data was obtained from the USGS database for each basin. This figure depicts the percentage of wells within each basin of the USGS database that were

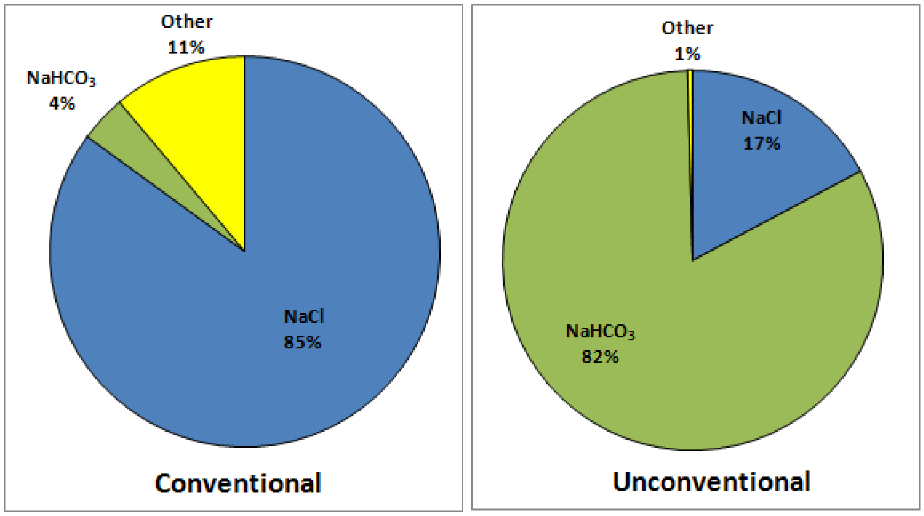


Figure 14. Dominant salt types of produced water.

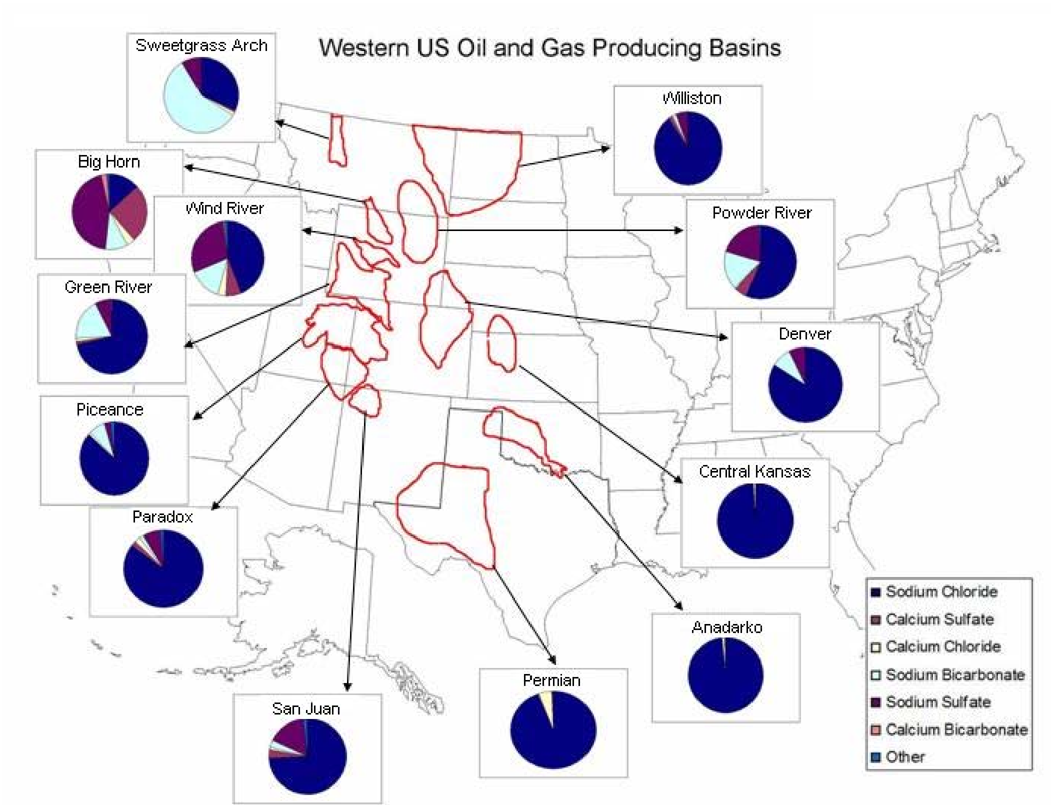


Figure 15. Western United States oil and gas basins: dominant salt type distribution.

dominated by each type of salt. The salt types include, in clockwise order on the pie charts, sodium chloride, calcium sulfate, calcium chloride, sodium bicarbonate, sodium sulfate, calcium bicarbonate, and other as any remaining salts unlisted.

Observed from figure 15, sodium chloride is the dominant salt in nearly all of the Western United States basins. The Big Horn and Sweetgrass Arch basins are the two main exceptions. The Big Horn basin has the largest makeup of sodium sulfate type waters; although the basin exhibits a variety of dominant salt types. Sodium bicarbonate is the dominant salt type in the Sweetgrass Arch, similar to the unconventional CBM basins. Kansas, Anadarko, and Permian basins show the least amount of subsequent salt types with most wells in those basins exhibiting sodium chloride type waters. The most common salts following sodium chloride across the Western United States basins include sodium bicarbonate and sodium sulfate. Dominant salt type is an important descriptive feature for produced water quality; however, other inorganic and organic constituents also exist at measurable concentrations in produced water.

6.2 Inorganic Constituents

Produced water has high concentrations of dissolved constituents that build up during extended contact with formation material. Produced water contains some of the chemical characteristics of the formation waters originally associated with the formation environment as well as manipulations to the water by subsurface processes (Van Voast 2003). Produced water is in contact with the formation environment for centuries, suggesting that mineral characteristics of the formation material will be reflected in the produced water quality (Veil 2004). These reflections can be in the form of mineral types, such as carbonate or silicate systems, but also can include minor heavy metals present in the subsurface including arsenic, lead, organic constituents, and naturally occurring radioactive materials (NORM). This section focuses on the inorganic characteristics of produced water, specifically commonly occurring, or major ions and lower concentration inorganic and organic constituents or minor ions.

6.2.1 Major Ions

Based on the salt composition observations from the previous sections sodium is consistently present in both conventional and unconventional produced water types. There is potentional, due to produced water composition, that high ranges of SAR likely are associated with each water type. SAR represents the ratio of specific cations to one another, focusing on the relationship of sodium with calcium and magnesium. The higher the calcium and magnesium concentrations with respect to the sodium, the lower the value of SAR becomes. High TDS concentrations associated with conventional wells translate to a high SAR when sodium is the dominant cation in the wells. Although unconventional wells have lower overall TDS concentrations, the lack of calcium and magnesium in the cation makeup also suggest elevated SAR values in unconventional wells.

To determine the impact of TDS on the SAR, SAR values were calculated for wells using the USGS database. These values were calculated by basin as, in conjunction with TDS; the SAR is also highly variable between basins. For the conventional basins included in figure 15, table 12 provides the median TDS and SAR values with the standard deviations for each basin. Large standard deviations in the data are a result of the variability associated with wells in each basin, while variations exist in TDS and SAR data for each basin may also be observed.

Trends in SAR with respect to TDS are present at the higher TDS concentrations. At higher TDS concentrations (> 50,000 mg/L), the SAR increases with TDS concentration. For example the Williston basin in North Dakota has the highest average TDS concentration of the basins, while it also has the highest average SAR. This trend suggests that, at TDS above 50,000 mg/L, increases in TDS are caused by the sodium cation. TDS concentrations also can be significantly different between regions or States that are contained within the same basin. For example, wells in the South Dakota portion of the Williston basin have very low TDS concentrations compared to the North Dakota portion. Geographic location within the basin influences the produced water quality. This may be due to the presence of a recharge zone along outcrops, confined areas of formation water, or the transmission of fresh water into the hydrocarbon bearing formation (Rice and Nuccio 2000; Clearwater, Morris et al. 2002).

Major inorganic constiuents identified in produced water include sodium, calcium, magnesium, potassium, chloride, bicarbonate, and sulfate. Barium and stronium also occur in produced water, although the concentration ranges can span from nondetect to elevated concentrations such as 850 mg/L for barium and 6,250 mg/L for strontium in conventional basins. Ranges of these prevalent inorganic constituents in produced water are presented in table 13 for conventional wells.

CBM water traditionally has lower sulfate concentrations than conventional wells. Barium sulfate forms a sparingly soluble salt, controlled by the amount of barium or sulfate present in the water. Since the sulfate concentration in CBM wells is relatively low, the barium concentrations in the water can remain relatively high. The barium concentration in conventional produced water has a range of 0–850 mg/L (Fillo, Koraido et al. 1992). The COGCC database reports a barium range from 0.5–125 mg/L. This trend is consistent for other ions as well. For instance, maximum calcium, magnesium, potassium, and sulfate concentrations are one to two orders of magnitude lower in CBM wells than conventional wells. Due to lower TDS concentrations, unconventional wells tend to have lower concentrations of all major ions.

Table 12. Conventional basins TDS and SAR statistics

Basin	State	TDS (mg/L)		SAR	
		Median	Standard Deviation	Median	Standard Deviation
Williston	Montana	74,300	113,200	127.7	144.4
	North Dakota	253,000	122,400	179.8	107.4
	South Dakota	8,200	36,000	35.5	45.8
Sweetgrass Arch	Montana	4,000	21,100	36.8	33.4
Powder River	Montana	7,000	5,400	70.3	42.1
	Wyoming	7,400	35,300	76.8	204.1
Big Horn	Montana	3,200	8,300	16.9	45.0
	Wyoming	4,900	12,900	10.5	31.3
Wind River	Wyoming	5,300	14,800	52.5	55.3
Green River	Wyoming	10,000	22,000	64.4	36.9
	Colorado	7,500	16,800	76.5	46.3
Denver	Colorado	10,100	19,600	96.8	56.1
	Nebraska	10,300	32,300	151.9	70.5
Piceance	Colorado	15,000	34,900	79.0	41.2
Paradox	Colorado	137,900	102,600	95.6	41.0
	Utah	55,700	87,300	62.2	98.1
Central Kansas	Kansas	58,400	70,500	65.4	46.8
San Juan	Colorado	14,900	37,000	103.9	90.6
	New Mexico	15,900	34,100	77.9	55.1
Anadarko	Kansas	108,300	81,300	98.0	50.6
	Oklahoma	142,000	90,500	112.3	29.8
	Texas	124,600	84,200	n/a[1]	n/a
Permian	New Mexico	63,300	83,100	81.5	98.8
	Texas	99,600	73,500	93.4	64.7

[1] n/a = data not available.

Table 13. Common inorganic constituents in conventional produced water

Constituent	Units	Concentration Range Low	High	Median	Reference
TDS	mg/L	100	400,000	50,000	USGS produced water database
Sodium	mg/L	0	150,000	9,400	USGS produced water database
Chloride	mg/L	0	250,000	29,000	USGS produced water database
Barium	mg/L	0	850	Not Available	Fillo 1992
Strontium	mg/L	0	6,250	Not Available	Fillo 1992
Sulfate	mg/L	0	15,000	500	USGS produced water database
Bicarbonate	mg/L	0	15,000	400	USGS produced water database
Calcium	mg/L	0	74,000	1,500	USGS produced water database

Inorganic chemical composition information can be represented graphically in the form of a Stiff diagram. A Stiff diagram plots the concentrations of major cations and anions of a water type. The diagrams in figure 16 represent cations on the right and anions on the left of the center axis. The distance of each point representing an ion type from the center access is the ions' equivalent concentration. The points are connected to outline a chemical pattern. By comparing the shape of the outlined figure, water types can be compared easily in a visual manner. Note that the scales are different on the conventional and unconventional diagrams and the concentrations compared are in milliequivalents per liter (meq/L).

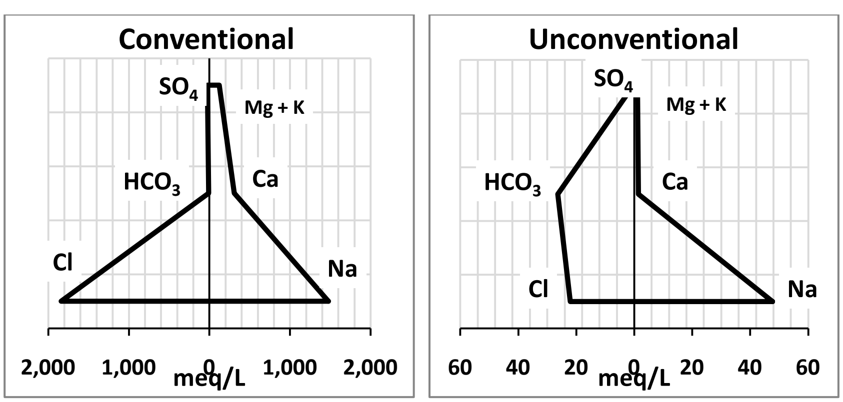


Figure 16. Geochemical fingerprints of conventional and unconventional basins.

Both cation sides of the diagrams are bottom heavy where sodium is the dominant cation. Calcium, magnesium, and potassium have a higher contribution, or deviation from the center axis in convention produced water. Bicarbonate is relatively absent by comparison to chloride in conventional produced water. Bicarbonate and chloride both exist in the unconventional system, where bicarbonate is more often the dominant anion. This diagram can be applied to the Western basins to observe variations and similarities between basins. Figure 17 shows the major Western conventional basins with the subsequent basinwide Stiff diagrams.

As a general theme, the geographic spatial distributions are similar across most basins. Generally, the conventional basin diagrams are bottom heavy with their sodium chloride type waters and small relative influences from other ions. In certain basins, such as the Permian, Central Kansas, and Paradox, cations such as potassium, magnesium, and calcium occur at visible concentrations on the Stiff diagrams. These three diagrams share the same scale and, therefore, comparable concentrations. Sweetgrass Arch and Big Horn also contain visible concentrations of the alternate cations; however, the smaller scale suggests these concentrations may be visible on the diagram due to relatively lower concentrations of sodium. The same is true in these basins for the bicarbonate and sulfate anions.

The Williston and Anadarko basins have the highest ion concentrations, although both are dominated by sodium chloride type waters. The lowest ion concentrations are found in the Sweetgrass Arch, Big Horn, and Wind River basins. The overall trends for Stiff diagrams over the Western United States include a general increase in diagram scale, which is consistent to the increase in ion concentrations or TDS towards the Southern United States. Again, the exception to this trend is the Williston basin in Montana, North Dakota, and South Dakota. Although occurring at higher relative concentrations, these major ions are a small subset of the inorganic constituents present in produced water. The following section focuses on the remaining inorganic constituents, or minor ions, present in conventional and unconventional CBM produced waters.

6.2.2 Minor Ions

Minor ions present in produced waters include inorganic constituents such as metals at varying ranges of concentrations as well as nonmetals such as fluoride and boron. These minor ions are found at relatively lower concentrations than the major ions, mentioned previously, in most wells (McBeth and Reddy 2003). Ranges of ions may reflect wells with elevated concentrations of certain constituents, but overall minor ions make up less than 1% of the overall constituent contribution to dissolved solids. Minor ions are of interest for a number of reasons including their regulation in beneficial use standards, potential hazardous nature if concentrated during treatment, recoverable quantity for constituents of value, and preserving natural systems during practices such as water application to soils in irrigation.

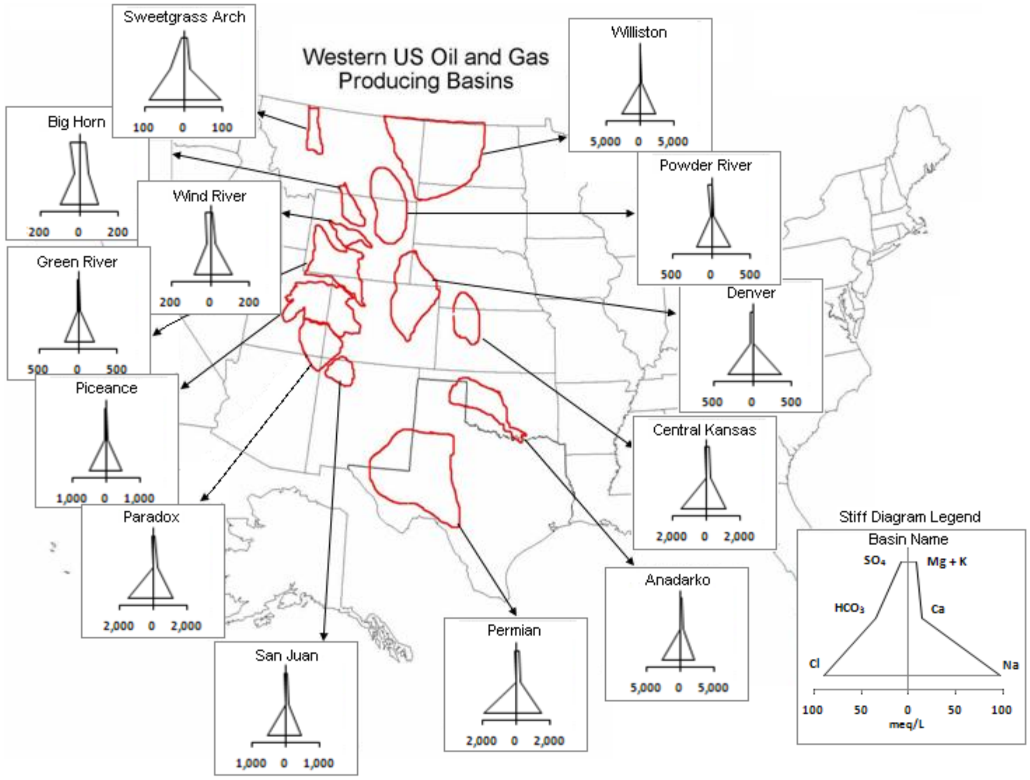


Figure 17. Western United States oil and gas basins: water geochemistry.

Interest exists to beneficially use CBM water for various applications due to lower TDS. These applications include irrigation, livestock watering, and streamflow augmentation. Dissolved chemicals in CBM produced water can differ greatly from those in surface waters because of their origin within coal seam aquifers (Clearwater, 2002 #80);(Van Voast, 2003 #45). Therefore, it is important to determine the coal seam water quality, particularly that of minor ions that may precipitate or concentrate upon release to the surface. McBeth et al. (2003) collected CBM product water samples from discharge points and associated discharge ponds. This study focused on identifying changes in CBM produced water quality upon release to surface ponds. Although this report does not go into detail regarding downstream changes in water quality, the values analyzed by that study for discharge points, which included aluminium (Al), arsenic (As), boron (B), barium (Ba), chromium (Cr), copper (Cu),fluorine (F), iron (Fe), manganese (Mn), molybdenum (Mo), lead (Pb), selenium (Se), and zinc (Zn), which are also included in table 14 to supplement COGCC database values for minor ion concentrations.

Table 14 includes a comprehensive list of inorganic constituents. Minor ion concentrations for conventional wells are provided from numerous studies in cooperation with the USGS database values. Fakhru'l-Razi et al. (2009) summarized oil and gas conventional water qualities separately (Fakhru'l-Razi, Pendashteh et al. 2009). Although those ranges have been combined for the

Table 14. Ranges of inorganic constituents in produced water[1]

Constituent List	Units	Conventional	Unconventional
Antimony	mg/L	n/a	ND – 0.005 [e]
Aluminum	mg/L	< 0.50 – 410 [b,d]	0.005 – 1.52 [f, g]
Arsenic	mg/L	0.004 – 151 [a,b,d]	ND – 0.158 [e]
Barium	mg/L	ND – 1740 [a,b,d]	0.445 – 125 [e, g]
Beryllium	mg/L	< 0.001 – 0.004 [d]	n/a
Bicarbonate	mg/L	ND – 14,750 [h]	4.53 – 49,031 [g]
Boron	mg/L	ND – 95 [a,d]	0.05 – 30.6 [e]
Bromide	mg/L	150 – 1,149 [a,b]	ND – 41.1 [e]
Cadmium	mg/L	< 0.005 – 1.21 [a,b,d]	ND – 0.076 [e]
Calcium	mg/L	ND – 74,185 [h]	ND – 5,530 [e, g]
Chloride	mg/L	2 – 254,923 [h]	ND – 52,364 [e, g]
Chromium	mg/L	ND – 1.1 [a,d]	ND – 3.71 [e, g]
Cobalt	mg/L	n/a	ND – 0.010 [e]
Copper	mg/L	< 0.002 – 5 [b,d]	0.001 – 1.448 [e]
Fluoride	mg/L	n/a	0.57 – 20 [f, g]
Iron	mg/L	ND – 1,100 [a]	0.001 – 258 [e, g]
Lead	mg/L	0.002 – 10.2 [b,d]	ND – 0.098 [e]
Lithium	mg/L	3 – 235 [b,d]	ND – 1.50 [g]
Magnesium	mg/L	ND – 46,656 [h]	1.2 – 918.9 [e]
Manganese	mg/L	< 0.004 – 175 [d]	ND – 3.11 [e, g]
Mercury	mg/L	< 0.001 – 0.002 [d]	ND – 0.014 [e]
Molybdenum	mg/L	n/a	ND – 0.448 [e]
Nickel	mg/L	< 0.08 – 9.2 [b]	ND – 0.082 [e]
Nitrogen, ammoniacal ($N-NH_3$)	mg/L	10 – 300 [d]	n/a
Nitrate ($N-N0_3$)	mg/L	n/a	ND – 26.1 [g]
Potassium	mg/L	0 – 14,840 [h]	ND – 1,100 [g]
Selenium	mg/L	n/a	ND – 1.27 [e]
Silver	mg/L	< 0.001 – 7 [b,d]	ND – 0.14 [g]
Sodium	mg/L	1 – 149,836 [h]	97.3 – 32,013 [e]
Strontium	mg/L	0.02 – 6,200 [a,d]	ND – 47.9 [g]
Sulfate	mg/L	ND – 14,900 [h]	ND – 2,200 [e, g]
Tin	mg/L	ND – 1.1 [a]	n/a
Titanium	mg/L	< 0.01 – 0.7 [d]	n/a
Uranium	mg/L	n/a	ND – 2.5 [g]
Vanadium	mg/L	n/a	ND – 0.290 [e]
Zinc	mg/L	0.01 – 35 [d]	0.005 – 5.639 [e]

[1] ND = nondetect; n/a = data not available; a = Fillo and Evans 1990; b = USEPA 2000; c = Shepard, Shore et al. 1992; d = Tibbetts, Buchanan et al. 1992; e = Cheung, Sanei et al. 2009; f = McBeth, Reddy et al. 2003; g = Colorado Oil and Gas Conservation Commission 2010; h = USGS 2002.

purpose of this report, the separated values can be found in table 1, natural gas produced water, and table 2, oilfield produced water, of that study.

In general, concentrations of minor ions are greater in conventional than unconventional CBM wells. Exceptions include bicarbonate as well as chromium and silver, although limited data is available for chromium and silver in conventional wells. Marine influences from the depositional environment may include boron, bromide, and chloride due to elevated concentrations in the source water. Conventional produced waters reflect marine influences containing elevated chloride and bromide concentrations ranging from 80–200,000 mg/L and 150–1,149 mg/L, respectively. Minor ions generally originate from natural sources in the system such as prolonged contact with source rock or depositional environment characteristics, such as those marine water types.

In addition to naturally occurring minor inorganic compounds, organic compounds and NORM also exist in produced water samples. These compounds also are naturally occurring and are significant in meeting regulations and treatment for use. The minor ions addressed in the following sections are attributes of the reservoir system, subsurface processes, and producing hydrocarbons. Byproducts of drilling or additives to aid in well production or completion are addressed in the section following NORM.

6.3 Organic Constituents

This section focuses on an explanation and overview of organic constituents present in produced water. Produced water is removed from an inherently organic system, where carbon sources have been converted to hydrocarbons over geologic time. This section will focus on organic constituents present from natural processes. Organic matter in produced water exists in two forms: dispersed oil and non-hydrocarbon organic material. Dispersed oil is small, discrete droplets suspended in the water. Nonhydrocarbon organic material is dissolved in the water (Stephenson 1992).

6.3 Organic Constituents

This section focuses on an explanation and overview of organic constituents present in produced water. Produced water is removed from an inherently organic system, where carbon sources have been converted to hydrocarbons over geologic time. This section will focus on organic constituents present from natural processes. Organic matter in produced water exists in two forms: dispersed oil and non-hydrocarbon organic material. Dispersed oil is small, discrete droplets suspended in the water. Nonhydrocarbon organic material is dissolved in the water (Stephenson 1992).

The amount and nature of soluble oil, or nonhydrocarbon organic materials in produced water is dependent on several factors: type of hydrocarbon being produced, volume of water production, artificial lift technique, and age of production. The only factor studied to any extent is the type of oil (paraffinic, asphaltenic, or gas condensate) (Stephenson 1992). Analysis of the organic content in produced water is complicated by interferences in the detection or measurement method. High inorganic content has been found to cause spectral interference and sample crystallization during the acid digestion process of metal analyses. Sample dilution is most often used to alleviate this problem.

Total organic carbon (TOC) ranges from nondetect concentrations to almost 2,000 mg/L. TOC includes suspended carbon or carbon that is not dissolved. Suspended carbon could include oils or high carbon mass particles that can be removed by filtration. The chemical oxygen demand is a measure of the oxygen consumed per liter of solution. Due to the deep confined nature of produced water, reservoirs systems are anoxic, although oxidation may occur during pumping and transport if the water comes in contact with the atmosphere. COD is a reflection of this anoxic system, but it also indicates the high carbon content. Table 15 lists the concentration ranges of organic material commonly found in produced water from oil operations (Tibbetts, Buchanan et al. 1992).

Insoluble carbon commonly identified as a part of total suspended solids (TSS) or total oil also is provided with concentrations in table 15. The total oil content in water generated from conventional crude oil extraction can range from 40–2,000 ppm depending on the water retention time in the three-phase separator (no chemicals or additional separation equipment used to generate these figures). Generally, polar water soluble organics found in produced water are distributed between the low and midrange of carbon content. The factor that most controlled the total water soluble organic content in produced water was aqueous phase pH. This study, conducted with water from oil operations, found that salinity had the least affect on the chemical character or the carbon size of water soluble organics in produced water.

Volatile compounds, compounds with low boiling points, include compounds such as nitrogen, carbon dioxide, hydrogen sulphide, and methane. These compounds likely are to be present at producing wells, but they also may be remnant as dissolved compounds in produced water. The organic components with the largest range of concentrations are the volatile fatty acids, which include acetate, propionate, and butyrate. Table 16 provides a breakdown of the volatile organics commonly found in produced water from natural gas extraction. These ranges of volatile organics were found in 75 to 80% of all gas produced water samples (Fillo, Koraido et al. 1992).   Volatile organics concentrations were not reported for water from oil extraction, because the concentrations are typically low or not observed. Conversely, semivolatile organics are rarely found in gas produced water and are much more prevalent in oil produced water. Semivolatile organics concentrations were not reported for water from gas extraction, because the concentrations are typically low or not observed.

Table 15. Organic material in produced water from oil operations[1]

Constituent	Units	Concentration Range			Technique (Method)
		Low	High	Median	
TOC	mg/L	ND	1,700	NA	UV Oxidation/IR (USEPA 415.1)
COD	mg/L	1,220		NA	Redox Titration (USEPA 410.3)
TSS	mg/L	1.2	1,000	NA	Gravimetric (USEPA 160.2)
Total Oil	mg/L	2	565	NA	Gravimetric (USEPA 413.1)
Volatiles	mg/L	0.39	35	NA	GC/MS (USEPA 1624 Rev B and USEPA 24 & CLP)
Total Polars	mg/L	9.7	600	NA	Florisil column/IR
Phenols	mg/L	0.009	23	NA	Silylation GLC/MS
Volatile Fatty Acids	mg/L	2	4,900	NA	Direct GLC/FID of water

[1] ND = below detection limit; NA = not available.

Table 16. Volatile organics in produced water from gas operations[1]

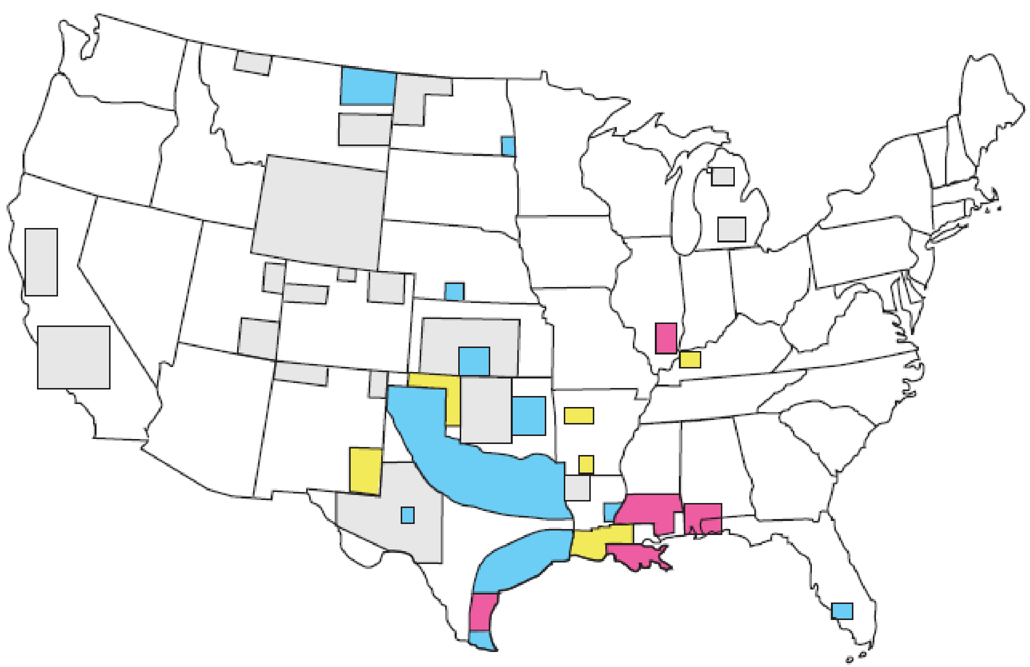
Constituent	Units	Concentration Range			Analytical Method	Reference
		Low	High	Median		
Benzene	mg/L	ND	27	NA	USEPA Method 1624 and 624	Fillo, 1992
Bis (2-chlorethyl) ether	mg/L	ND	0.03	NA	NA	GRI report, 1988
Ethylbenzene	mg/L	ND	19	NA	USEPA Method 1624 and 624	GRI report, 1988
Phenol	mg/L	ND	2.6	NA	NA	GRI report, 1988
Toluene	mg/L	ND	37	NA	USEPA Method 1624 and 624	Fillo, 1992
2-Butanone	mg/L	ND	0.37	NA	NA	GRI report, 1988

[1] ND = below detection limit; NA = not available.

Produced water from gas production tends to have higher contents of low molecular-weight aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX) than water from oil production. Studies indicate that the produced waters discharged from gas/condensate platforms are about 10 times more toxic than produced waters discharged from oil platforms (Jacobs, Grant et al. 1992). The chemicals used in processing typically include dehydration chemicals, hydrogen sulfide removal chemicals, and chemicals to inhibit hydrates. Well-stimulation chemicals such as mineral acids, dense brines, and additives also can be found in gas produced water (Stephenson 1992). These additional compounds are discussed in a following section.

6.4 Naturally Occurring Radioactive Materials

Naturally occurring radioactive elements include uranium, thallium, radium, and radon. These elements dissolve into water at low concentrations while water is in contact with rock or soil. Naturally occurring radioactive materials (NORM) in oil and gas production are primarily in the form of radon 226 and 228. Beneficial use of produced water containing NORM can contaminate soil, ground water, and surface water. NORM also is present in scale deposits that coat pipes and storage tanks conveying and containing produced water. Radium accumulation in equipment became apparent in the United States in the 1980s when unacceptable levels of radioactivity were found in oilfield pipe shipments (Zielinski and Otton 1999). In 1999, the USGS published Fact Sheet 0142-99, which focuses on the occurrence, regulations, and health concerns dealing with NORM in produced water. Figure 18 and the following information are summarized from this source.



Color Legend: White = no data; gray to yellow = at background or marginally detectable; blue = less than five times the median background for all sites; pink = greater than five times the median background for all sites.

Figure 18. Radioactive oilfield equipment (USGS Fact Sheet 0142-99).

Figure 18 demonstrates the severity of radioactivity geographically by categorizing United States basins through comparing radioactive concentrations in oilfield equipment to natural background concentrations. The sampling indicated that gamma ray radiation levels exceeded natural background radiation levels at 42% percent of the sites. Along the gulf coast, in Texas, Illinois, and Kansas, radioactivity levels were found to be greater than five times the median background, and these elevated areas represented 10% of the study sites. Radon 226 and 228 were reported to range from 4.93–720 pCi/L and 22.2–723 pCi/L in produced water outfalls in the Gulf of Mexico (Moatar, Shadizadeh et al. 2010).

Pipe, casing, fittings, and tanks with prolonged contact with produced water were more likely to contain radioactive deposits than other parts of the plumbing system. Leakage or spills of produced water in the vicinity of production sites may affect soils. Radon (226+228) is regulated at a maximum concentration of 5 pCi/L in drinking water sources; therefore, most sources require treatment to lower levels in produced water to meet this standard.

6.5 Chemical Additives

In addition to naturally occurring compounds mentioned in previous sections, chemical additives also are present in produced water. Chemical additives used in chemical treatments for produced water are commonly employed for problems such as hydrate formation, water vapor, mineral deposits, chemical corrosion, bacterial corrosion, emulsions, foaming, and paraffin. Table 17 contains a brief description of each problem encountered, sources of the issue, treatment chemicals, and concentrations. The data in table 17 is not comprehensive but provides a general background on chemical treatment compounds that may be present in produced water streams (Hayward Gordon Ltd.).

6.6 Beneficial Use Potential

Given the information on water quality for produced water from oil and gas as well as unconventional gas wells, it is apparent the treatment is required to meet most beneficial use scenarios. The following sections provide information on applicable scenarios for beneficial use given produced water quality. The section compares standards mentioned previously in the report, section 5. This information is calculated based on database values and assimilated tables. Comparison to each scenario is based on untreated water quality. Specific technologies capable of meeting these beneficial use requirements are available in the following report section 8.

Generalizing the TDS requirements for five particular beneficial uses allows for comparing database wells to the following TDS standards: drinking water 500 mg/L, ground water recharge 625 mg/L, surface water discharge 1,000 mg/L,

Table 17. Chemicals added for treatment of produced water

Problem	Cause	Chemical Treatment	Chemical Concentrations
Chemical corrosion	Hydrogen sulfide gas, carbon dioxide or oxygen	Corrosion inhibitor: amine imidazolines, amines and amine salts, quaternary ammonium salts, and nitrogen	Active ingredient concentration 3 –40%
Bacterial corrosion	Sulfate reducing bacteria reducing sulfate to hydrogen sulfide	Bactericides: quaternary amine salt, amine acetate, and gluteraldehyde	Concentrations ranging from 10–50%
Hydrate formation	Natural gas hydrates formed in the presence of water usually at high pressure and low temperature	Hydrate inhibition: ethylene glycol and methanol	5–15 gallons per million cubic feet of produced gas
Water Vapor	Water vapor present in natural gas is removed to meet sales specifications	Dehydration: Triethylene glycol (TEG)	n/a
Mineral deposits	Inorganic mineral compounds causing scale or deposits, such as calcium carbonate, calcium sulfate (gypsum), strontium sulfate, and barium sulfate	Scale inhibitor: phosphate esters, phosphonates, and acid polymers	Treatment concentrations from 3–5 ppm, but depend on the water type
Emulsion (normal and reverse)	Normal – water droplets dispersed in the oil phase Reverse – oil droplets suspended in the continuous water phase	Emulsion breakers: oxyalklated resins, polyglycol esters, and alkl aryl sulfonates	Bulk concentrations of 30–50%
Foaming	Oil froth	Defoamers: silicones and polyglycol esters	Treatment concentrations are 5–25 ppm

irrigation 1,920 mg/L, and agriculture livestock watering 10,000 mg/L. These values are the least conservative concentrations allowable for each use. Utilizing this breakdown, figure 19 was created to depict the percentage of wells in each database suitable for each use. This chart is based purely on TDS concentration and does not take into account SAR or minor ions.

Results from comparing database TDS concentrations to use alternatives indicate that water quality of produced water from both conventional and unconventional wells is unsuitable for drinking or ground water recharge untreated. Only 4% of the unconventional wells meet these criteria. Meanwhile 10% of the unconventional wells meet the 1,000-mg/L surface criteria for discharge. In the Powder River basin in Wyoming, a significant amount of produced water is discharged into watersheds (Clearwater, Morris et al. 2002). Numerous studies

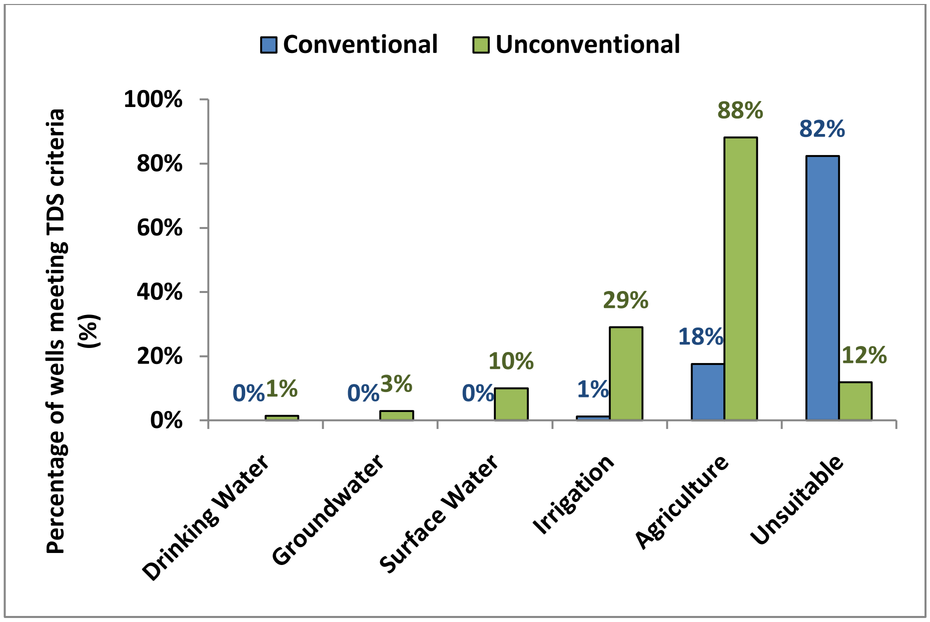


Figure 19. Conventional versus unconventional well distribution in the TDS requirement categories for each beneficial use.

are available on the Powder River that consider effects beyond salinity of surface discharges of produced water. Given the high maximum TDS concentration for livestock watering of 10,000 mg/L, 18% of conventional wells and 88% of unconventional wells meet this requirement. For unconventional CBM wells, 29% of that 88% also meets TDS standards. Of the two databases, 82% and 12% of the conventional and unconventional wells, respectively, do not meet any of the above listed standards. These waters may meet subsequent beneficial use opportunities such as dust control, hydraulic fracturing, or enhanced oil recovery, but requirements for these processes are not explored or compared in this report.

Potential use for these wells in the previous categories varies by location of the basin as well. By grouping drinking, ground water and surface water requirements into a single category, due to the low percentage of wells capable of meeting these standards, figure 20 was created. Using the same bar chart format, with consolidated categories, red bars represent water requiring treatment or water exceeding 10,000 mg/L TDS, yellow bars represent agriculture, green represents irrigation, and blue represents drinking, ground water or surface discharge. The results of the bar chart subsets are provided for the Western United States basins in figure 20.

Figure 20 shows that only four basins have a majority of wells with a TDS level unsuitable for use without treatment; Permian, Anadarko, Central Kansas, and Williston. Given the poor water quality in these basins, treatment is required to meet uses originating in this region. Recall Texas is also the largest generator of

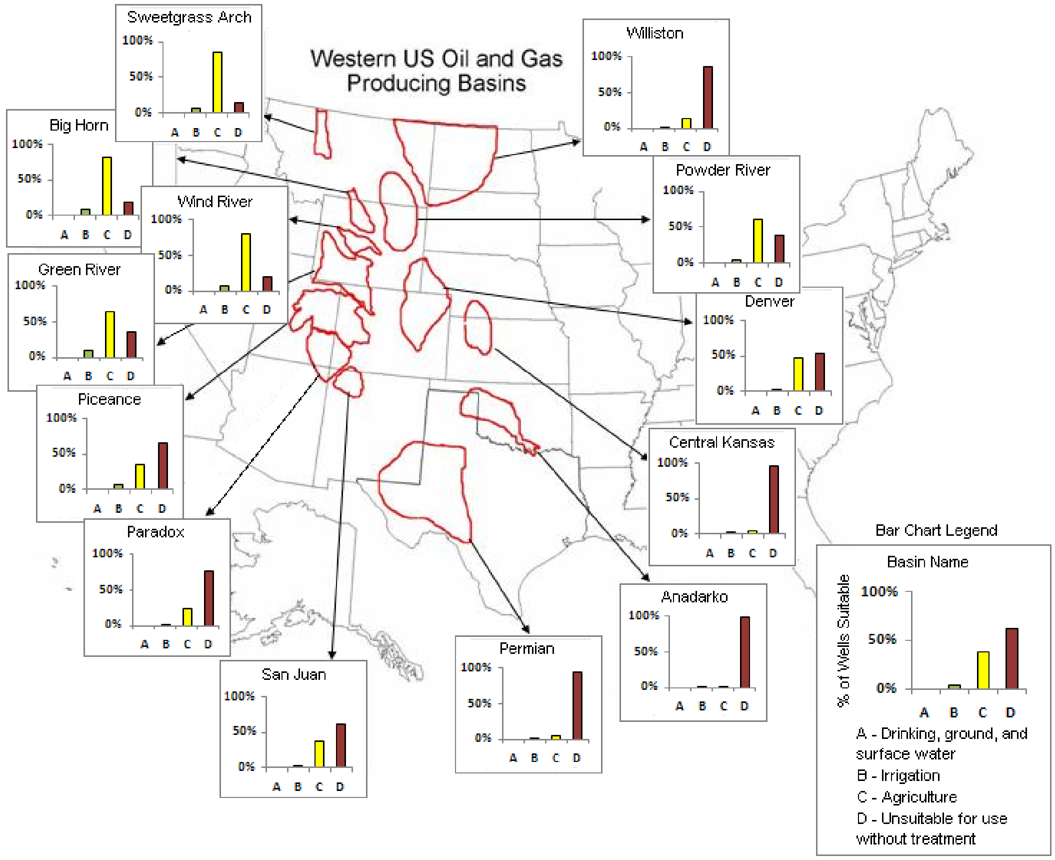


Figure 20. Western United States oil and gas basins: percentage of wells in various beneficial use categories.

produced water in the Western United States (Clark and Veil 2009). Although water generation of poor quality may be representative of this dataset, the amount of oil and gas production in the State suggests that onsite uses for production, enhanced well recover, and hydraulic fracturing could be accomplished through the treatment and use of produced water resources, thereby limiting requirements for fresh water resources in the State.

The Williston basin in Montana, North Dakota, and South Dakota is also of poor quality; however, given the relatively lower TDS concentrations in South Dakota, a small portion of the basins water resource does meet standards for agriculture livestock watering. The Denver, Piceance, Paradox, and San Juan basins also contain a certain number of wells fit for agricultural purposes, although a majority of wells are unsuitable for these uses without treatment. The Powder and Green River basins all exceed unsuitable wells with wells meeting TDS requirements for agriculture. The Big Horn, Sweetgrass Arch, and Wind River basins are all dominated by agricultural type waters, with multiple wells meeting irrigation water qualities.

TDS can be broken into subcategories based on specific irrigation and livestock requirements. Although the least conservative TDS values were used for the previous comparison, many less wells meet more stringent water quality requirements. For example, although 88% of the unconventional CBM wells meet the 10,000-mg/L criteria for livestock water, only 10% meet the satisfactory level preventing illness and mortality. Less than 1% of the conventional wells meet this satisfactory criterion. Although the TDS is acceptable in most wells for short periods of time, treating or blending water with a fresh water resource would be required to sustain this application.

Table 18. Suitability statistics for produced water for agricultural uses

			% of Wells in TDS Range	
Irrigation TDS Categories			**Conventional**	**Unconventional**
Class 1	Excellent	< 160	0 %	0 %
Class 2	Good	160 – 480	0 %	1 %
Class 3	Permissible	486 – 1,280	0 %	14 %
Class 4	Doubtful	1,286 – 1,920	1 %	14 %
Class 5	Unsuitable	> 1,920	99 %	71 %
Livestock Watering TDS Categories			**Conventional**	**Unconventional**
Level 1	Satisfactory	< 1,000	0 %	10 %
Level 2	Satisfactory, slight temporary illness	1,000 – 2,999	4 %	37 %
Level 3	Satisfactory for livestock, increased poultry mortality	3,000 – 4,999	5 %	15 %
Level 4	Reasonable for livestock, unsafe for poultry	5,000 – 6,999	3 %	12 %
Level 5	Unfit for poultry and swine, acceptable short term for livestock	7,000 – 10,000	5 %	14 %
Level 6	Not recommended	> 10,000	82 %	12 %

TDS concentration is not the only requirement specific for irrigation applications. SAR is as important as TDS when considering applications. Irrigation requirements for SAR can be split into four categories: low 1–9, medium 10–17, high 18–25, and very high > 26. Low SAR values may not be used on sodium sensitive crops; medium values require soil amendments such as gypsum; high values are generally unsuitable for continuous use; and very high values generally are unsuitable for use (Davis, Waskom et al. 2007). Figure 22 compares calculated SAR values for convention and unconventional wells to the aforementioned categories.

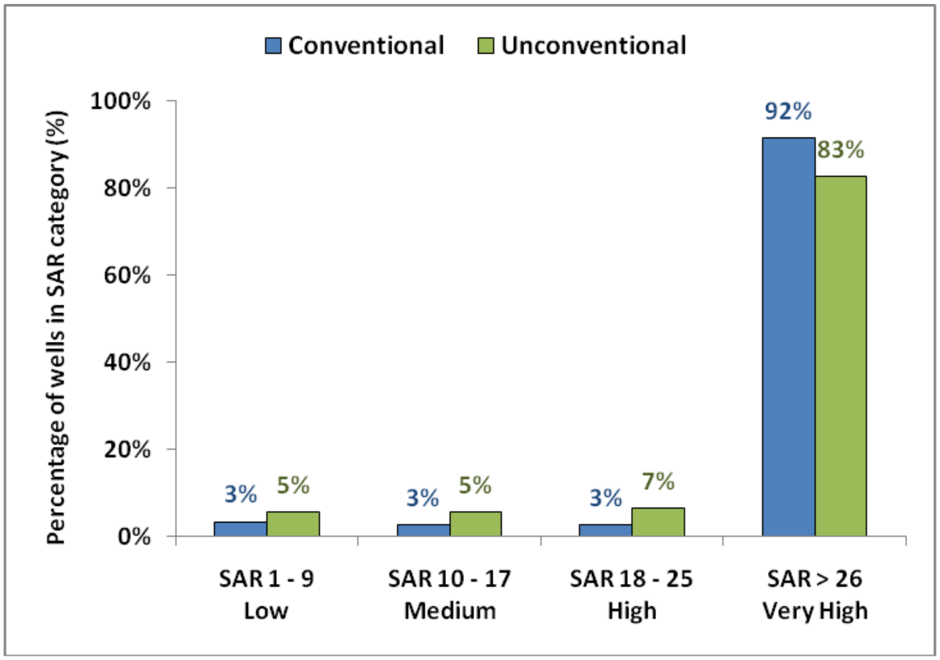


Figure 21. Conventional versus unconventional well distribution in the irrigation requirement categories for SAR.

Although 29% of CBM wells were suitable for irrigation based on TDS concentrations, only 10% meet the required low or medium SAR values. Conversely, although only 1% of the conventional wells met TDS requirements 6% meet the low or medium SAR criteria. Since SAR is a calculation of the ratio between sodium, magnesium, and calcium conventional wells with higher TDS, but also high calcium and magnesium concentrations, increase the relative amount of wells meeting SAR standards.

A similar figure for SAR distribution of wells among basins was created for figure 22. Utilizing SAR as the qualities for irrigation demonstrates that only the Sweetgrass Arch, Bighorn, Wind River and Powder River basins contain wells meeting the low or medium categorical value. The remainder of the basins contains mostly unsuitable waters for irrigation purposes. The mapping of these criteria is helpful to determine the geographic variation of not only water quality, but potential uses in the area. A combined prediction of wells meeting the full extent of concentrations for all constituents and parameters would be beneficial to targeting beneficial use applications in specific basins and areas.

Minor ions are regulated for a variety of types of beneficial uses. Table 19 denotes minor ions potentially present at concentrations that exceed beneficial use standards based on recorded concentration ranges for three common beneficial use applications—drinking water, livestock watering, and irrigation. Drinking water standards consider primary and secondary national maximum contaminate levels in evaluation of water quality constituents. Note that not all wells will exceed these standards; but by using the range of concentrations spanning over

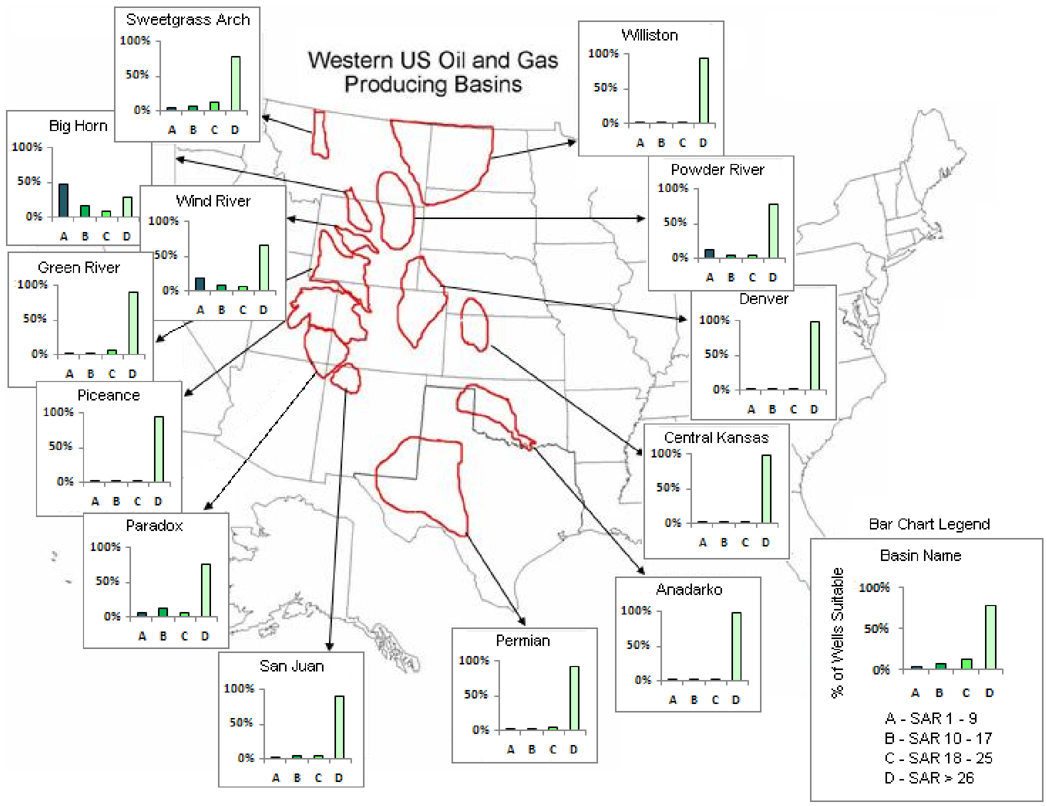


Figure 22. Western United States oil and gas basins: percentage of wells in SAR irrigation categories.

the maximum levels, there is a potential for wells to exceed standard requirements. Only beryllium (conventional) and antimony (unconventional) standards are not exceeded for drinking water within the range of recorded concentrations, table 19. For livestock watering, mercury is not exceeded in conventional wells; while aluminium, cobalt, and zinc are the only constituents not exceeded in unconventional wells. All other constituent levels are potentially exceeded for livestock watering including TDS, pH, and alkalinity as the recorded concentration ranges exceed standards.

TDS concentrations and SAR values exceed most standard requirements for beneficial use. To use these resources, more produced waters will require treatment. Treatment processes, particularly those focused on removing salt from the system to lower TDS concentration, concentrate rejected ions into a brine stream. Concentration of certain minor ions, such as heavy metals, challenges the easy disposal of a potentially hazardous waste stream. Metals also may accumulate in soils. Metals at low concentrations in produced water, continuously applied to irrigation fields or streams, may deposit metals into the subsurface. These metals may concentrate in the subsurface contaminating the soil and also may be transported into potable shallow ground water sources at concentrations exceeding standards for use. Concentrations of minor ions present in solution are important considerations for both treatment design and usage applications. The following section outlines a variety of treatment processes currently applied or applicable to treating this water composition to meeting standards for beneficial use applications.

Table 19. Constituents with the potential to be detected above requirements[1]

	Conventional			Unconventional		
Constituent List	**Drinking Water**	**Livestock Watering**	**Irrigation**	**Drinking Water**	**Livestock Watering**	**Irrigation**
Antimony	n/a	—	—	No	—	—
Aluminum	Yes	Yes	—	Yes	No	—
Arsenic	Yes	Yes	—	Yes	Yes	—
Barium	Yes	—	—	Yes	—	—
Beryllium	No	—	—	n/a	—	—
Boron	—	Yes	Yes	—	Yes	Yes
Cadmium	Yes	Yes	—	Yes	Yes	—
Chloride	Yes	—	Yes	Yes	—	Yes
Chromium	Yes	Yes	—	Yes	Yes	—
Cobalt	—	n/a	—	—	No	—
Copper	Yes	Yes	—	Yes	Yes	—
Fluoride	n/a	n/a	—	Yes	Yes	—
Iron	Yes	—	—	Yes	—	—
Lead	Yes	Yes	—	Yes	Yes	—
Manganese	Yes	—	—	Yes	—	—
Mercury	—	No	—	—	Yes	—
Nitrate ($N-N0_3$)	n/a	n/a	n/a	Yes	Yes	Yes
Selenium	n/a	n/a	—	Yes	Yes	—
Silver	Yes	—	—	Yes	—	—
Sodium	—	—	Yes	—	—	Yes
Strontium	—	—	—	—	—	—
Sulfate	Yes	Yes	Yes	Yes	Yes	Yes
Uranium	—	—	—	—	—	—
Vanadium	—	n/a	—	—	Yes	—
Zinc	Yes	Yes	—	Yes	No	—

[1] Considered with respect to the ranges provided in table 14.

7. Assessment of Technologies for Treatment of Produced Water

Because produced water may contain many different types of contaminants and the concentration of contaminants varies significantly, numerous types of treatment technologies have been proposed to treat produced water. Most often, an effective produced water treatment system will consist of many different types of individual unit processes used in series to remove a wide suite of contaminants that may not be removed with a single process. Organic and particulate removal, desalination, and disinfection are the major classifications of produced water treatment technologies.

A qualitative comparison of produced water treatment technologies is presented to provide an assessment of the benefits and limitations of each technology for produced water applications. The criteria used to compare the technologies are robustness, reliability, mobility, flexibility, modularity, cost, chemical and energy demand, and brine or residual disposal requirements.

- Robustness refers the ability of the equipment to withstand harsh environmental conditions, have high mechanical strength, and represents a technology in which the failure of an individual component does not significantly affect the overall performance of the technology.

- Reliability means that the technology will require minimal down time, can produce consistent water quality, and is not prone to failure.

- Mobility measures the ease with which the equipment can be moved from one site to another.

- Flexibility is the measure of the capability of the technology to accommodate a wide range of feed water qualities and to handle an upset in water quality without failure or reduced product water quality.

- Modularity refers to the ability to implement the technology as a unit process in a train of treatment technologies and the ability of ease with which the system can be modified to handle changing water volumes.

Based on industry research and communication with industry contacts, these criteria were deemed most important for produced water applications.

7.1 Organic, Particulate, and Microbial Inactivation/Removal Technologies

Organic chemical and particulate removal is most often required as a pretreatment step when desalination technologies must be employed to treat produced water. The technologies considered in this assessment are as follows: biological aerated filter, hydrocyclone, dissolved air flotation, adsorption, media filtration, oxidation, settling ponds, air stripping, surfactant modified zeolites, constructed wetlands, granular activated carbon, ultraviolet (UV) disinfection, and ceramic and polymeric micro- and ultrafiltration.

The technologies were evaluated based on the whether they are an emerging technology or an established technology and whether they have previously employed for treatment of produced water. The size and type contaminants removed by the technology and the overall process recovery are presented. The technologies were then compared qualitatively based on the following criteria: chemical and energy requirements, maintenance requirements, ease of operation, cost, robustness, reliability, flexibility, mobility, modularity, volume of residuals generated, and the size of the plant or footprint.

The qualitative technology assessment and comparison is presented in tabular format; see table 20. A very brief summary of the current status of the technologies listed in the table is provided below; however, for more detailed information on each technology, please refer to other sources.

7.1.1 Biological Aerated Filters

The term biological aerated filter (BAF) refers to a class of technologies, including fixed film and attached growth processes, roughing filters, intermittent filters, packed bed media filters, and conventional trickling filters. A BAF consists of permeable media, such as rocks, gravel, or plastic media. The water to be treated flows downward over the media and, over time, generates a microbial film on the surface of the media. The media facilitates biochemical oxidation/removal of organic constituents. This is an aerobic process, and aerobic conditions are maintained by pumps and fans in the system. The thickness of the microbial layer continues to increase as the filter is used. Eventually, the microbial layer becomes thick enough that part of the slime layer becomes anaerobic and the microbial layer begins to slough off in the filter effluent (USEPA 1991). Media should have high a surface area per unit volume, be durable, and inexpensive. The type of media often is determined based on what materials are available at the site. Media can be field stone or gravel, and each stone should be between 1–four inches in diameter to generate a pore space that does not prohibit flow through the filter and will not clog when sloughing occurs (EPA 1980).

BAF can remove oil, suspended solids, ammonia, and nitrogen, chemical oxygen demand, biological oxygen demand, iron, manganese, heavy metals, soluble

Table 20. Comparison of organic contaminant and particulate removal technologies for treatment of produced water

Technology	Emerging Technology	Previously Employed for Produced Water	Overall Process Recovery (%)	Contaminants removed	Organic Matter Removal	Particulate Removal (min size removed)	Heavy Metals	Low Chemical Demand	Low Energy Demand	Minimal Maintenance	Ease of Operation	Minimal Posttreatment Requirement	Low Cost	Robustness[1]	Reliability[2]	Flexibility[3]	Mobility[4]	Modularity[5]	Waste Disposal Requreiments	Small Footprint
Biological aerated filters	No	Yes	100%	oil, nitrogen, COD, BOD	++	++	+	+++	+++	+++	+++	+	+++	+++	+++	+++	-	+	++	-
Hydroclone	No	Yes	98%	particulates	NA	5-15 um	-	+++	+	+++	+++	+++	+	+++	+++	+	+	-	++	++
Centrifuge	No	Yes	98%	particulates	NA	2 um	-	+++	+	+++	+++	+++	+	+++	+++	+	+	-	++	++
API gravity separator	No	Yes	98%	particulates	NA	150 um	-	+++	+	+++	+++	+++	+	+++	+++	+	+	-	++	++
Corrugated plate separator	No	Yes	98%	particulates	NA	40 um	-	+++	+	+++	+++	+++	+	+++	+++	+	+	-	++	++
Dissolved air/gas flotation	No	Yes	100%	TOC, oil and grease, particulates, hydrogen sulfide	+++	3-25 um	-	+++	++	++	+++	+++	++	++	+++	+	+	-	++	++
Adsorption/media filtration	No	Yes	98%	particulates, BTEX, oil, TOC, iron, manganese, heavy metals	+++	5 um	++	+++	+++	++	+++	+++	++	+++	+++	+++	+++	+++	++	++
Oxidation	No	Yes	100%	manganese, iron, sulfur, color, odor, synthetic organic compounds	++	NA	++	++	++	++	++	+++	++	+++	+++	+++	+++	+++	+++	+++
Settling pond	No	Yes	100%	particulates, iron, manganese	NA	+++	++	+++	+++	+++	+++	+++	+++	+++	+++	++	-	-	+++	-
Air stripping	No	Yes	100%	TOC, volatile organics	+++	NA	-	+++	++	++	++	+++	++	+++	+++	+	++	+	+++	++
Surfactant modified zeolite vapor phase bioreactor	Yes	Yes	95%	TOC, volatile organics	+++		++	++	+++	+++	+++	+++	ND	ND	ND	ND	ND	+++	++	++
Constructed wetlands	No	Yes	100%	TOC, dissolved organic compounds (increased calcium and slighly increased TDS)	+++	+++	++	+++	+++	+++	+++	+++	+++	+++	+++	++	-	-	+++	-
Granular activated carbon fluidized bed reactor	No	Yes	100%	TOC, volatile organics	+++	++	+++	+++	+++	++	+++	+++	+	+++	+++	+++	+++	+++	+	+++
UV disinfection	No	Yes	100%	inactivation of microbial contaminants	NA	NA	NA	+++	+	+	+++	+++	+	+	+++	+++	+++	+++	+++	+++
Ceramic MF/UF membrane	Yes	Yes	85 to 95%	particulates, dissolved (with coagulation) and suspended organics, biological contaminants	++	0.01 um	-	++	++	++	++	+++	++	+++	++	++	+++	+++	++	++
Polymeric MF/UF membrane	No	Yes	85 to 95%	particulates, dissolved (with coagulation) and suspended organics, biological contaminants	++	0.01 um	-	++	++	++	++	+++	++	+	++	++	+++	+++	++	++

Legend: Excellent | Good | Fair | Poor

Notes:
[1]Robust: Ability of equipment to withstand harsh conditions, mechanical strength, able to accommodate multiple design criteria, failure of an individual. component does not significantly affect the overall performance
[2]Reliable: Minimal equipment downtime, technology not prone to failure and produces consistent product water quality.
[3]Mobile: Easily moved from one site to another.
[4]Flexible: Able to accommodate a wide range of water quality.
[5]Modularity: Ability to implement technology as a unit process in a treatment train, and accommodate changing influent volumes.
ND - No data
NA - Not applicable
1 bbl = 42 gallons

organics, trace organics, and hydrogen sulfide. Iron and manganese removal in BAFs is mainly due to chemical oxidation rather than a biological process. Since BAFs do not remove dissolved constituents, however, high concentrations of salts can decrease the effectiveness of this technology due to salt toxicity effects. At chloride levels below 6,600 mg/L, there is no diminished contaminant removal with BAFs; and at 20,000 mg/L chloride levels, there will be a reduction in slime growth and BOD removal (Ludzack and Noran 1965). This technology can be used to treat water with much greater organic contaminant concentrations than typically found in CBM produced water.

BAF is a well established technology and has been used for produced water treatment for many years (Doran 1997; Su, Wang et al. 2007). Because of this technology's ability to remove oil and grease, it has been primarily used for oilfield produced water treatment (Su, Wang et al. 2007). Informal versions of BAFs require minimal equipment and can be made by flowing water over rock beds. These types of BAFs also have been used in CBM produced water treatment for iron removal and suspended solids removal.

BAF is most effective on waters with chloride levels below 6,600 mg/L (Ludzack and Noran 1965), oil concentrations less than 60 mg/L; COD less than 400 mg/L, and BOD less than 50 mg/L. The maximum feed water constituent concentration for which this technology can be employed depends on desired removal and target water quality requirements. Removal capability of BAFs is dependent on the hydraulic loading rate on the filter and the raw water quality. The following are approximate removal capabilities of this technology:

- 60 to 90% nitrification
- 50 to 70% total nitrogen (USEPA 1991; Ball 1994)
- 70 to 80% oil (Su, Wang et al. 2007)
- 30 to 60% COD (Su, Wang et al. 2007)
- 85 to 95% BOD (Su, Wang et al. 2007)
- 75 to 85% suspended solids (Su, Wang et al. 2007)

There is nearly 100% water recovery from this process. The residuals generated are from the settling of the microbial layer that sloughs off the media. The residuals generation, which is highly dependent on the water quality, is approximately 0.4–0.7 pounds of dry solids per 1,000 gallons of water treated (for wastewater treatment) (Ball 1994). Solids disposal is required for the sludge that accumulates in the sedimentation basins, and solids disposal can account for up to 40% of total cost of technology.

This technology has a long expected lifespan. BAFs require upstream and downstream sedimentation; therefore, they have a large footprint and are not very mobile or modular. Very little monitoring is required, and occasional emptying of sedimentation ponds is required; the use of this technology does not require skilled operators. BAF can easily accommodate highly varying water quantity and quality. There is little down time or need for maintenance. Electricity is required for pumps and for fans for aeration and circulating water. The majority of the overall cost of this technology is capital, and operation and maintenance (O&M) costs are very low.

Primary sedimentation should be employed upstream of BAFs to allow the full bed of the filter to be used for removing nonsettling, colloidal, and dissolved particles if the water requires a large degree of contaminant removal. Sedimentation also should follow BAFs to remove the microbial layer that sloughs off of the filter. In addition to pumps and fans for aeration, other equipment such as distribution nozzles may be required. The estimated energy demand for BAFs is 1–4 kilowatt-hours per day (kWh/day). No chemicals are necessary for this treatment process (USEPA 1980).

7.1.2 Hydrocyclone

Hydrocyclones are used to separate solids from liquids based on the density of the materials to be separated. Hydrocyclones normally have a cylindrical section at the top where the liquid is fed tangentially and a conical base. The angle of the conical section determines the performance and separating capability of the hydrocyclone. Hydrocyclones can be made from metal, plastic, or ceramic and have no moving parts. The hydrocyclone has two exits—one at the bottom, called the underflow or reject for the more dense fraction and one, called the overflow or product at the top for the less dense fraction of the original stream (K. Wagner 1986).

Hydrocyclones can be used to separate liquids and solids or liquids of different densities. Hydrocyclones can be used to remove particulates and oil from produced water. Depending on the model of hydrocyclone employed, they can remove particles in the range of 5–15 micrometers (µm) (NETL). Hydrocyclones will not remove soluble oil and grease components (T. Hayes 2004).

Hydrocyclones have been used extensively to treat produced water and are marketed by numerous companies for produced water treatment (Veil ; Sinker 2007). Hydrocyclones were used to treat fracturing brine in the Barnett Shale play (Burnett 2005). In this research study, hydrocyclones were used in combination with organo-clays as a pretreatment to reverse osmosis.

Hydrocyclones can be used to treat water with high solids and organic chemical concentrations and can reduce oil and grease concentrations to 10 ppm. High product water recovery is possible with this technology. The waste generated from a hydrocyclone is a slurry of concentrated solids. This is the only residual that requires disposal.

Hydrocyclones do not require any pre- or post-treatment. The hydrocyclone itself does not require any chemicals or energy; however, a forwarding pump may be necessary to deliver water to the hydrocyclone or to recover pressure lost through the hydrocyclone. The hydrocyclone is the only piece of equipment necessary. There are no energy requirements unless the plant setup requires a forwarding pump to deliver water to the hydrocyclone. Depending on the size and configuration of the hydrocyclone, a large pressure drop can occur across the hydrocyclone.

Hydrocyclones have a long operational life due to the fact that they have no moving parts; however, they may suffer from abrasion when treating water with high particulate concentrations. Solid material can block the inlet, and scale formation can occur requiring cleaning; however, typical cleaning is minimal.

7.1.3 Flotation

Flotation is a process in which fine gas bubbles are used to separate small, suspended particles that are difficult to separate by settling or sedimentation. Gas is injected into the water to be treated, and particulates and oil droplets suspended in the water are attached to the air bubbles, and they both rise to the surface. As a result, foam develops on the surface, which is commonly removed by skimming. The dissolved gas can be air, nitrogen, or another type of inert gas. Dissolved air/gas flotation also can be used to remove volatile organics and oil and grease. Dissolved air flotation units have been widely used for treatment of produced water (Casaday 1993; Hayes 2004; Çakmakce, Kayaalp et al. 2008).

Gas flotation technology is subdivided into dissolved gas flotation (DGF) and induced gas flotation (IGF). The two technologies differ by the method used to generate gas bubbles and the resultant bubble sizes. In DGF units, gas (usually air) is fed into the flotation chamber, which is filled with a fully saturated solution. Inside the chamber, the gas is released by applying a vacuum or by creating a rapid pressure drop. IGF technology uses mechanical shear or propellers to create bubbles that are introduced into the bottom of the flotation chamber (Veil). Coagulation can be used as a pretreatment to flotation.

The efficiency of the flotation process depends on the density differences of liquid and contaminants to be removed. It also depends on the oil droplet size and temperature. Minimizing gas bubble size and achieving an even gas bubble distribution are critical to removal efficiency (Casaday 1993). Flotation works well in cold temperatures and can be used for waters with both high and low TOC concentrations. It is excellent for removing natural organic matter (NOM) and can be used to treat water containing TOC, oil and grease, and particulates < 7% solids (Burke).

It is not ideal for high temperature feed streams.

Dissolved air flotation (DAF) can remove particles as small as 25µm. If coagulation is added as pretreatment, DAF can remove contaminants 3–5 µm in size (NETL). In one reported study, flotation achieved an oil removal of 93%

(ALL 2003). Flotation cannot remove soluble oil constituents from water. Product water is nearly 100% with this technology.

Because flotation involves dissolving a gas into the water stream, flotation works best at low temperatures. If high temperatures are present, a higher pressure is required to dissolve the gas in the water.

Energy is required to pressurize the system to dissolve gas in the feed stream. Coagulant chemical may be added to enhance removal of target contaminants. Chemical coagulant and pumping costs are the major components of O&M costs for flotation. Treatment costs are estimated to be $0.60 per cubic meter (Çakmakce, Kayaalp et al. 2008). Solids disposal will be required for the sludge generated from flotation.

7.1.4 Adsorption

Adsorption can be accomplished using a variety of materials, including zeolites, organoclays, activated alumina, and activated carbon. Chemicals are not required for normal operation of adsorptive processes. Chemicals may be used to regenerate media when all active sites are occupied. Periodically, the media is backwashed to remove large particulates trapped between the voids in the media. Typically, these processes can be gravity fed and do not require an energy supply, except during backwash.

Adsorbents are capable of removing iron, manganese, total organic carbon, BTEX compounds, heavy metals, and oil from produced water. Adsorption is generally utilized as a unit process in a treatment train rather than as a stand-alone process. The adsorbent can be easily overloaded with large concentrations of organics, so this process is best used as a polishing step rather than as a primary treatment process (Veil). Adsorption is capable of removing over 80% of heavy metals (Spellman 2003) and can accomplish nearly 100% product water recovery.

Media usage rate is one of the main operational costs for adsorptive processes and may require frequent replacement or regeneration depending on media type and feed water quality. When all active sites of the adsorptive material have been consumed, the material must either be regenerated or disposed of. Regenerating the materials will result in a liquid waste for disposal. Solid waste disposal is necessary when the material needs to be replaced entirely.

There will be a pressure loss incurred across the filter; however, depending on the plant configuration, this may not require any additional pumps. Pumps will be necessary to backwash the filters. Adsorption is best used as a polishing step to avoid rapid usage of adsorbent material. Waste disposal is required for spent media or the waste produced during regeneration of the media.

7.1.5 Media Filtration

Filtration can be accomplished using a variety of different types of media: walnut shell, sand, anthracite, and others. Filtration is a widely used technology for produced water, especially walnut shell filters for removing oil and grease. There are many vendors available that market filtration technologies specifically for produced water.

Filtration does not remove dissolved ions, and performance of filters is not affected by high salt concentrations; therefore filtration can be used for all TDS bins regardless of salt type. Filtration can be used to remove oil and grease and TOC from produced water with greater than 90% oil and grease removal. Removal efficiencies can be improved by employing coagulation upstream of the filter. Nearly 100% water recovery is achieved with filtration; some filtrate may be used for backwashes.

Minimal energy is required for these processes. Energy is required for backwashing the filter. Coagulant may be added to the feed water to increase particle size and enhance separation. Chemicals may be required for media regeneration. There will be a pressure loss incurred across the filter; however, depending on plant configuration, this may not require any additional pumps. Pumps will be necessary to backwash the filters. Solid waste disposal is required for spent media or the waste produced during regeneration of the media.

7.1.6 Oxidation

Chemical oxidation treatment can be used to remove iron, manganese, sulphur, color, tastes, odor, and synthetic organic chemicals. Chemical oxidation relies on oxidation/reduction reactions, which consist of two half-reactions: the oxidation reaction in which a substance loses or donates electrons, and a reduction reaction in which a substance accepts or gains electrons. Oxidation and reduction reactions will always occur together since free electrons cannot exist in solution and electrons must be conserved (AWWA 2005). Oxidants commonly used in water treatment applications include chlorine, chlorine dioxide, permanganate, oxygen, and ozone. The appropriate oxidant for a given application depends on many factors including raw water quality, specific contaminants present in the water, and local chemical and power costs (AWWA 2005). Chemical oxidation is well established, reliable, and requires minimal equipment (Reclamation 2003). Oxidation can be employed to remove organics and some inorganic compounds (i.e., iron and manganese) from produced water. The removal or oxidation rate may be controlled by applied chemical dose and contact time between oxidants and water with 100% feed water recovery.

Chemical metering is required. Energy usage usually accounts for approximately 18% of the total O&M for oxidation processes coupled with high chemical cost. Critical components of the oxidation process are the chemical metering pumps. Chemical metering equipment can have a life expectancy of 10 years or greater. Periodic calibration and maintenance of chemical meter pumps are required.

Capital costs can be near to $0.01 per gallon per day (gpd), and O&M costs can be approximately $0.05 per kilogallon (kgal) (>$0.01 per bbl). No waste is generated from oxidation processes.

No pretreatment is required for oxidation. Solid separation post-treatment might be required to remove oxidized particles. Chemical metering pumps are required for dosing. Some equipment may be required to generate the oxidant onsite, and chemical costs may be high.

7.1.7 Settling

Settling can be achieved using a pond or a basin. In this process, particulates are removed by gravity settling. Settling ponds require a large footprint and environmental mitigation to protect wildlife. The volume of the settling basin required depends on the hydraulic residence time required for the desired level of contaminant removal. Settling ponds most likely will be used in combination with other treatment processes. There are no chemical requirements, but chemicals can be used to enhance sedimentation. Infrastructure requirements include liners. Settling ponds are used to remove large particulates from water sources. The degree of particle removal and size of particles removed depends on the water detention time in the pond.

7.1.8 Air Stripping

Air stripping primarily is used for removing volatile organic chemicals (VOCs), oxidizing contaminants such as iron and manganese, improving taste, or removing odor. Air stripping is an USEPA BAT for some organic chemicals (VOCs) including benzene, toluene, xylene, tri/tetrachloroethylene, trihalomethanes, vinyl chloride and many others.

Air stripping is the process of transferring a contaminant from the liquid phase to the gas phase. In the air stripping process, air and water are contacted in a packed column designed to maximize the contact surface area between the water and air. Air stripping performance depends on factors such as:

- Characteristics of the volatile material (partial pressure, Henry's constant, gas-transfer resistance, etc.) (AWWA 2005, Water Treatment Plant Design)
- Water and ambient air temperature
- Turbulence in gaseous and liquid phases
- Area-to-volume ratio
- Exposure time

Appropriate design of the packed column is necessary to ensure the desired level of contaminant removal based on the process operating temperature and the

Henry's Constant of the target contaminant**.** Scaling can occur when calcium exceeds 40 mg/L, iron exceeds 0.3 mg/L, magnesium exceeds 10 mg/L, and manganese exceeds 0.05 mg/L. Biological fouling also may occur depending on the feed water quality (U.S. Army Corps of Engineers 2001.

Spray aerators dissipate water in a vertical or inclined angle breaking the water into small drops. Multiple-tray aerators use uniquely designed trays to increase the surface area for aeration. Cascade and cone aerators allow water to flow in a downward direction over a series of baffles or pans (AWWA 2005).

There are two main types of pressure aerators—one that sprays water on top of a tank that is constantly supplied with compressed air and one that injects compressed air directly into a pressurized pipeline adding fine air bubbles into the flowing water (AWWA 2005).

Diffusion type aerators are similar to pressure aerators but are designed to allow air bubbles to diffuse upward through the tank of water to help produce turbulence and mixing (AWWA 2005).

Mechanical aerators use a motor driven impeller to achieve air mixing. Occasionally, it also is used in combination with an air injection device (AWWA).

Air stripping is a proven and widely used technology**,** able to be a low profile addition to a treatment process**,** with a high contaminant removal efficiency (> 99%) (U.S. Army Corp of Engineers, 2001). Air stripping systems must be properly designed to provide the proper air and water balance to prevent flooding or excess air flow (U.S. Army Corp of Engineers, 2001); scaling, and biological fouling may impact the performance of the air stripper.

7.1.9 Surfactant Modified Zeolite Vapor Phase Bioreactor

Zeolites are naturally occurring hydrated aluminosilicates with a large surface area. Because of the natural shape and size of zeolites, they are suitable for flow through applications or media for fluidized beds. Treatment of zeolites with cationic surfactants changes the surface chemistry of the zeolites, allowing them to absorb nonpolar organic solutes. These materials also are capable of cation or anion exchange; however, their usefulness as a desalination technology is questionable.

A substantial amount of research has been conducted on using surfactant modified zeolites for organic chemical removal from produced water. This research suggests that this process is a promising produced water treatment technology (Ranck, Bowman et al. ; Bowman 2003; Altare, Bowman et al. 2007).

7.1.10 Constructed Wetlands

One of the major benefits of constructed wetlands is that these systems have low construction and operating costs. The estimated cost of constructed wetlands treatment is $0.01 to $0.02 per bbl. However, these systems are not efficient and the treatment rate is slow compared to other technologies. The average lifespan of a constructed wetland is approximately 20 years (Shutes, 2001).

A study was conducted to look at a hybrid reverse osmosis (RO) constructed wetland system for produced water treatment. This study showed that, while RO removes the majority of organic and inorganic constituents, it does not sufficiently remove dissolved organic compounds. These compounds were removed by the constructed wetland. Toxicity tests were conducted with a few different types of bacteria. All species of bacteria experienced a greater survival rate with water that had been passed through the constructed wetland. Many water quality parameters were increased following the wetland construction, such as TDS and calcium. SAR was decreased. Boron removal was not addressed in this study, and mention was made that for irrigation, the levels of boron in the treated water may be too high (Murry-Gulde 2003).

7.1.11 Granular Activated Carbon

Granular activated carbon (GAC) can be used to remove the following contaminants from produced water: mercury, cadmium, natural organic matter, BTEX compounds, synthetic organic chemicals—specifically benzo(a)pyrene, di(2-ethylhexyl)adipate, di(2-ethylhexyl)phthalate, hexachlorobenzene, dioxin, and radionuclides.

For source water with a large amount of bacteria, pretreatment in the form of filtration and disinfection prior to carbon treatment may be required. Filtration prior to GAC also may be required when dealing with high TSS waters.

GAC has an extremely large amount of adsorption surface area, generally around 73 acres per pound (acre/lb) (650 square meters per gram [m^2/gram]) to 112 acres/lb (1,000 m^2/gram) (AWWA, 2005, Water Treatment Plant Design). GAC is made of tiny clusters of carbon atoms stacked upon one another and is produced by heating the carbon source (coal, lignite, wood, nutshells, or peat) in the absence of air, which produces a high carbon content material. The adsorption isotherm for carbon and the source water will determine the total contaminant removal capacity.

The physical removal of a contaminant by adsorption on to the carbon surface is done in the mass transfer zone. Breakthrough is defined as the point at which the concentration of a contaminant in the effluent adsorption unit exceeds the treatment requirement (AWWA, 2005, Water Treatment Plant Design). This breakthrough time is important to note so that treatment goals are not exceeded and that backwashing rates can be optimized. Backwashing a GAC system follows the same general procedures as a conventional granular gravity filter system. The GAC typically will expand up to 75–100% in volume, but it may be only as much as 50% (AWWA, 2005, Water Treatment Plant Design). Empty bed contact time is the volume of the empty bed divided by volumetric flow rate of water through the carbon. A typical bed depth can contain up to 50% freeboard excess capacity beyond the designed capacity to allow for bed expansion during backwashing. Surface loading rates, or the volume of water that is passing though a given area, typically range from 2–6 gallons per minute per square foot (5–15 meters per hour) (AWWA, 2005, Water Treatment Plant Design).

Biological growth can be desirable within GAC, which results in what is known as biologically active carbon (BAC). BAC can be beneficial by removing assimilable organic carbon (AOC) and other biodegradable compounds. If it is intended to have BAC, the GAC filters typically are preceded by ozonation that breaks down the organic carbon into a more assimable form. This process can enhance the overall contaminant removal of the GAC process. However, the biological growth needs to be controlled with frequent backwashing (once every 5 days). The use of chlorine prior to the beds will not prevent growth, will produce DBPs that take up more GAC adsorption sites, and will make the carbon more brittle. Disinfection is recommended after the GAC filters to prevent biological growth in the distribution system and to achieve the highest removal of AOC within the plant. If biological growth is not controlled and anaerobic conditions develop, odor problems will occur, and undesirable organisms will begin to grow. Significant head loss and shorter filter runs can occur with too much biological growth. These two factors will be impacted even with beneficial biological growth and should be accounted for in GAC design (AWWA, 2005, Water Treatment Plant Design).

Regular reactivation or replacement of carbon media is required. If a GAC plant is large enough, regeneration can be done onsite, but it is typically performed off site. Onsite regeneration is typically not effective unless the carbon exhaustion rate is larger than 910 kg/day (AWWA, 2005, Water Treatment Plant Design). Reactivation frequency is dependent on contaminant type, concentration, rate of water usage, and type of carbon used. Careful monitoring and testing to ensure contaminant removal is achieved is necessary around the time of startup and breakthrough. Flushing is required if the carbon filter is not used for several days, and regular backwashing may be required to prevent bacterial growth (AWWA, 2005, Water Treatment Plant Design).

Disposal of spent media is typically the responsibility of the contractor providing the media replacement or reactivation service. Backwash/flush water disposal is a required waste stream if it is included in the design of the filter (AWWA, 2005, Water Treatment Plant Design).

Benefits:

- Well established treatment technique
- Suitable for many organic chemicals, NOM, and trihalomethanes (THMs).

- Suitable for home use.
- Able to improve taste and odor and removes chlorine.

Limitations:

- Relatively expensive O&M cost for regeneration.
- Effectiveness is based on contaminant type, concentration, rate of water usage, and type of carbon used.
- Requires careful monitoring when nearing breakthrough times.

7.1.12 Ultraviolet Disinfection

Ultraviolet (UV) radiation disinfection is a popular form of primary disinfection because of its ease of use, no need of chemicals, and no formation of disinfection byproduct (DBP). Water is pumped through a UV reactor, which is equipped with an array of UV lamps providing disinfection dosages of 30–50 megajoules per square centimeter. As pathogens path through the reactor, they are inactivated. They are exposed to the UV light for a predetermined period of time, depending on the desired level of disinfection. UV reactors typically are closed channel for potable water treatment and are installed in open channel for wastewater treatment. There are several types of UV lamps, with low pressure-high output and medium pressure mercury vapor lamps being the most commonly used (Reclamation 2003). The lamps are housed inside of quartz lamp sleeves in the reactor to protect the lamp from breaking.

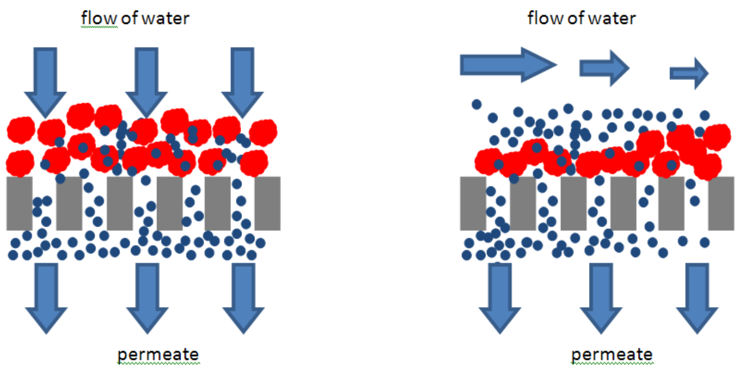
The mechanism of UV disinfection is inactivation through UV damage of the microorganism's deoxyribonucleic acid (DNA) and/or ribonucleic acid (RNA). Removal of suspended solids from the feedwater to UV is important to avoid shielding of microorganisms from the UV by suspended solids. This phenomenon is called "shadow effect." UV disinfection does not provide a disinfectant residual. Therefore, addition of chlorine or chloramine as a secondary disinfectant might be required (Reclamation 2003).

Disinfection is typically the last treatment step in most water treatment facilities, most suspended solids and/or dissolved ions, if any, should have been removed prior to disinfection. No waste is generated in UV disinfection. UV equipment including lamps must be properly checked to ensure they are working according to technical specifications. The lamps age with time and require periodic replacement. A cleaning system also must be installed on the lamp sleeves, because the sleeve itself reacts with compounds in water and would decrease the UV transmittance if they are not cleaned (Reclamation 2003). This disinfection has a high capital cost; with the USEPA estimated cost as $0.13 per gpd.

7.1.13 Microfiltration/Ultrafiltration

Microfiltration (MF) has the largest pore size (0.1–3 µm) of the wide variety of membrane filtration systems. Ultrafiltration (UF) pore sizes range from 0.01–0.1 µm. In terms of pore size, MF fills in the gap between ultrafiltration and granular media filtration. In terms of characteristic particle size, the MF range covers the lower portion of the conventional clays and the upper half of the range for humic acids. This is smaller than the size range for bacteria, algae, and cysts, and larger than that of viruses. MF also typically is used for turbidity reduction and removal of suspended solids, *Giardia*, and *Cryptosporidium*. UF membranes are used to remove viruses, color, odor, and some colloidal natural organic matter (Technologies 2008). Both processes require low transmembrane pressure (1–30 pounds per square inch [psi]) to operate, and both now are used as a pretreatment to desalination technologies such as reverse osmosis, nanofiltration, and electrodialysis but cannot remove salt themselves (Reclamation 2003).

MF membranes can operate in either cross-flow separation as shown in figure 23 and also dead-end filtration where there is no concentrate flow. There are also two pump configurations, either pressure driven or vacuum-type systems.



a) Dead-End b) Cross-flow

Figure 23. Dead-end versus cross flow filtration.

Pressure driven membranes are housed in a pressure vessel, and the flow is fed from a pump. Vacuum-type systems are membranes submerged in nonpressurized tanks, and product water is extracted by a vacuum pump on the product side. Typical recoveries can range from 85–95% (AWWA 2005). Flux rates range from 20–100 gallons per day per square foot depending on the application. Backwash usually is used to clean the membranes, and it is carried out for short durations (3–180 seconds) in relatively frequent intervals (5 minutes to several hours) (AWWA 2005). The frequency and duration of backwash depend on the specific application. A clean in place (CIP) also can be performed as a periodic major cleaning technique. Typical cleaning agents are sodium hypochlorite, citric acid, caustic soda, and detergents. They can be initiated manually and automatically controlled. CIP is initiated when backwashing and chemically enhanced backwash are not effective in restoring desirable performance (Reclamation 2003).

Factors affecting membrane selection are:

- Cost
- Percent recovery
- Percent rejection
- Raw water characteristics
- Pretreatment

Factors affecting performance are:

- Raw water characteristics
- Pressure
- Temperature
- Regular monitoring and maintenance

A self-backwashing 100-μm strainer is often used to protect the membranes and moderate particulate loading. Depending on the raw water quality, a coagulant may be added to form pin-sized floc and help improve rejection (Reclamation 2003).

7.1.13.1 Ceramic MF/UF Membrane

Ceramic UF and MF membranes are made from oxides, nitrides, or carbides of metals such as aluminum, titanium, or zirconium (Mulder 2003). Ceramic membranes are much more resilient than polymeric membranes and are mechanically strong, chemically and thermally stable, and can achieve high flux rates. Typically, a tubular configuration is used with an inside-out flow path, where the feed water flows inside the membrane channels and permeates through the support structure to the outside of the module. These membranes typically are comprised of at least two layers—a porous support layer and a separating layer.

Ceramic membranes are capable of removing particulates, organic matter, oil and grease, and metal oxides. Ceramic membranes alone cannot remove dissolved ions and dissolved organics. Precoagulation, injection of a chemical coagulant upstream from the membrane, improves removal efficiencies of dissolved organic carbon and smaller particulates. As with conventional UF and MF, a strainer or cartridge filter is necessary as pretreatment for ceramic membranes.

Numerous research studies have been conducted on using ceramic membranes to treat oil-containing wastewater and produced water (Faibish and Cohen 2001; Faibish and Cohen 2001; Konieczny, Bodzek et al. 2006; Lobo, Cambiella et al.

2006; Gutierrez, Lobo et al. 2008). These research studies have shown that ceramic membranes perform better than polymeric membranes on oil-containing waters. Ceramic membranes also have been employed commercially to treat oil produced water (Wallace 2005). Ceramic membranes are employed as part of a large treatment train consisting of a multiple unit process at the Wellington Water Works to treat oilfield produced water.

Energy requirements for ceramic membranes are lower than those required for polymeric membranes. Infrastructure requirements for ceramic membranes are similar to other membrane processes and include a break tank for the feed water, a feed pump, a rack for holding the membrane modules, a chemical metering system if necessary, a tank for the filtrate water, and a pump and valves for the backwash and cleaning systems.

Ceramic membranes have a higher capital cost than polymeric membranes. The use of ceramic membranes is increasing as more research and pilot studies are conducted. The capital cost of ceramic membranes will continue to decrease as they become a more widely used technology. Ceramic membranes do require frequent backwashes; backwash waste will require disposal. If ceramic membranes are operated in a cross-flow mode, then there will be a residual process stream requiring disposal.

6.1.11.2 Polymeric MF/UF Membrane

Polymeric MF/UF membranes are made from materials like polyacrylonitrile (PAN) and polyvinylidene (PVDF). Because there is a large market for polymeric ultrafiltration membranes, there are many vendors and suppliers for these membranes. They also are relatively inexpensive. Typically, package systems are purchased and installed by the vendor.

An important consideration for polymeric MF/UF membranes is integrity testing to ensure that the membrane is not damaged and is operating properly. Typically, the filtrate turbidity is monitored to give a rough indication of membrane integrity. Membrane integrity can be tested through a pressure decay test. In this test, pressurized air is applied to the membranes at a pressure less than would cause the air to flow through the membrane, and the pressure decay is measured. Regular monitoring of membrane performance is necessary to ensure that the membrane system is operating at the most effective loading rate and backwash regime. Membrane life typically is estimated at 7+ years with manufacturer warranties covering 5 years in municipal applications.

Product water is free of suspended solids. DOC removal is approximately 10%. Nearly all nondissolved organic carbon is removed, with 95% hydrocarbon removal—85–100% depending on feed water quality and mode of operation (dead-end versus crossflow).

Waste includes pretreatment waste, backwash flow, retentate flow (if applicable), and CIP waste. Waste streams are either discharged to the sewer or treated if discharging to surface waters. Waste streams being discharged to surface waters typically are processed for turbidity removal through settling ponds or other treatment systems. CIP waste is neutralized and usually combined with the rest of the waste.

Capital cost for polymeric UF systems vary based on the size of the plant and feed water quality. Approximate capital costs will be near $1–2 per gpd, and O&M costs will be approximately $1–2 per kgal.

Bierle et al. performed a three-pass UF membrane pilot study to treat produced water at a temperature of 130 degrees Fahrenheit (°F) to reduce the total organic carbon concentration of the produced water from 29 mg/L to 11.9 mg/L (Bierle).

7.2 Desalination Technologies

Desalination technologies are necessary to lower the total dissolved solids concentration and the concentration of ions that are too high for the desired beneficial use of co-produced water. Desalination technologies fall into the following categories: membrane, thermal, and alternative technologies. Desalination technologies, combined together and called hybrid technologies, are often employed to reduce the energy cost of the process or to enhance the product water recovery. The following membrane processes were evaluated: reverse osmosis, nanofiltration, and electrodialysis (ED). Hybrid membrane processes considered are two pass nanofiltration, dual RO with chemical precipitation, dual RO with HERO™, dual RO with seeded slurry precipitation, and high efficiency electrodialysis. The thermal desalination technologies included in this report are: membrane distillation, multistage flash distillation, multieffect distillation, vapor compression, and freeze-thaw evaporation. Commercial processes evaluated are as follows: CDM HERO process, Veolia OPUS, Altela Rain, and 212 Resources.

The technologies were evaluated based on the whether they are an emerging technology or an established technology and whether they previously have been employed for treatment of produced water. The TDS range of applicability of these technologies and their salt rejection and product water recoveries are also presented. Specific sodium, organic, and heavy metal rejection capabilities are also presented. The technologies then were compared qualitatively based on the following criteria: pretreatment requirements, chemical and energy requirements, maintenance requirements, ease of operation, cost, robustness, reliability, flexibility, mobility, modularity, volume of residuals generated, and the size of the plant or footprint.

The qualitative technology assessment and comparison are presented in tabular format, see table 21. A very brief summary of the current status of each technology is described below; however, for more detailed information and a description of the technology, please refer to other sources.

Table 21. Comparison of desalination technologies for treatment of produced water

Technology	Emerging Technology	Previously Employed for Produced Water	Application Range	Overall TDS Rejection (%)	Overall Process Recovery (%)	Na Removal	Organics	Heavy Metals	Minimal Pretreatment Required	Low Chemical Demand	Low Energy Demand	Minimal Maintenance	Ease of Operation	Low Cost	Robustness[1]	Reliability[2]	Flexibility[3]	Mobility[4]	Modularity[5]	Residual Disposal/ Manage-ment	Footprint
Membrane																					
NF	No	Yes	1,000 to 35,000	> 99	60 to 80	+	+	++	-	++	+	+	+	++	++	+++	++	++	Yes	+	++
RO	No	Yes	1.000 to 35.000	> 99	30 to 60	+++	+	+++	-	++	-	+	+	++	++	+++	++	++	Yes	+	++
ED/EDR	No	Yes	500 to 1,500	55 to 75	80 to 90	+	-	++	++	+++	+	++	+	+++	+	+++	+	++	Yes	+	+
FO	Yes	No	> 500	95	ND	++	+	ND	-	ND	ND	ND	+	ND	ND	ND	ND	ND	Yes	ND	ND
Membrane Hybrid																					
NF/NF	No	No	25,000 - 50,000	> 99	30 to 44	++	-	++	-	+	+	+	+	ND	++	+++	++	++	Yes	+	++
Dual RO w/ Chemical Precip	Yes	No	1000 to 35,000	> 94	90	+++	+	+++	-	-	ND	+	+	ND	++	+++	++	++	Yes	+	++
Dual RO w/HERO	Yes	No	1000 to 35,000	> 94	90	+++	+	+++	-	++	+	+	+	ND	++	+++	++	++	Yes	+	++
Dual RO/w SPARRO	Yes	No	1000 to 35,000	> 94	90	+++	+	+++	-	++	ND	+	+	ND	++	+++	++	++	Yes	+	++
HEED	Yes	Yes	> 500	ND	ND	+	-	++	++	+++	+++	+	+	-	+	ND	+	++	Yes	+	+
Electro-deionization																					
Thermal																					
MSF	No	?	5 000 to 50.000	> 99.9	27 to 40	+++	-	++	+	-	-	-	-	++	++	-	-	-	No	-	+
MED	No	?	1 500 to 50.000	> 99.9	27 to 40	+++	-	++	+	-	-	-	-	++	++	-	-	-	No	-	+
VC	No	Yes	1.500 to 50.000	> 99.9	90	+++	-	++	+	-	-	-	-	++	++	-	-	-	Yes	-	+
MED-VC	No	?	1.500 to 50.000	> 99.9	27 to 40	+++	-	++	+	+	-	+	-	++	++	-	-	-	No	+	+
MD	Yes	No	500 to 50,000	> 99.5	ND	++	+	ND	+	++	ND	ND	+	++	ND	ND	ND	ND	Yes	ND	ND
Freeze-Thaw	No	Yes	> 5 000	> 94	94	+++	+	+++	++	+++	++	+	++	++	++	+++	+	-	No	+	-
Alternative																					
CDI	Yes	Yes	500 to 5,000	99	20 to 80	+++	-	ND	-	-	++	-	+	-	+	-	+	+	Yes	-	+
IX	No	Yes	< 750	95	99.9	++	-	+++	+	-	+++	+	++	++	++	++	+	+++	Yes	+	++
Chemical softening																					
Commercially available																					
CDM HERO	No	Yes	> 1 250	NA	NA	NA	NA	+++	+++	+++	+++	+	++	+++	+++	+++	-	-	No	+++	-
Veolia OPUS	Yes	No	> 1 250	NA	NA	NA	NA	+++	+++	+++	ND	ND	+++	ND	++	ND	-	-	Yes	+	+
Altela Rain	Yes	Yes	800 to 45,000	NA	NA	NA	NA	+++	++	+++	+++	++	++	+	ND	ND	ND	ND	Yes	+++	-
212 Resources	Yes	?	> 7 500	NA	NA	NA	NA	+++	+++	NA	ND	ND	++	-	ND	ND	ND	ND	No	+++	-
Disposal																					
Evaporation	No	Yes	> 1.250	NA	NA	NA	NA	+++	+++	+++	+++	+	++	+++	+++	+++	-	-	No	+++	-
WAIV	Yes	No	> 1.250	NA	NA	NA	NA	+++	+++	+++	ND	ND	+++	ND	++	ND	-	-	Yes	+	+
Dewvaporation	Yes	Yes	800 to 45,000	NA	NA	NA	NA	+++	++	+++	+++	++	++	+	ND	ND	ND	ND	Yes	+++	-
SAL-PROC™	Yes	?	> 7 500	NA	NA	NA	NA	+++	+++	NA	ND	ND	++	-	ND	ND	ND	ND	No	+++	-

Legend

Excellent	Good	Fair	Poor
+++	++	+	-

Notes:
[1]Robust: Ability of equipment to withstand harsh conditions. mechanical strength, able to accommodate multiple design criteria, failure of an individual. component does not significantly affect the overall performance
[2]Reliable: Minimal equipment downtime. technology not prone to failure and produces consistent product water quality.
[3]Mobile: Easily moved from one site to another.
[4]Flexible: Able to accommodate a wide range of water quality.
[5]Modularity Ability to implement technology as a unit process in a treatment train, and accommodate changing influent volumes
ND - No Data
NA - Not applicable

7.2.1 Reverse Osmosis and Nanofiltration

Reverse osmosis and nanofiltration membranes also can be used to remove salt from produced water. Reverse osmosis membranes work on the premise that a pressure, greater than the osmotic pressure of the feed solution, must be applied to the system to force water through the membrane and reject the salt. The osmotic pressure is a function of the salinity of the water. For water with very high salinity, the osmotic pressure and, hence, the required system operating pressure are very high. For waters with high salinity, reverse osmosis is not a practical solution. Reverse osmosis generally is considered a cost effective treatment technology to use with seawater or the salinity up to 40,000 ppm TDS.

Current research on the use of RO and NF membranes for produced water treatment emphasizes the tendency for organic fouling to increase the treatment cost and reduce the process efficiency (Mondal and Wickramasinghe 2008). Effect pretreatment technologies and appropriate membrane materials must be selected to make produced water treatment with RO and NF effective.

Melo et al. investigate RO and NF use for treatment of produced water. They employed oil/water separation, warm softening, sand filters, ion exchange, and cartridge filtration as pretreatment to the RO and NF. The RO and NF were successful in meeting the treatment goals; however, fouling data was not presented, and further study is required to determine suitability of the water for beneficial use, the optimum process operating conditions, and the effects of the product water on soil for irrigation purposes (Melo, Schluter et al.).

Mondal, et al. observed significant organic fouling on RO and NF membranes from treatment of produced water. They found that large MWCO, smooth, hydrophilic membranes experienced the least amount of fouling (Mondal and Wickramasinghe 2008).

Sagle, et al. have been developing fouling resistant coatings for RO membranes to minimize the fouling potential of produced water using polyethylene hydrogels (Sagle, Van Wagner et al. 2009).

7.2.2 Electrodialysis/Electrodialysis Reversal

Electrodialysis is an electrically driven process consisting of a stack of alternating cation-transfer membranes and anion-transfer membranes between an anode and a cathode. An electrical current is passed through the water. The dissolved salts in the water exist as ions and migrate toward the oppositely charged electrode. The anion-transfer membrane only allows passage of negatively charged ions, and the cation-transfer membrane only allows passage of positively charged ions. Alternating anion and cation transfer membranes are arranged in a stack. The membranes are impermeable to water. These systems are operated at a very low pressure, usually below 25 psi. Electrodialysis reversal also can be implemented where the charge on the electrodes is frequently reversed. This prevents buildup of scale, biofilm, and other foulants on the membrane surface.

The energy required for ED treatment is related to the TDS of the water—the higher the TDS, the more energy required for treatment. Current research suggests that ED is not cost competitive for treating water with a TDS greater than 1,500 mg/L. Sirivedhin et al. tested ED on five simulated produced water types of high and low TDS using Neosepta® membranes. They found that at 6.5 volts per stack, ED was not capable of producing water with an SAR that would be suitable for irrigation because ED removes divalent ions to a greater extent than monovalent ions (Sirivedhin, McCue et al. 2004). If ED, using divalent selective membranes, is to be used to treat produced water for beneficial use as irrigation water, calcium and/or magnesium will need to be added back to the water to lower the SAR.

7.2.3 Forward Osmosis

Forward osmosis is an osmotically driven membrane process. Forward osmosis uses the feed water to be treated as the dilute process stream and water is moved across the membrane from the dilute feed water stream to a concentrated brine stream with a high osmotic pressure. The concentrated brine stream is called a draw solution. To enable forward osmosis to be cost effective, the components that contribute to the high osmotic pressure in the brine stream must be removed easily to leave behind the fresh water product.

7.2.4 Hybrid Membrane Processes

7.2.4.1 Two Pass Nanofiltration

Two pass nanofiltration involves treating produced water with nanofiltration and then further treating the permeate water with nanofiltration again. This process is used to obtain a permeate stream with an even lower TDS than a single pass NF process and is less energy intensive than reverse osmosis. Western Environmental pilot tested this process for produced water (Bierle).

7.2.4.2 Dual RO with Chemical Precipitation

Dual RO with chemical precipitation consists of a primary RO process. The concentrate from the first RO is further treated with lime softening and is then fed to a second stage RO. The permeate streams from both RO processes are collected and provide the product water from this process. Reported recoveries using this process are 95% and higher for brackish water applications. Utilizing this process enhances the recovery of the RO process but requires additional chemicals, additional equipment, and an increased footprint.

7.2.4.3 Dual RO with Softening Pretreatment and Operation at High pH

This patented process is called HERO™ and consists of chemical softening as a pretreatment step, primary RO, and ion exchange, degasification, and pH increase on the concentrate from the first RO stage. The treated concentrate stream then is treated with a secondary RO. The product water from the primary and secondary

RO units is combined to make up the product water for this process. As with the dual RO with chemical precipitation, this process is designed to increase the product water recovery of the process. Reported recovery rates range from 90–95%.

7.2.4.4 Dual RO with Slurry Precipitation and Recycling RO (SPARRO)

In this process, a single stage reverse osmosis membrane unit is used, and the concentrate from the RO process is treated using a seeded crystalline slurry to precipitate sparingly soluble salts from the water. The crystals then are separated from the concentrate process stream using a cyclone separator, and the remaining water then is recycled back to the RO feed.

7.2.4.5 High Efficiency Electrodialysis (HEED®)

HEED® is an electromembrane process in which the ions are transported through a membrane from one compartment to another under the influence of an electrical potential. HEED® consists of dual or multiple side-by-side ion exchange membranes and contains an improved gasket design that results in greater efficiency than traditional ED processes (Corporation 2008). HEED® is more resistant to organic fouling than RO or NF.

7.2.4.6 Electrodeionization

Electrodeionization (EDI) involves ion exchange resins, ion exchange membranes, and a direct current electrical current. The major difference between ED and EDI is that desalting compartments of EDI are filled with an ion exchange resin. Ions are transported to the ion exchange resin by diffusion; they are then transported through the resin by the current. The current flows through the ion exchange resin because this path is more electrically conductive. This process is capable of removing weakly ionized species and desalting water to very low concentrations.

7.2.5 Thermal Processes

7.2.5.1 Multistage Flash Distillation

Multistage flash distillation converts water to steam at low temperatures in a vacuum. At vacuum pressures, the boiling point of water is lower than at atmospheric pressure, requiring less energy. The water is preheated and then subjected to a vacuum pressure that causes vapor to flash off the warm liquid. The vapor then is condensed to form fresh water while the remaining concentrated brine that does not flash is sent to the next chamber where a similar process takes place. The multiple stages are designed to improve the recovery of the process. Many of the older seawater desalination plants use the multistage flash distillation process.

7.2.5.2 Multieffect Distillation

In multieffect distillation, vapor from the first evaporator is condensed in the second evaporator and the heat of condensation is used to evaporate the water in the second evaporator. Each evaporator in the series is called an "effect."

7.2.5.3 Vapor Compression

In the vapor compression process, the feed water is preheated in a heat exchanger by the product and reject streams from the process. This process uses a still that contains tubes. The water then is fed to the inside of the tubes, and the vapors then are fed to the outside of the tubes to condense. The gases that do not condense are removed from the steam-condensation space by a vent pump or ejector. The mechanical pump or ejector is a requirement of this process and is necessary to increase the pressure of the vapor to cause condensation. Vapor compression has been used for produced water treatment, and commercially available products currently are marketed for this application.

7.2.5.4 Membrane Distillation

Membrane distillation is a thermally driven membrane processes that uses the vapor pressure gradient between the feed solution and the product solution as the driving force. The membrane is hydrophobic and microporous. The flux and salt rejection of this process is independent of feed water salinity. There are many different configurations for the application of membrane distillation.

7.2.6 Alternative Desalination Processes

Alternative desalination processes do fall within the thermal or membrane categories and use other materials and mechanisms for desalination.

7.2.6.1 Capacitive Deionization

In capacitive deionization, water is passed through pairs of high surface area carbon electrodes that are held at a potential difference of 1.2 volts. Ions and other charged particles are attracted to the oppositely charged electrode. When the electrodes have become saturated with ions, they must be regenerated by removing the applied potential and rinsing the ions out of the system.

The carbon aero gel electrodes have a relatively high surface area (500 m^2/g) and provide high electrical conductivity, and have a high ion permeability. The electrodes are, however, expensive and have a relatively low ion storage capacity.

7.2.6.3 Softening

Softening can be used to remove hardness and silica from the water. Generally, if the water is to be used for agricultural purposes, softening would not be advised because, like nanofiltration, the SAR will be higher following treatment due to removing the divalent ions.

7.2.6.4 Ion Exchange

The Higgins Loop™ is a sodium ion exchange technology for water with a high concentration of sodium. This process is beneficial if there are no other ions of concern besides sodium and if SAR adjustment is necessary. The cation exchange resin in the Higgins Loop™ process exchanges sodium ions for hydrogen ions. Up to 90% exchange levels are achieved. As the resin becomes loaded with sodium, the flows to the adsorption portion of the process temporarily are interrupted. The resin then is advanced by a pulsing action through the loop in the opposite direction of the liquid flow. The loaded resin then is regenerated with hydrochloric acid and rinsed before being advanced back into the adsorption portion of the loop. Treated water is slightly acidic because H^+ ions are added to the water. Therefore, the pH is raised, and calcium is added by passing the treated water through a limestone bed in the pH controlling process step.

For many produced waters, removing the sodium ions will have a large effect on the total dissolved solids concentration to render the water suitable for beneficial use.

Other ion exchange resins also may be employed to target specific ions for removal. The resin may or may not be able to be regenerated.

7.3 Commercial Processes

Numerous companies currently market package produced water treatment technologies. Most of these companies tailor their package plant to meet the specific treatment need for each individual application. The following sections contain a brief summary of some of the commercially available produced water treatment systems.

7.3.1 Freeze-Thaw/Evaporation (FTE®)

BC Technologies and Crystal Solutions utilizes the FTE® process to treat produced water for full scale facilities. In this process, when the outdoor air temperature is less than 32 °F, the water to be treated is sprayed or dripped onto a freezing pad, forming a large pile of ice. This process exploits the fact that saline water has a lower freezing point than fresh water; therefore, at temperatures cooler than 32 °F, the runoff from the ice pile will be salty brine. When the temperature is such that melting occurs, the runoff will be fresh water.

This process has been used successfully to treat produced water and is considered an established process for produced water treatment.

7.3.2 CDM Produced Water Technology

CDM has developed a process for treating produced water containing TDS levels up to 20,000 mg/L. The technology is not specific for coal bed methane produced water and has been pilot tested with tight sands produced water in the Piceance basin and with CBM produced water in the Powder River basin. CDM also is marketing the technology for treating flow-back water from subsurface hydraulic fracturing.

The treatment process is comprised of a train of different technologies in series to meet site-specific treatment goals (figure 24). The specific processes included in the treatment train are dictated by the feed water quality and the desired product water quality. Some of the technologies that may be used include: advanced filtration, weak acid cation IX softener, UV disinfection, low-pressure RO, antiscalant addition, seawater/high pressure RO, evaporation, and crystallization. The feed stream is kept anoxic to minimize oxidation of iron and other metals and to reduce the fouling potential of the water. Depending on the feed water quality, the process can achieve more than 97% recovery. A computer program was developed that assists in selecting the required technologies and predicts the performance and scale formation within the system based on feed water quality.

The pretreatment for the process consists of media filers and polymeric hollow fiber UF membranes to remove particulates, silt, oil, grease, coal fines, clay, and bacteria. The filtration system is backwashed using RO permeate. A weak acid cation (WAC) IX softener is used to reduce hardness and other metals. The resin is regenerated using hydrochloric acid. The water is then disinfected using UV. The calcium and magnesium-rich WAC regeneration solution is combined with the filter backwash and is either treated separately or combined with the product streams from the membrane processes and discharged, depending on the scenario and the feed water quality.

After pretreatment, low-pressure RO (capable of achieving 85% recovery) is employed. The train size and type of membrane employed is tailored based on the feed water quality. An antiscalant (approximately10 mg/L) is added to the concentrate stream to stabilize the silica and to prevent scale formation in the next high-pressure RO stage. The second RO stage consists of high-pressure or seawater RO membranes that can achieve 80% water recovery. The RO permeate is combined with the low-pressure RO permeate for discharge or beneficial use. The concentrate, approximately 2–3% of the initial feed volume, is either disposed of as a waste, or can be treated for zero liquid discharge (ZLD).

Because many produced waters contain high levels of sodium and low levels of divalent ions, the SAR may be too high, even after treatment, for beneficial use of the water. In these cases, a limestone bed is used to add calcium to the water and lower the SAR.

The following cost estimates were presented based on the pilot testing experience in the Powder River basin: $0.14 per bbl or $3.33 per 1,000 gal (not including energy or brine disposal); $0.08 per bbl or $1.90 per 1,000 gal for brine disposal. Cost estimates were not provided for the pilot test on tight sands produced water.

To accommodate changing water volumes, modular systems can be designed to treat volumes from 5,000 bbl/day (200,000 gpd or 145.8 gpm) to 20,000 bbl/day (840,000 gpd or 583 gpm) with additional units added or removed, as necessary. A schematic diagram of the CDM process is provided in figure 24.

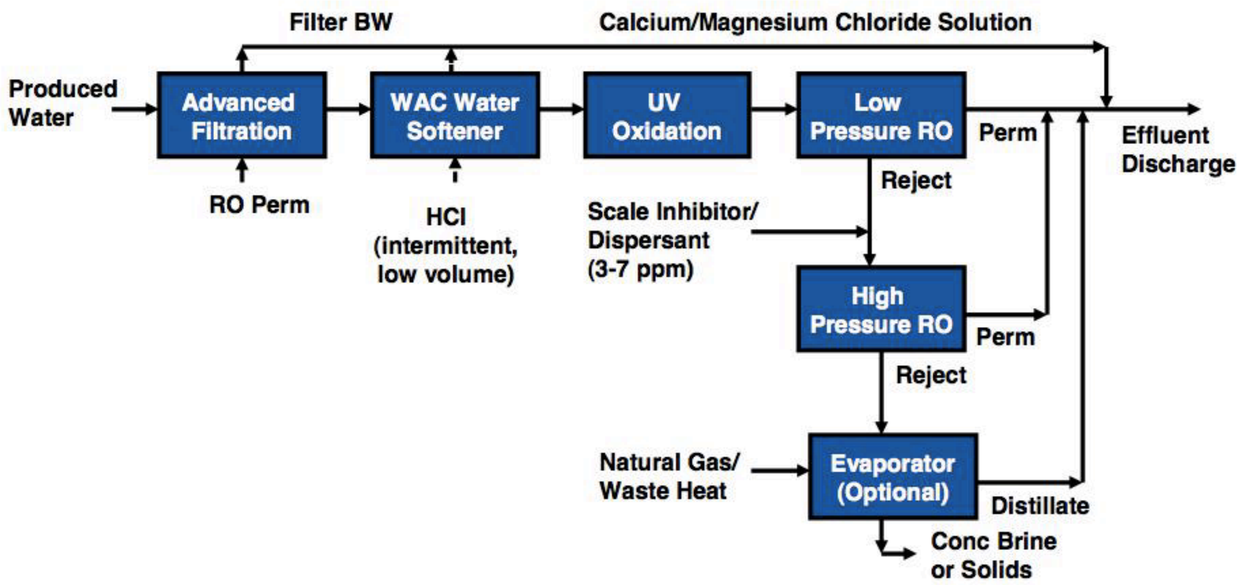


Figure 24. Schematic diagram of CDM produced water treatment process.

7.3.3 Veolia OPUS™

Veolia water currently is marketing their produced water treatment system, called OPUS™, which stands for optimized pretreatment and unique separation. OPUS™ uses filtration and ion exchange as pretreatment to an RO system operated at a high pH. The process may be modified slightly depending on the specific water quality of produced water application.

7.3.4 Altela Rain℠ (Dewvaporation)

This process utilizes a humidification-dehumidification cycle to produce distilled water. Feed water is evaporated by hot air on one side of a heat transfer wall, and fresh water is condensed on the other side. The condensate or dew collects on the other side of the wall represents the purified water stream. This process has been utilized for produced water treatment and has undergone several pilot tests.

7.3.5 212Resources

212Resources is currently marketing a produced water treatment system. The core component to the process is vapor compression. The package treatment system also utilizes other unit processes in a package treatment system; however, the specific details of the process are proprietary. 212Resources claims the treatment system can produce clean water and recover marketable hydrocarbons and methanol.

7.4 Implications of Water Quality for Treatment Technologies

Many application specific and water quality specific factors should be taken into account when selecting a produced water treatment process. For example, the temperature of the feed water may help determine which type of desalination treatment should be employed since some technologies work more efficiently at high temperatures, while others use a low temperature feed stream. Also, if ion removal is necessary, one must consider the type of ions that need to be removed. Membrane processes most often remove divalent ions to a greater extent than monovalent ions, which may make the sodium adsorption ratio higher and render the water less suitable for beneficial use as irrigation water or surface discharge.

8. GIS-Based Approach to Produced Water Management

Produced water management strategies should consider the geographical relationship between the produced water source and potential beneficial uses. Ideally, beneficial use of produced water will require minimal water conveyance. Geographic data can be used to describe the location of produced water and water uses.

8.1 Produced Water GIS Database

A GIS database has been compiled to describe the location of oil and gas producing wells and the water quality of produced water associated with the wells. From this database, a series of maps has been generated to qualitatively describe the potential for different types of produced water beneficial use. The database was designed such that data of interest can be viewed by selecting the corresponding data layers. Map layers were constructed to include a base map and reference data, petroleum basin and well locations, and water consumption by use.

8.1.1 Base Map and Reference Data

Shape files for State boundaries, city/town data, rivers, and lakes are contained within the database to provide a base map and to serve as a reference for the oil and gas data. City and town location data were obtained from ESRI Redlands, California, (www.esri.com), and population data were gathered from the U.S. Geological Survey (http://nationalatlas.gov/atlasftp-na.html). Shape files for rivers, streams, lakes, and reservoirs were obtained from the U.S. Geological Survey (http://edc2.usgs.gov/geodata/index.php). Figure 25 shows the base map with reference data.

8.1.2 Oil and Gas Distribution, Well and Basin Data

USEIA collects, analyzes, and publishes unbiased energy information for policymaking, market studies, and public knowledge. These data, which include energy production values, stock prices, energy demand, import and export volumes, and current prices, are intended to improve the understanding of energy and interaction with the economy and environment.

Each year, USEIA publishes a list of the top 100 producing oil and gas well, based on proved reserves. We have used these data to identify areas with substantial amounts of petroleum production and, therefore, water production. USEIA also gathers data on the distribution of oil and gas production within the

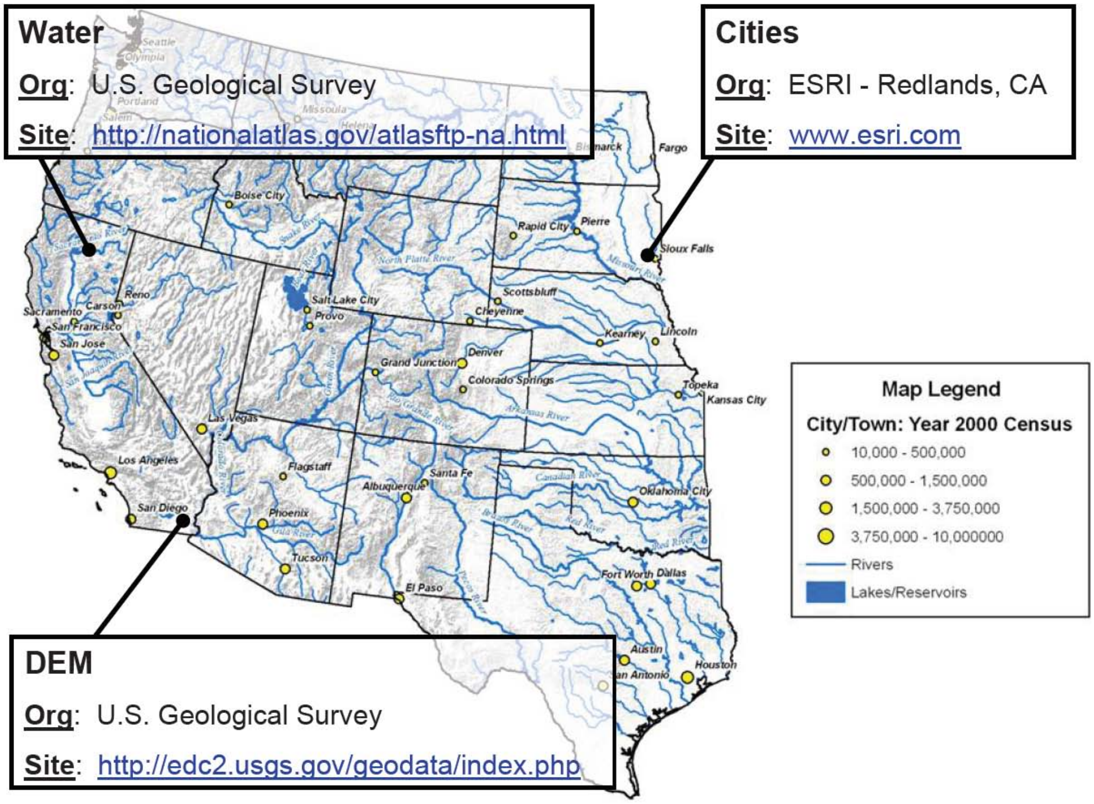


Figure 25. Base map with reference data and sources.

United States. This data can be used to infer information about the general distribution of petroleum from all wells, not only the top producing wells. Many basins produce both oil and gas. The latitude and longitude data for these top 100 wells and the shape files for the distribution data are available by request from USEIA (www.eia.doe.gov). Figure 26 shows the top producing wells, petroleum basin boundaries, and distribution of oil and gas wells for the Western United States along with the base map with the reference data.

8.1.3.1 Hydrologic Units

Hydrologic units represent natural and manmade watersheds. A watershed is a geographic area of land, water, and biota within the confines of a drainage divide. Watershed boundaries define the aerial extent of surface water drainage to a specific location. These watersheds divide regions based on the area drained by a river system, section of river, and its tributaries. Different levels of hydrologic units are defined based on the scale at which the drainage is evaluated. Hydrologic data was used as a layer on the base map.

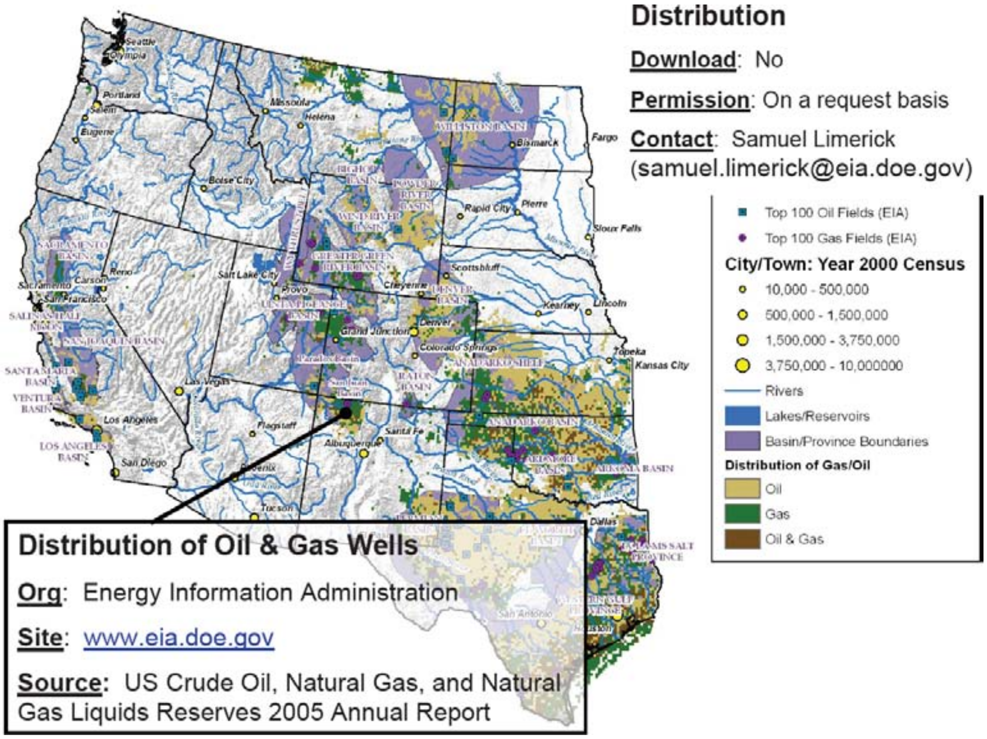


Figure 26. Location of oil and gas producing basins and the top 100 producing oil and gas wells in the Western United States.

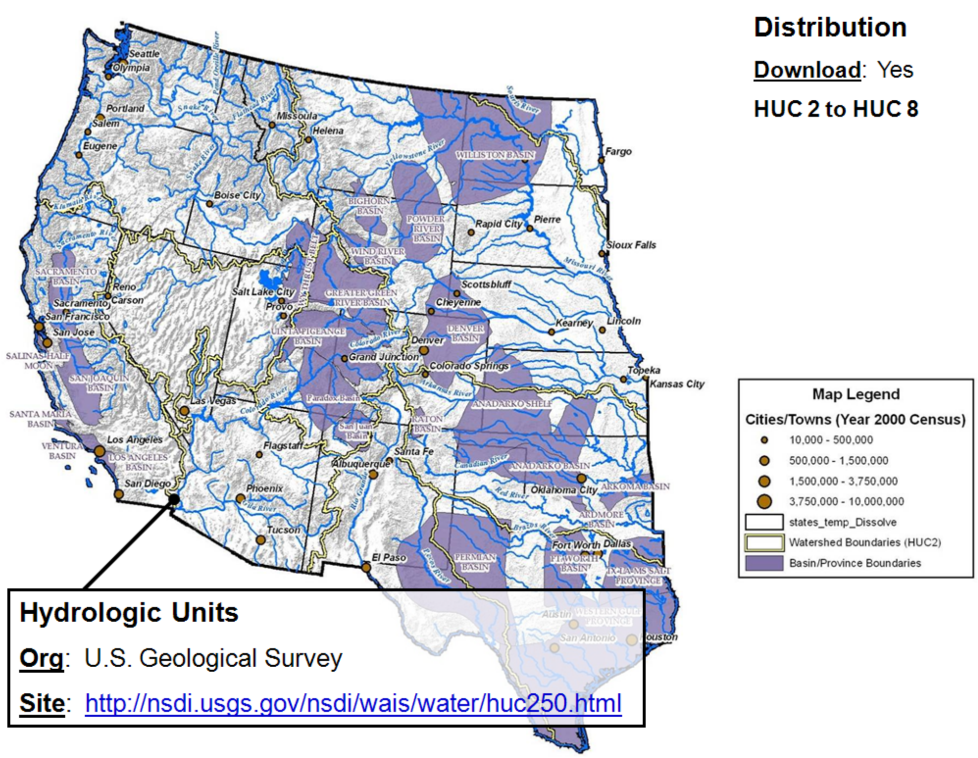


Figure 27. Geographic relationship between hydrologic units and petroleum basins.

Hydrologic units are important for employing watershed approaches to water management. A watershed approach is a comprehensive interrelated approach to watershed and natural resources management because it is sensitive to the needs of all resources: soil, water, air, plants, animals, and people in relation to local social, cultural, and economic factors (2007). Most watershed efforts are focused on an eight-digit hydrologic unit basis.

8.1.3.2 Overall Need for Additional Water Supplies

Water shortage and water-use conflicts have become increasingly common in many areas of the United States, even in normal water years. As competition for water resources grows—for irrigation of crops, growing cities and communities, energy production, and the environment—the need for information and tools to aid water resource managers also grows. Water issues and challenges are increasing across the Nation but particularly in the West and Southeast due to prolonged drought.

These water issues are exacerbating the challenges facing traditional water management approaches, which by themselves no longer meet today's needs. Beneficial use of produced water is new tool that can be used in the Western United States to increase water supplies. Additionally, produced water often occurs in areas that also have a high potential for water conflict, as identified by Water 2025, figure 28.

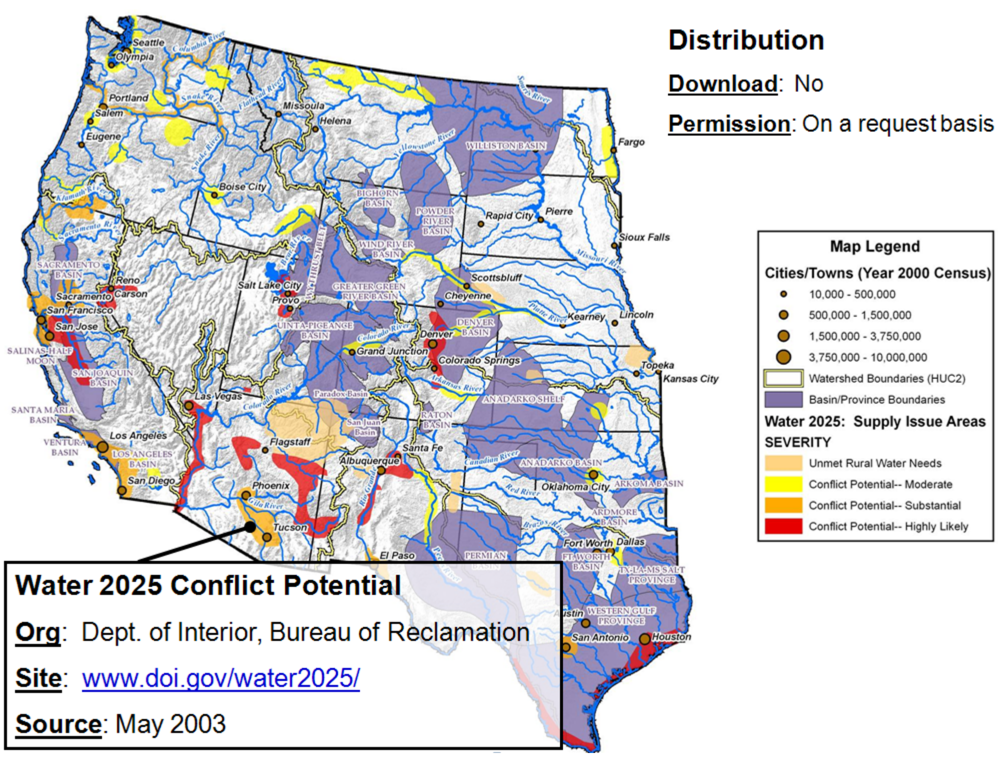


Figure 28. Potential water conflict and produced water generation.

8.1.3.3 Agricultural Water Demand

Produced water, which can be generally described as brackish ground water, could easily be put to use as agricultural water for irrigation or livestock watering. Data was obtained for the U.S. Department of Agriculture to describe the amount of irrigation in the Western United States. These data were mapped on the base map, figure 29.

The maps presented in figures 28 and 29 can be used to draw general conclusions about the use of produced water for streamflow augmentation, municipal uses, general water supply augmentation, and agricultural uses. At the macroscopic level, it does appear that there is a geographical relationship between produced water generation and beneficial uses of produced water.

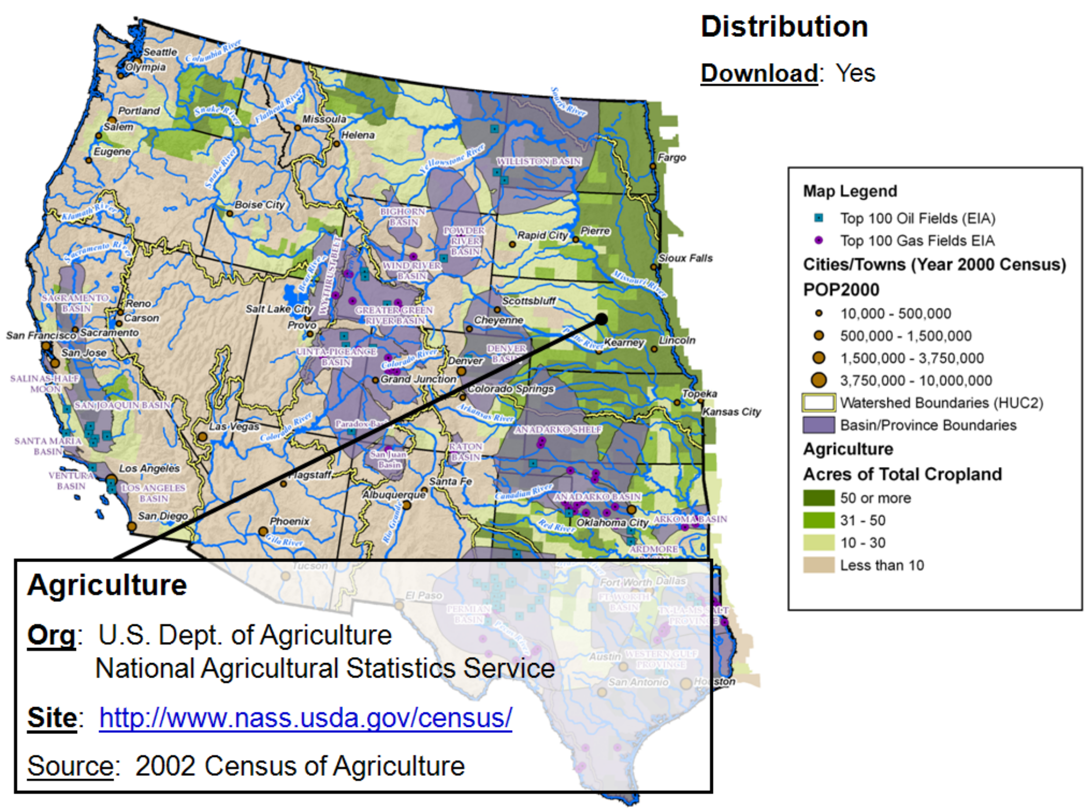


Figure 29. Areas of irrigated agriculture compared to produced water generation.

8.2 Examples of GIS-Based Approach

The Geographic Information System (GIS) database was used to identify produced water management options for three different geographic locations: conventional oil production in the Denver basin, coal bed methane production in the Powder River basin, and conventional gas production near a tributary of the Colorado River. This section is intended to illustrate the potential for use; legal and regulatory considerations are outside of the scope of this study. The need for treatment to render the produced water to the quality dictated by the different beneficial uses was not considered, since this is purely a conceptual analysis. In many cases, the actual beneficial use for produced water would be dependent upon the raw water quality of the produced water and the degree and cost of treatment required for the water to meet beneficial use water quality standards.

8.2.1 Denver Basin Example

Produced water generated in the Denver basin could potentially be used to augment the water supply in an urban area. The Denver basin falls within one of the areas outlined in the Water2025 study that has a large potential for water conflict by the year 2025. The Denver basin contains one of the USEIA top producing oil wells and a top producing gas well, figure 30.

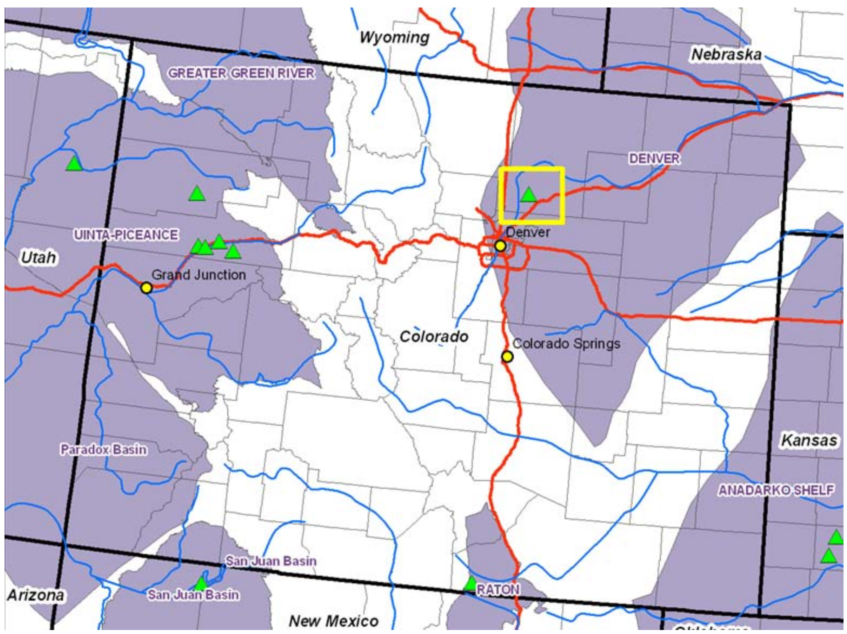


Figure 30. Selection of top 100 producing well in the Denver basin.

Within the study area, the conventional water supply is from the Colorado-Big Thompson (CBT) Project. The Colorado-Big Thompson Project is the largest transmountain water diversion project in Colorado and is used to supplement the water supplies of 30 cities east of the Continental Divide with water from the west of the Continental Divide. The Colorado-Big Thompson Project annually delivers 213,000 acre-feet of water to northeastern Colorado for agricultural, municipal, and industrial uses. For the purposes of this analysis, we will consider the use of produced water only to augment conventional supplies, not to replace or compete with conventional supplies. Therefore, it is important to note that, within the study area, it is not possible to purchase additional water (that is not already allocated) from the Colorado-Big Thompson Project. Therefore, to render produced water useful as a new water source, it does not need to be compared on the same cost basis as water from the Colorado-Big Thompson Project.

The boundary conditions for this example are a 5-mile radius surrounding the well of interest. Agricultural data was obtained for this study area from the National Agricultural Imagery Program, figure 31.

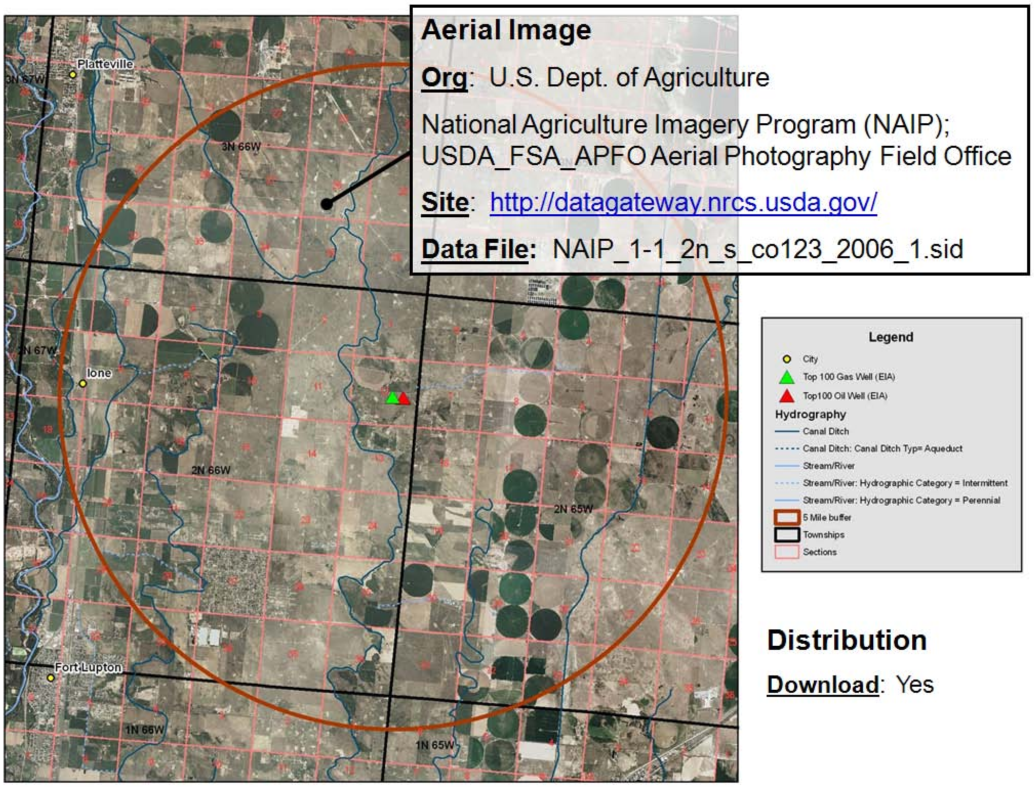


Figure 31. Agricultural data within the study area.

Oil and gas well locations were obtained from the Colorado Oil and Gas Conservation Commission, figure 32. Abandoned wells are identified by a black cross, and producing wells are identified by a red cross. It is important to note that not only is there a top 100 producing gas wells, but also a top 100 producing oil wells and over 1,000 other producing wells within the study area.

The next layer added to the study area map shows the type of irrigation used—sprinkler and flood, figure 33. Each sprinkler irrigated circle on the map is roughly 130 acres. Within the study area, there are 5,565 acres of flood irrigated land and 10,809 acres of sprinkler irrigate land.

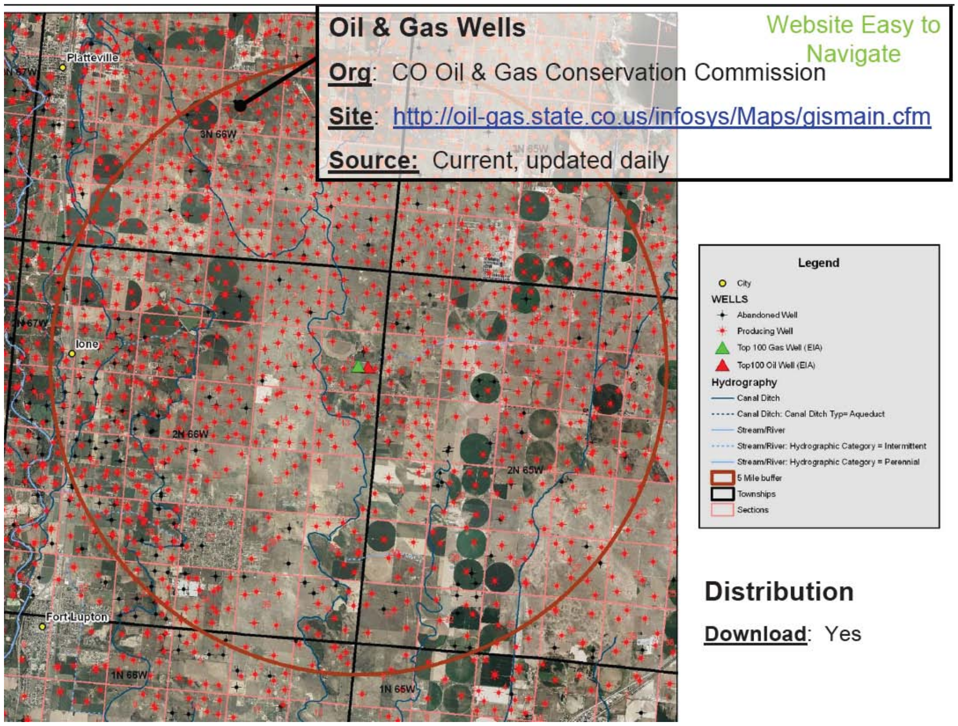


Figure 32. Oil and gas well location data within the study area.

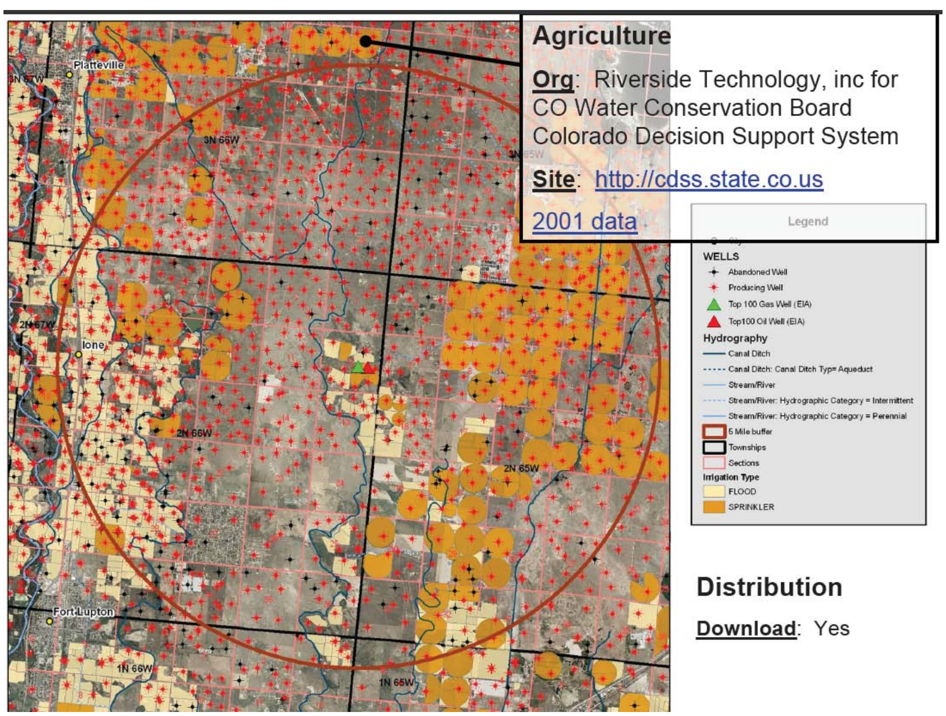


Figure 33. Irrigated land within the study area.

Within the study area, the most likely use for produced water is irrigation water. As can be seen from figure 33, there are approximately four producing wells within the sprinkler irrigated areas. Depending on the quality of the produced water, treatment may be required to treat the water to irrigation water standards. Another option is to use a pipeline to transport the produced water to the irrigations canal within the study area. The irrigation canals are shown as blue lines in figure 33.

8.2.2 Powder River Basin Example

Another example looked at the top 100 producing well locations within the Powder River basin in northeastern Wyoming, figure 34.

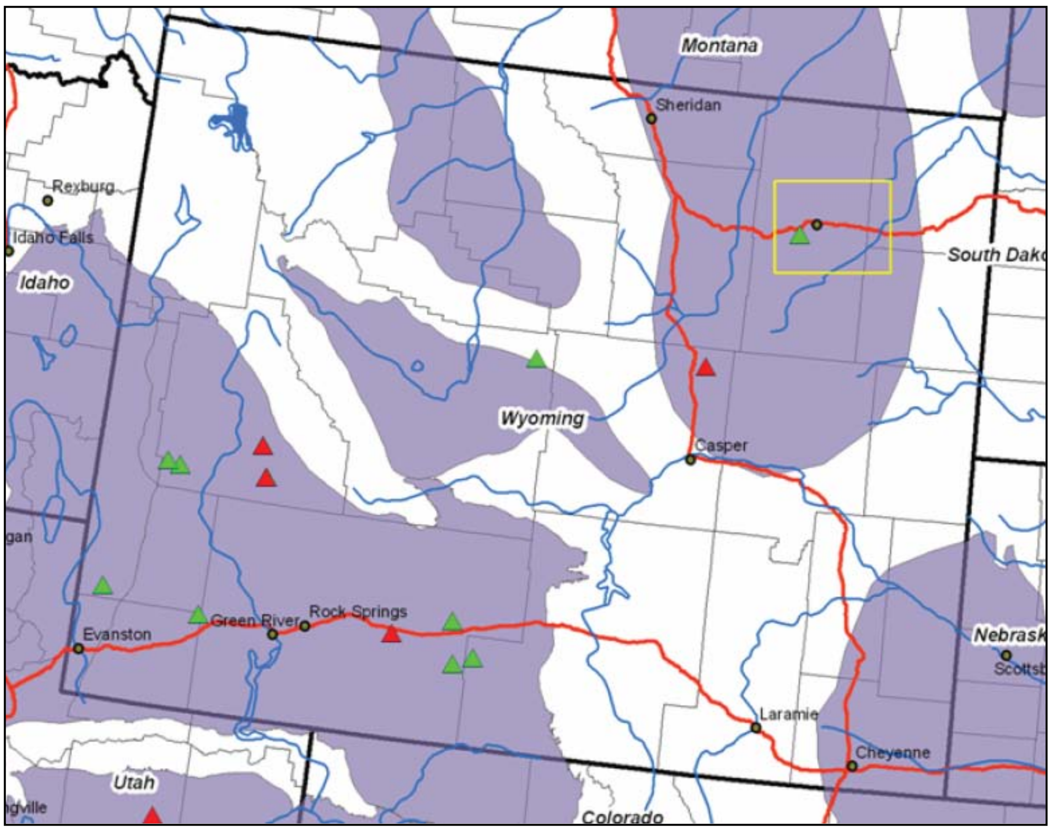


Figure 34. Powder River basin example area.

Well location data was obtained from the Wyoming Oil and Gas Conservation Commission; producing wells are shown with a red cross, and abandoned wells are identified by a black cross, figure 35.

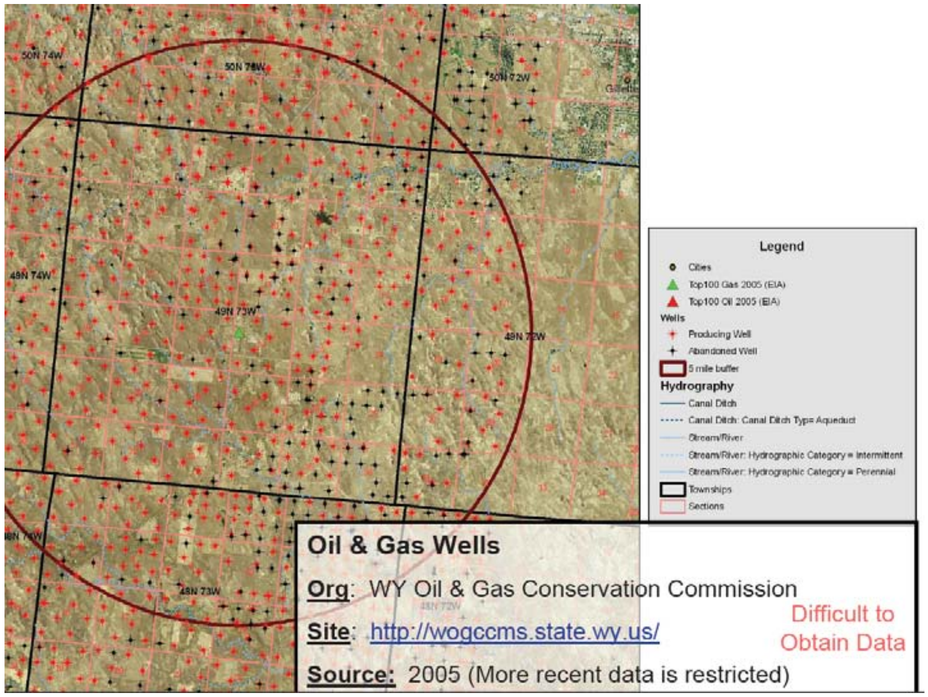


Figure 35. Location of oil and gas wells within 5-mile radius of top producing well in the Powder River basin.

Irrigation data was obtained from the Wyoming Water Resources Center to identify irrigated agriculture and nonirrigated agriculture within the study area, figure 36. Within the 5-mile radius study area, there are 1,075 acres of irrigated agriculture and 6,219 acres of nonirrigated agriculture.

Based on the map data, produced water could be used locally within the study area to irrigate land or to convert nonirrigated land to irrigated land. It also could be possible to use pipelines to transport water to streams and rivers, identified by blue dashed lines in figure 36. There is also municipal and industrial water use within the study area that could be augmented with produced water.

8.2.3 Uinta-Piceance Basin Example

The map example was conducted within the Uinta-Piceance basin in eastern Utah, figure 37.

Oil and gas well location data for this study area was obtained from the Utah Department of Natural Resources – Oil, Gas, and Mining Division, figure 38.

There is limited agricultural water use in this area, so the most realistic beneficial use of produced water in this area is for streamflow augmentation by discharge from a pipeline, see figure 39. Surface discharge in this area falls within the Colorado River Basin and, therefore, has important implications for water managers within the Colorado River Basin.

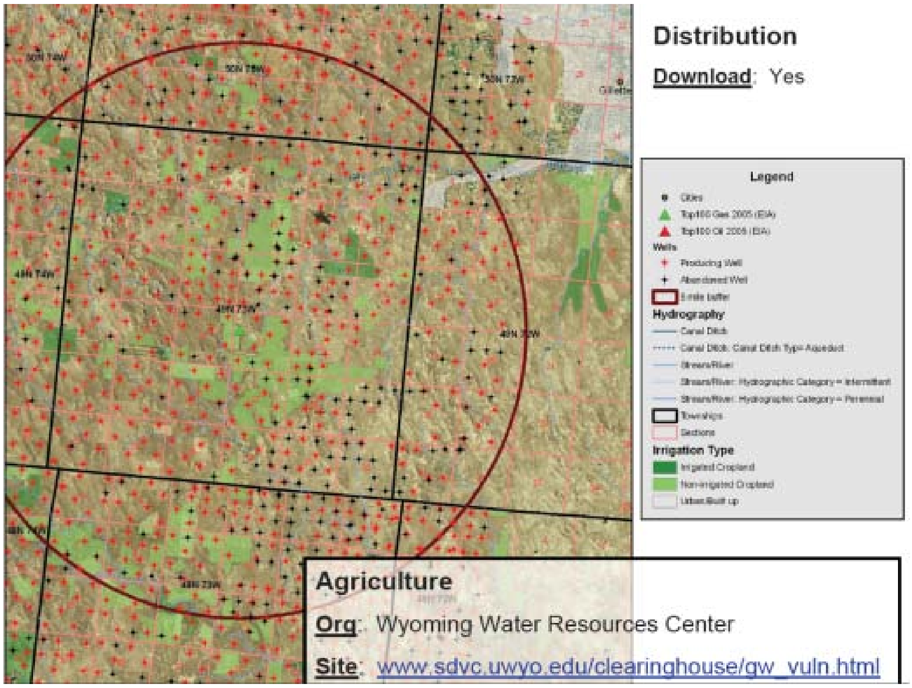


Figure 36. Irrigated and nonirrigated agriculture within the study area.

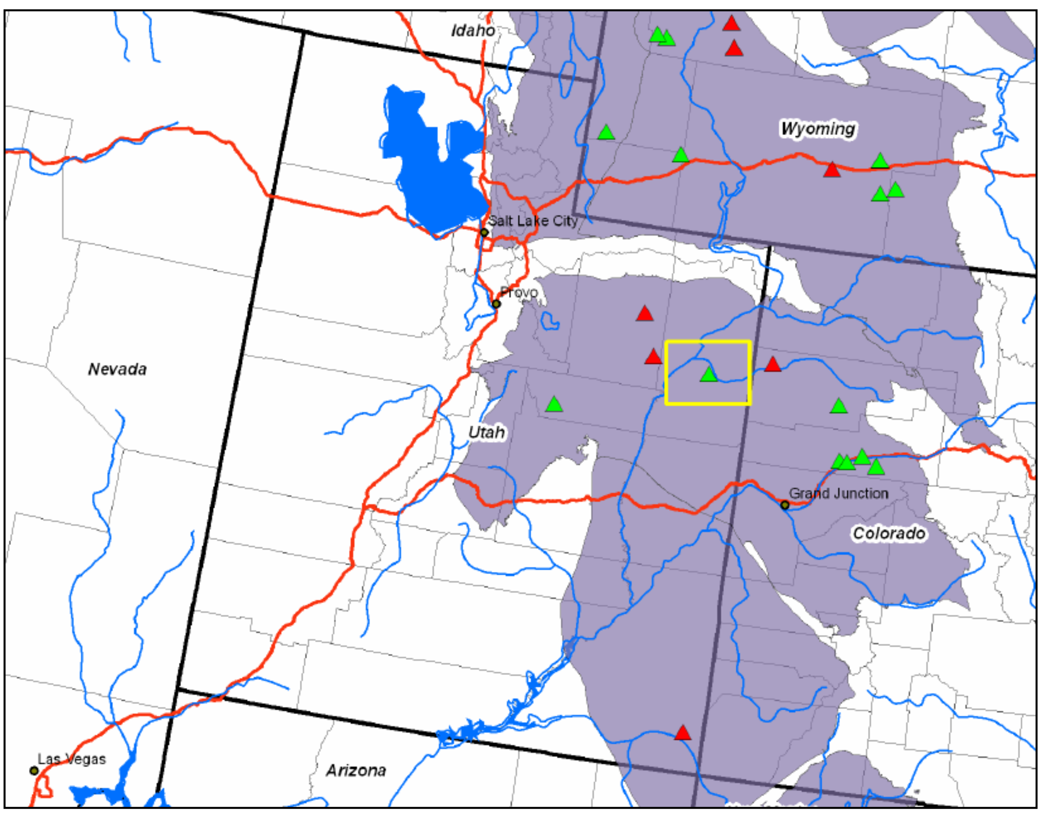


Figure 37. Uinta-Piceance basin example study area.

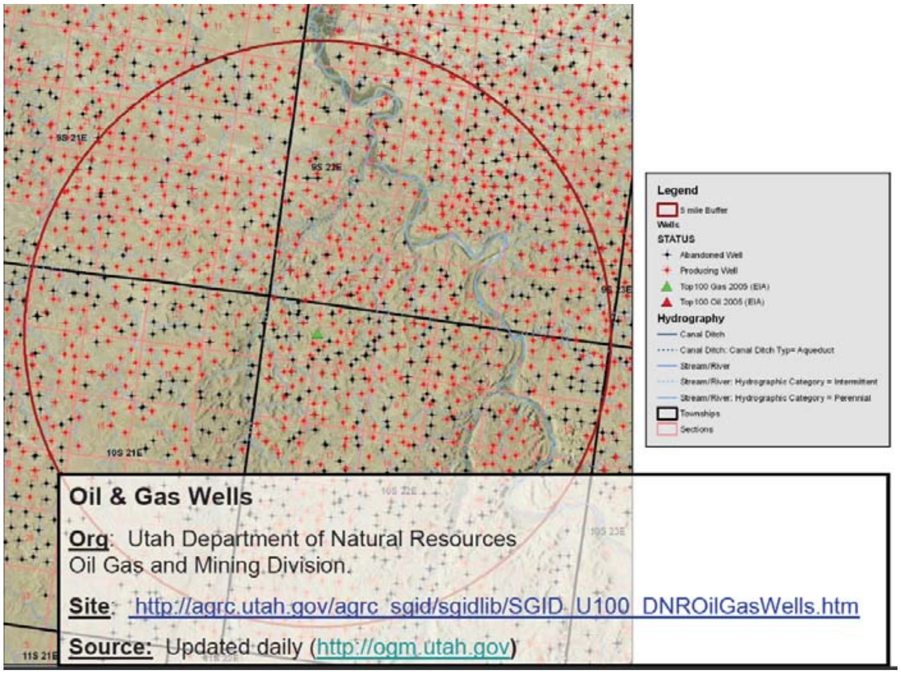


Figure 38. Five-mile study radius for Piceance basin example.

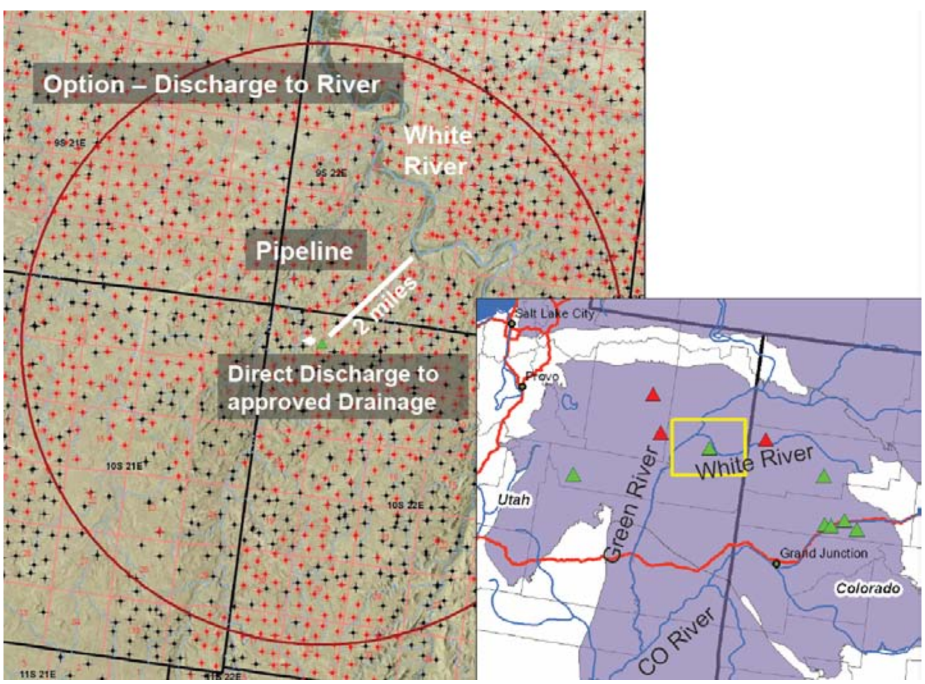


Figure 39. Surface discharge beneficial use option for Uinta-Piceance study area.

While the maps presented in this section do not provide quantitative information regarding the feasibility or economics of treating and reusing produced water for beneficial uses, they do provide evidence that there is potential for multiple beneficial use options in many areas throughout the Western United States.

9. References

ALL Consulting. 2003. *Handbook on Coal Bed Methane Produced Water: Management and Beneficial Use Alternatives*. Prepared by ALL Consulting for the Ground Water Protection Research Foundation, U.S. Department of Energy, and U.S. Bureau of Land Management. Accessed from http://www.all-llc.com/CBM/BU/index.htm.

Altare, C.R., R.S. Bowman, et al. 2007. "Regeneration and long-term stability of surfactant-modified zeolite for removal of volatile organic compounds from produced water." *Microporous and Mesoporous Materials* **105**(3): 305–316.

AWWA. 2005. *Water Treatment Plant Design*. New York, McGraw-Hill.

Ayers, R.S., and D.W. Westcot. 1994. "Water quality for agriculture." *Food and Agriculture Organization of the United Nations*.

Ball, H.L. 1994. *Nitrogen Reduction in an On-Site Trickling Filter/Upflow Filter Wastewater Treatment System*. Seventh International Symposium on Individual and Small Community Sewage Systems.

Bierle, A. *Produced Water Membrane Technology*.

Bowman, R.S. 2003. "Applications of surfactant-modified zeolites to environmental remediation." *Microporous and Mesoporous Materials* **61**(1–3): 43–56.

Bureau of Reclamation. 2003. *Water Treatment Primer for Communities in Need*. Accessed at www.usbr.gov/pmts/water/media/pdfs/report068.pdf.

Burke, D. *Application of the Anoxic Gas Flotation Process*.

Burnett, D., and M. Barrufet. 2005. *Membranes used in Produced Brine Desalination*. DOE/PERF Project Review, Annapolis, MD.

Çakmakce, M., N. Kayaalp, et al. 2008. "Desalination of produced water from oil production fields by membrane processes." *Desalination* **222**(1–3): 176–186.

Casaday, A.L. 1993. *Advances in Flotation Unit Design for Produced Water Treatment*, Society of Petroleum Engineers. **SPE #25472**.

Cheung, K., H. Sanei, et al. 2009. "Produced fluids and shallow groundwater in coalbed methane (CBM) producing regions of Alberta, Canada: Trace element and rare earth element geochemistry." *International Journal of Coal Geology* **77**: 338–349.

Clark, C.E., and J.A. Veil. 2009. *Produced Water Volumes and Management Practices in the United States*. A.N. Laboratory.

Clearwater, S.J., B.A. Morris, et al. 2002. "A comparison of coalbed natural gas product water quality versus surface water quality in the Powder River Basin of Wyoming, and an assessment of the use of standard aquatic toxicity testing organisms for evaluating the potential effects of coalbed natural gas product waters." The Department of Zoology and Physiology, University of Wyoming**:** 135, Laramie, Wyoming.

Colorado Department of Public Health and Environment. 2010. "The Basic Standards and Methodologies for Surface Water." *5 CCR 1002-31*. Water Quality Control Commission.

Colorado Oil and Gas Conservation Commission. 2010. *Colorado Oil and Gas Information System (COGIS)*. Accessed at http://cogcc.state.co.us/.

Corporation, E. 2008. *HEED Summary*. Accessed at http://www.eetcorp.com/lts/HEEDsumm.htm.

Davis, J.G., R.M. Waskom, et al. 2007. "Managing Sodic Soils." *Crop Series*.

Doran, G. 1997. *Developing a Cost Effective Environmental Solution for Produced Water and Creating a New Water Resource*. Department of Energy DE-FC22-95MT95008 Report.

Faibish, R.S., and Y. Cohen. 2001. "Fouling-resistant ceramic-supported polymer membranes for ultrafiltration of oil-in-water microemulsions." *Journal of Membrane Science* **185**(2): 129–143.

Faibish, R. S. and Y. Cohen. 2001. "Fouling and rejection behavior of ceramic and polymer-modified ceramic membranes for ultrafiltration of oil-in-water emulsions and microemulsions." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **191**(1–2): 27–40.

Fakhru'l-Razi, A., A. Pendashteh, et al. 2009. "Review of technologies for oil and gas produced water treatment." *Journal of Hazardous Materials* **170**(2–3): 530–551.

Fillo, J. P. and J. M. Evans. 1990. "Characterization and management of produced waters from underground natural gas storage reservoirs." *American Gas Association Sction Proceedings*: 448–459.

Fillo, J.P., S.M. Koraido, et al. 1992. "Sources, characteristics, and management of produced waters from natural gas production and storage operations." *Produced Water*. J.P. Ray and F R. Engelhardt. New York, Plenum Press. **46**.

Fox, W.E., and D. Burnett. 2002. *Produced Water: An oasis for arid and semi-arid rangeland restoration*. Groundwater Protection Council.

Gutierrez, G., A. Lobo, et al. 2008. "Influence of Coagulant Salt Addition on the Treatment of Oil-in-Water Emulsions by Centrifugation, Ultrafiltration, and Vacuum Evaporation." *Separation Science and Technology* **43**(7): 1884–1895.

Hayes, T., and D. Arthur. 2004. *Overview of Emerging Produced Water Treatment Technologies*. 11th Annual International Petroleum Conference, Albuquerque, New Mexico.

Hayward Gordon Ltd. "Oil & Gas Industry - Produced Water Chemical Treatment 101." Accessed at http://www.haywardgordon.com/documents/PRODUCED_WATER_CHEMICAL_TREATMENT_101.pdf.

Jacobs, R.P. W.M., and R.O.H. Grant, et al. 1992. "The composition of produced water from Shell operated oil and gas production in the North Sea." *Produced Water*. J.P. Ray and F.R. Engelhardt. New York, Plenum Press. **46**.

Konieczny, K., M. Bodzek, et al. 2006. "A coagulation-MF system for water treatment using ceramic membranes." *Desalination* **198**(1-3): 92–101.

Lardy, G., C. Stoltenow, et al. 2008. *Livestock and Water*. N.D. S.U.E. Service. Fargo, North Dakota State University**:** 8.

Lobo, A., A. Cambiella, et al. 2006 . "Ultrafiltration of oil-in-water emulsions with ceramic membranes: Influence of pH and crossflow velocity." *Journal of Membrane Science* **278**(1–2): 328–334.

Ludzack, F. J. and D. K. Noran (1965). "Tolerance of high salinities by conventional wastewater treatment processes." *Water Environment Federation*.

McBeth, I., and K.J. Reddy. 2003. "Chemistry of trace elements in coalbed methane product water." *Water Research* **37**(4): 884–890.

Melo, M., H. Schluter, et al. "Advanced performance evaluation of a reverse osmosis treatment for oilfield produced water aiming reuse." *Desalination* **250**(3): 1016–1018.

Moatar, F., S.R. Shadizadeh, et al. 2010. "Determination of naturally occurring radioactive materials (NORM) in formation water during oil exploration." Radioanal Nucl Chem **283**: 3–7.

Mondal, S., and S.R. Wickramasinghe. 2008. "Produced water treatment by nanofiltration and reverse osmosis membranes." *Journal of Membrane Science* **322**(1): 162–170.

Mulder, M. H.V. 2003. *Basic Principles of Membrane Technology*. Norwell, Kluwer Academic Publishers.

Murry-Gulde, C. 2003. "Performance of a hybrid reverse-osmosis-constructed wetland treatment system for brackish oil field produced water." *Water Research*, Volume 37, Issue 3, pp. 705–713.

National Research Council (NRC) Committee on Management and Effects of Coalbed Methane Development and Produced Water in the Western United States. 2010. *Management and Effects of Coalbed Methane Produced Water in the United States*. Washington, DC, The National Academies Press.

Natural Resources Conservation Service. 2007. Watersheds, Hydrologic Units, Hydrologic Unit Cose, Watershed Approach, and Rapid Watershed Assessments. United States Department of Agriculture, Natural Resoures Conservation Service.

NETL. "Produced Water Management Technology Descriptions Fact Sheet." Accessed at http://www.netl.doe.gov/technologies/pwmis/techdesc/.

Otton, J. K. 2006. *Environmental Aspects of Produced-water Salt Releases in Onshore and Coastal Petroleum-producing Areas of the Conterminous U.S. – A Bibliography*. U.S. Geological Survey. U.S. Department of the Interior. Reston, Virginia. **Open-File Report 2006-1154**.

Petroleum Technology Transfer Council Enhanced Oil Recovery.

R.W. Harden & Associates, I. 2007. Northern Trinity/Woodbine Aquifer Groundwater Availability Model. Accessed at http://www.twdb.state.tx.us/gam/trnt_t/trnt_n.asp. Texas Water Development Board.

Ranck, J.M., R.S. Bowman, et al. *Removal of BTEX from produced water using surfactant-modified zeolite*. National Ground Water Association.

Rice, C.A., R.M. Flores, et al. 2008. "Chemical and stable isotopic evidence for water/rock interaction and biogenic origin of coalbed methane, Fort Union Formation, Powder River Basin, Wyoming and Montana U.S.A." *International Journal of Coal Geology* **76**(1–2): 76–85.

Rice, C.A., and V. Nuccio. 2000. Water Produced with Coal-Bed Methane. United States Geological Survey. Denver, Colorado, U.S. Department of the Interior. **USGS Fact Sheet FS-156-00**.

Sagle, A.C., E.M. Van Wagner, et al. 2009. "PEG-coated reverse osmosis membranes: Desalination properties and fouling resistance." *Journal of Membrane Science* **340**(1–2): 92–108.

Shaver, E., R.R. Horner, et al. 2007. *Fundamentals of Urban Runoff Management: Technical and Institutional Issues.*

Shepard, M.C., F.L. Shore, et al., eds. 1992. *Characterization of produced waters from natural gas production and storage operations: regulatory analysis of complex matrix*. Produced Water: Technological/ Environmental Issues and Solutions. New York, Plenum Publishing Corp.

Sinker, A. 2007. *Produced Water Treatment Using Hydrocyclones: Theory and Practical Applications*. 14th Annual International Petroleum Environmental Conference, Houston, Texas.

Sirivedhin, T., J. McCue, et al. 2004. "Reclaiming produced water for beneficial use: salt removal by electrodialysis." *Journal of Membrane Science* **243**(1–2): 335–343.

Spellman, F.R. 2003. *Handbook of water and wastewater treatment plant operations*. CRC Press.

Stephenson, M.T. 1992. A survey of produced water studies. *Produced Water*. J.P. Ray and F.R. Engelhardt. New York, Plenum Press. **46**.

Su, D., J. Wang, et al. 2007. "Kinetic Performance of Oil-field Produced Water Treatment by Biological Aerated Filter." *Chinese Journal of Chemical Engineering* **15**(4): 591–594.

Taulis, M. 2007. "Groundwater characterization and disposal modelling for coal seam gas recovery." *Environmental Engineering*. Christchurch, New Zealand University of Canterbury. **PhD:** 334.

Trussel Technologies. 2008. "Desalination Technologies." Accessed at http://www.trusselltech.com/tech_desalination.asp.

Texas Coorperative Extension. 2003. Irrigation Water Quality Standards and Salinity Management Strategies.

Tibbetts, P.J.C., I.T. Buchanan, et al. 1992. "A comprehensive determination of produced water composition." *Produced Water*. J.P. Ray and F.R. Engelhardt. New York, Plenum Press. **46**.

United States Army Corps of Engineers. 2001. *Engineering and Design: Air Stripping*. Design Guide No. 1110-1-3.

United States Energy Information Administration. 2007. *U.S. Coalbed Methane Past, Present, and Future*. U.S. Energy Information Administration.

USEPA. 1980. Onsite Wastewater Treatment and Disposal Systems Design Manual. EPA. Washington, DC, U.S. Environmental Protection Agency. **EPA/625/1-80-012**.

USEPA. 1991. *Assessment of Single Stage Trickling Filter Nitrification*. Washington DC, EPA Office of Water. **EPA 430/09-91-005**.

USEPA. 2000. "Profile of the Oil and Gas Extraction Industry." *EPA Office of Compliance Sector Notebook Project* **EPA/310-R-99-006**.

USEPA. 2010. "Hydraulic Fracturing." Accessed at http://water.epa.gov/type/groundwater/uic/class2/hydraulicfracturing/wells_hydrowhat.cfm.

USEPA. (2010). "Hydraulic Fracturing Research Study." *EPA/600/F-10/002*. Accessed at http://www.epa.gov/safewater/uic/pdfs/hfresearchstudyfs.pdf.

USGS. 2002. Produced Waters Database. U.S. Department of the Interior.

USGS. 2005. "Water Use in the United States."

Van Voast, W. A. (2003). "Geochemical signature of formation waters associated with coalbed methane." *AAPG Bulletin* **87**(4): 667–676.

Veil, J. "Produced Water Management Technology Descriptions." Accessed at http://www.netl.doe.gov/technologies/pwmis/techdesc/physep/index.html.

Veil, J.A. "Produced Water Management Information System, Fact Sheet - Industrial Use."

Veil, J.A., M.G. Pruder, D. Elcock, R.J. Redweik, Jr. 2004. A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane, Department of Energy, National Energy Technology Laboratory.

Wagner, K. et al.. 1986. *Remedial Action Technology for Waste Disposal Sites*, William Andrew Inc.

Wallace, B. 2005. *Project Example: Wellington Water Works - Production Water Reuse*. FIDIC Annual Conference, Beijing, China.

Zielinski, R.A., and J.K. Otton. 1999. *Naturally Occurring Radioactive Materials (NORM) in Produced Water and Oil-Field Equipment — An Issue for the Energy Industry*. USGS.