RCSP
Regional Carbon Sequestration Partnerships
Water Working Group

PLAINS CO_2 REDUCTION (PCOR) PARTNERSHIP PHASE III – TASK 14: REGIONAL CARBON SEQUESTRATION PARTNERSHIP WATER WORKING GROUP WHITE PAPER ON THE NEXUS OF CARBON CAPTURE AND STORAGE AND WATER

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EXECUTIVE SUMMARY

Carbon capture and storage (CCS) are promising technologies that have the potential to drastically reduce anthropogenic carbon dioxide (CO_2) emissions into the atmosphere. In 2003, the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) established the Regional Carbon Sequestration Partnership (RCSP) Program, the goal of which is to develop the infrastructure, regulations, and technology for large-scale CCS from a regional perspective. The program comprises seven regional partnerships that encompass nearly all of the U.S. power- and industry-related carbon emission sources as well as nearly all of the nation's potential geologic storage. In order to investigate the relationship between water and CCS, members of the RCSPs have formed the Water Working Group (WWG). Each RCSP has its own unique set of challenges related to water utilization and the implementation of CCS activity, and the WWG will help to address those concerns. The goal of this white paper is to summarize the influence CCS is expected to have on water issues and the influence of water issues on CCS.

The CCS process comprises the capture of CO_2 gas at large stationary sources such as fossil fuel-based power plants and the subsequent injection of the captured CO_2 into depleting/depleted oil and gas reservoirs, deep saline formations, or unminable coal seams. Large stationary sources are preferred because of the large volume of CO_2 that is produced on-site and/or the concentration of CO_2 present in their flue gas streams. CO_2 capture may be carried out through a variety of processes that are optimized for specific types of fuel and combustion processes. They can be generally classified as precombustion, where carbon species are chemically separated from a fuel prior to combustion; postcombustion, where carbon-containing species are separated from the combustion waste gas, typically with chemical or physical solvents; and oxycombustion, in which the fuel is combusted in a nearly pure oxygen environment, producing a flue gas with a very high concentration of CO_2 that requires little purification. Once captured, it is necessary to compress the CO_2 to a supercritical state to allow for efficient transport and storage. The supercritical fluid is then transported, typically via pipeline, to the storage site and injected into a storage formation.

Water is of utmost importance in every step of the CCS process, from the industrial sources where CO_2 is generated to long after the CO_2 is injected into the ground. Water is relied upon heavily for cooling, especially in power generation facilities, but is also needed for other processes, such as boiler operation and during the regeneration of solvents used during CO_2 capture. Each technique for capture and compression may require water for cooling the additional equipment and for makeup water in the various processes. Currently, a majority of the water used by power plants is provided by surface water and groundwater resources which face competition from agricultural and municipal uses across the United States. The additional water load required for CCS may be problematic or require other solutions in water-stressed areas.

New technological developments in capture and compression technologies also promise to reduce the impact of these technologies on increasing water demand.

CO_2 may be stored through injection into three primary types of formations: depleting/depleted oil and gas reservoirs, saline formations, and unminable coal seams. When injected into oil and gas reservoirs as well as saline formations, the gas permeates the rock and occupies a portion of the pore spaces while at the same time dissolving into the formation fluids. If one of the formation fluids is oil, dissolved CO_2 can reduce the viscosity and improve the volumetric properties of the hydrocarbon, which aids in its extraction, a process known as CO_2 enhanced oil recovery (EOR). The most common form of CO_2 EOR is known as the water alternating gas (WAG) method in which slugs of CO_2 are injected into the oil reservoir followed by larger alternating slugs of water. The water slugs push or drive the oil liberated by CO_2 toward the extraction well where all three fluids are separated and the water and CO_2 are reused. In this way, recycled and remaining source CO_2 can be stored in the reservoir once EOR operations are completed.

When CO_2 is injected into a deep saline formation, the supercritical CO_2 plume will displace the formation fluids and rise until it contacts the bottom of the cap rock (top of the storage formation), as it will be less dense than the saline formation water. The plume will first be trapped through physical traps and residual gas-trapping mechanisms. Then solubility trapping will occur over thousands of years as the CO_2 dissolves into the formation water. As the CO_2 dissolves, the formation water’s pH will be altered, allowing for the possibility of mineral dissolution, mobilization, and precipitation. These processes must be carefully modeled to assess a formation’s CO_2 storage capacity and security.

CO_2 may also be stored through the practice of enhanced coalbed methane (ECBM) recovery, whereby the production of methane gas from unminable coal beds can be improved. To produce CBM, the coal seam is depressurized by reducing the hydrostatic pressure within the coal, a process known as dewatering. First water and then methane gas are produced from this process. The produced water is often of high quality and, in many cases, may even be potable or usable for agriculture. When gas production drops, CO_2 may be injected to stimulate gas production as CO_2 is preferentially adsorbed onto the surfaces of the coal, liberating additional methane. If properly managed, CO_2 may be stored in the coal seams once methane extraction is completed, although this remains an area of continuing research.

In all cases, once injected, the CO_2 may become a reactive substance. It rapidly dissolves in formation water forming carbonic acid (H_2CO_3), reducing the formation fluid’s overall pH. Consequently, the dissolution of minerals or engineered materials (e.g., well metal casing and cements) may occur, and the chemical composition of the formation water may be altered. When properly designed and engineered to industry standards, negative effects can be mitigated. These same reactions in the long term remove free-phase CO_2 from the formation, eventually trapping it through dissolution and mineral-trapping mechanisms, which offer much higher storage security. Therefore, it is important to take into consideration the potential for future use of the water within the formation suggested for CO_2 injection, and as a result, injection of CO_2 into potentially usable sources of drinking water is prohibited, as described by the U.S. Environmental Protection Agency (EPA) Underground Injection Control (UIC) Program.

Large amounts of water are typically removed from oil and gas pools as a result of normal oil and gas operations, as water commonly coexists with oil and gas in the subsurface. This water, frequently referred to as produced water, can have salinity concentrations that exceed 300,000 ppm total dissolved solids (TDS), much higher than the average TDS concentrations of seawater, which is approximately 35,000 ppm. Common dissolved constituents in produced water include salts, hydrocarbons, and dissolved organics. Produced water can have an adverse effect on surface and groundwater resources, so care is required in its handling and disposal. The majority of produced water is either reinjected into the formation from which it was produced or into another deep saline formation. Water produced from oil fields may also be reused in other oil production activities, such as secondary oil recovery (waterflood), WAG, or hydrofracturing treatments. Such recycling is not uncommon in oil fields located in regions of the country where there is limited access to additional water resources. In all water disposal cases, regulations already exist for the safe reinjection of produced fluids from oil and gas production, and EPA has proposed new regulations to manage injections associated with large-scale CCS activities.[1] Individual states are also moving forward with their own sets of regulations to accommodate future CCS projects.

When CO_2 storage is combined with EOR or ECBM recovery operations, water will likely be produced as part of the hydrocarbon recovery process. In current oil and gas operations, this water is typically separated and reinjected, resulting in the majority of the water being recycled to the formation. When the quality of produced water is such that surface reuse is advantageous, it may be part of the overall CCS strategy to intentionally produce water. CO_2 storage in deep saline formations does not require the production of water, although there may be circumstances where the production of water is beneficial to the overall CO_2 storage strategy. Water may be produced to increase the storage capacity, reduce formation pressure, or control free-phase CO_2 movement. The simplest management option for produced water is to minimize production, but if production of water is necessary, subsurface reinjection is the most direct disposal option. Reinjection activities are regulated through the UIC Program,[2] which provides rules and guidelines for determining where produced waters may be reinjected and controls on the construction and operation of the reinjection wells. In conjunction with state and local regulators, UIC’s regulations protect underground sources of drinking water from unintentional contamination. Beneficial use of CCS produced water may also be a cost-reducing or even energy-offsetting option and should be considered on a case-by-case basis. Potential for reuse will be determined primarily by the quality of the CCS produced water and local water demand.

Produced water from CCS activities has many potential surface applications, although it may contain many constituents that may require treatment prior to use such as unacceptable concentrations of salt, trace metals, hydrocarbons, and dissolved organics. A variety of treatment processes exist that are applicable to produced water, notably reverse osmosis, ion exchange,

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[1] U.S. Environmental Protection Agency Office of Water, 2008, EPA proposes new requirements for geologic sequestration of carbon dioxide: EPA 816-F-08-032, p. 3, www.epa.gov/OGWDW/uic/pdfs/fs_uic_co2_ proposedrule.pdf (accessed July 2009).

[2] U.S. Environmental Protection Agency, 2008, Oil and gas-related injection wells (Class II), www.epa.gov/safewater/uic/wells_class2.html#additional (accessed June 2009).

thermal desalinization mechanical vapor recompression, and innovative treatment technologies such as freeze–thaw/evaporation and constructed wetland treatment. The utility of these and other processes will vary, depending on the quality of the produced water input and the required quality of the treated water output, as the costs are highly dependent on the application.

A broad range of potential produced water applications exist for beneficial use, from nearby oil field operations to treatment and use for supplemental drinking water. Oil field applications include use for waterflooding and hydraulic fracturing. A variety of industrial processes may benefit from the use of CCS produced waters, such as use in power plant cooling, wood and pulp production, textile and tannery processes, chemical production, and cement production. Produced water may also have applications for geothermal power generation, as recent technological advances have lowered the minimum required temperature of geothermal fluids. Agriculture and livestock production may also benefit from the availability of produced water, particularly in arid regions, as the water quality requirements of crops and livestock are typically less than those for human consumption. Finally, CCS produced water may also be of such quality (with or without treatment) that it may be utilized for artificial recharge of aquifers that provide drinking water or to protect such aquifers from saltwater intrusion.

RCSP Regional Carbon Sequestration Partnerships
Water Working Group

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INTRODUCTION

The U.S. Department of Energy’s (DOE) National Energy Technology Laboratory (NETL) has been developing the technology, infrastructure, and regulations to implement large-scale carbon capture and storage (CCS) from a regional perspective through the resources of its Regional Carbon Sequestration Partnership (RCSP) Program, which consists of seven regional partnerships. Members of these partnerships have formed the Water Working Group (WWG), whose goals are to address the concerns of the public and industry regarding CCS technology and its potential relationships with water resources. Members of the WWG represent different regions of North America, and each region has its own unique set of challenges surrounding water resources and CCS. For example, the implementation of CCS technology has the potential to increase the withdrawal and consumption of water at the site of carbon dioxide (CO_2) generation through the use of additional equipment and technology. At the site of geologic carbon storage in deep underground formations, however, impacts on water supplies will likely be minimal since most storage activities will occur in formations much deeper than those typically utilized for potable water supplies. Furthermore, a regulatory framework established by the U.S. Environmental Protection Agency (EPA) presently exists that protects all surface and underground sources of drinking water (USDW) from potential pollution. CCS activity will be required to operate within this framework, as careful implementation of all environmental regulations is paramount to the overall vision and ultimate success of CCS programs.

Water is an important factor at every step of the CCS process. Many industrial sources of CO_2, including power generation facilities, already use large volumes of water every day. The implementation of CCS will impact this water requirement, often increasing it. Carbon capture processes and technologies have a variety of water requirements depending on their size and type, and water may also be used for interstage cooling during CO_2 compression. Furthermore, carbon capture technologies will impose a parasitic load on power facilities, which may also increase the volume of water used for cooling and other plant processes. As CCS technology is implemented, stakeholders may need to consider water-conserving practices and processes, such as air-cooling, particularly in water-stressed regions.

Water is also an important factor for geologic storage. Water is routinely produced in conjunction with the production of oil and gas. This process is nearly unavoidable, as the liquids regularly coexist in underground formations. Often this produced water has high concentrations of dissolved solids including salts and other constituents that make it unfit for consumption. As a result, strategies and technologies for managing these waters have been developed by the oil and gas industry and have been implemented for decades. These strategies include the reinjection of water into deep underground saline formations and various water treatment methods that may allow the beneficial use of the CCS produced water. During the storage phase of CCS activities, there may be circumstances in which the production of water from storage formations is beneficial if not necessary. In these situations, the same strategies that have proven successful for managing water produced from oil and gas production can and will be applied to the water produced from CCS activities. This affords both the protection of drinking water sources and the opportunity for water reuse. For example, in some locations it may be possible to utilize the water produced from underground formations to satisfy the additional water demand necessary for the implementation of CCS technology. This report summarizes the processes and technologies of CCS that pertain to water usage, describes the types of water that exist in deep formations targeted for storage, and describes the likely impacts of CO_2 storage on existing formation fluids as well as potable water resources. The treatment technologies that may be applied to water produced from these deep formations during CO_2 storage are also addressed, and finally, opportunities to utilize produced water resources are described.

BACKGROUND

Terms and Definitions

The terms and definitions used in this report pertaining to water quality and industry terminology or concepts are presented in this section.

Water Quality Classification

Water quality is a property of water pertaining to the combination of total dissolved solids (TDS), turbidity, hardness, pH, sodicity, organics, dissolved metals, radioactive compounds, etc., that define the uses available or treatments required to make the water usable. For the purposes of this paper, water quality is broken up into four categories (Figure 1): potable water, protected water, saltwater, and brine.

Potable water **–** Water that is safe and suitable for human consumption and cooking as defined by local health officials, generally containing under 500 ppm TDS (modified from U.S. Department of Energy Energy Efficiency and Renewable Energy, 2009, and U.S. Environmental Protection Agency, 2008b, c). Local regulations may vary.

Protected water – Water with TDS up to 10,000 ppm that is protected by the Safe Drinking Water Act (SDWA) as potentially usable for applications including human consumption after treatment.

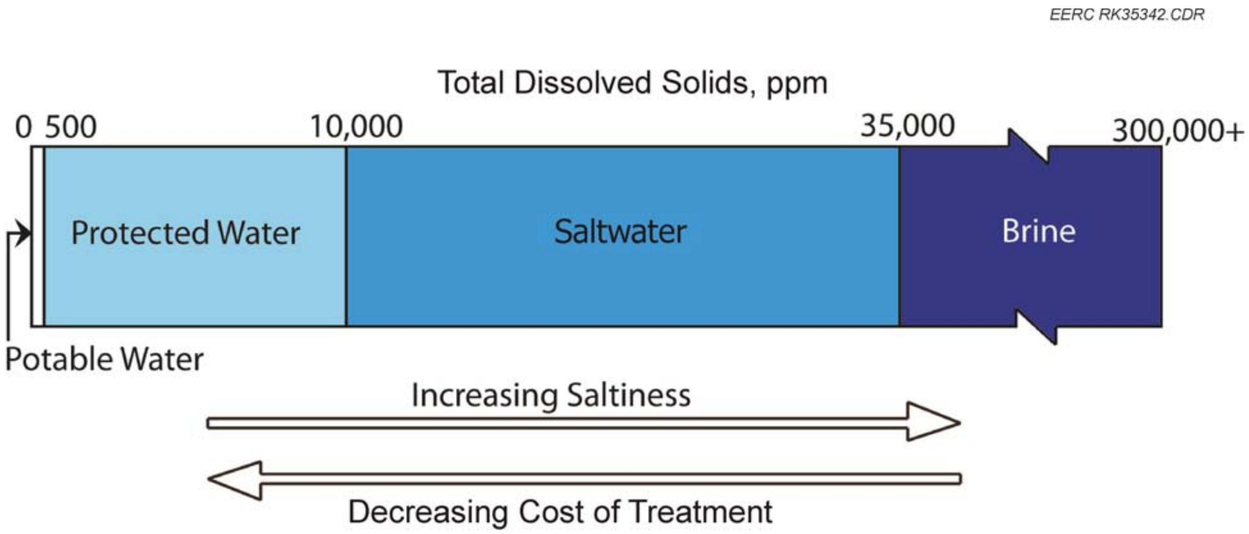


Figure 1. Relative salinity and ranges for water quality categories.

Saltwater – Water with salinity approaching ocean water, with salinity between 10,000 and 35,000 ppm TDS. This water is potentially usable in desalinization applications using current technology but at a greater cost than less saline protected water. Water in this range is occasionally referred to as brackish.

Brine – Natural formation fluids consisting of water that has been enriched in various salts, especially sodium chloride, at concentrations greater than 35,000 ppm TDS and may contain over 300,000 ppm TDS (modified from U.S. Environmental Protection Agency, 2008b, and U.S. Department of Energy Energy Efficiency and Renewable Energy, 2009).

Industrial Terms

Beneficial use – A concept wherein one aims to take advantage of an opportunity (a benefit) by utilizing part or the entirety of a waste product before disposal. Some examples include dust control, harnessing the heat from produced water in a binary turbine to produce electricity before reinjection, or applying minor treatments to the water for agricultural use. Beneficial use reduces demands on valuable groundwater supplies that are used for drinking water and irrigation, helps reduce pollutant loading in surface waters, postpones costly investments for development of new water sources, allows multiple uses of land, and can reduce costs (New Jersey Department of Environmental Protection, 2005).

Carbon capture and storage – A process involving the capture of CO_2 from large stationary sources and subsequent storage in geologic formations in lieu of venting the gas to the atmosphere. The CO_2 then is compressed and transported to an injection site, or “sink,” where it is stored indefinitely. CCS also covers enhanced oil recovery (EOR) and enhanced gas recovery (EGR) operations, where CO_2 is put to the beneficial reuse of increasing production in oil and gas reservoirs while simultaneously being stored.

Produced water – Water or brine that has been brought to the surface through mineral or resource extraction activities, such as oil, gas, or coalbed methane (CBM). This term also applies to water removed from a formation to increase the storage effectiveness of the pore space and, therefore, capacity. Depending on the circumstances, especially water quality and temperature, produced water may be put to a number of beneficial uses.

Saline formation – Also known as a brine formation, which is an underground geologic unit containing saltwater or brine as the primary pore fluid. Saline formations are considered to represent a substantial storage resource worldwide because of their size, properties, and prevalence and have been used to store CO_2 in the subsurface on a large scale.

Water withdrawal – A volume of water removed from a source, either surface or subsurface, which is utilized by humans. This refers to the gross amount of water extracted, either temporarily or permanently from a given source. When considering water withdrawals for power plants, it is important to note that the total amount of water withdrawal required for a given power plant must be available for a plant to operate at full capacity, regardless of whether or not the water is returned to its source. In times of stressed water supply, the ability to withdraw water, and the associated power production capacity, may be limited (Kimmell and Veil, 2009) (compare to *water consumption*).

Water consumption – The portion of withdrawn water that is evaporated, transpired, or incorporated into products or crops (U.S. Geological Survey, 1998). This water is, therefore, permanently removed from its source (compare to *water withdrawal*).

Underground source of drinking water – Defined as an aquifer or its portion that contains potable or treatable water (with a TDS content of less than 10,000 ppm) as the primary pore fluid and serves as a source of drinking water for human consumption or contains a sufficient quantity of water to supply a public water system (U.S. Environmental Protection Agency, 2008b, c).

Enhanced oil recovery – A variety of practices used to increase the production of oil from a reservoir. Typically, these practices are employed when the reservoir is considered depleted using pumping (primary) or waterflood (secondary) processes. When EOR is combined with CCS, supercritical CO_2 is used to stimulate oil production while simultaneously storing injected CO_2. The CO_2 may become miscible with oil, reducing its viscosity, increasing its volume, and increasing its rate of flow toward production wells. The most common form of EOR utilizing CO_2 is the water alternating gas (WAG) method, where alternating slugs of CO_2 and water are used to push oil toward production wells (Figure 2). If engineered for storage, CO_2 will remain trapped in the reservoir once oil recovery diminishes. This practice is predominantly utilized in the western states.

Enhanced coalbed methane (ECBM) recovery – A process that utilizes CO_2 to increase the production of methane naturally adsorbed onto the surfaces of unminable coal seams. The CO_2 is preferentially adsorbed onto the surface of the coal, liberating additional quantities of methane gas. Water production associated with traditional CBM recovery is very high. The additional

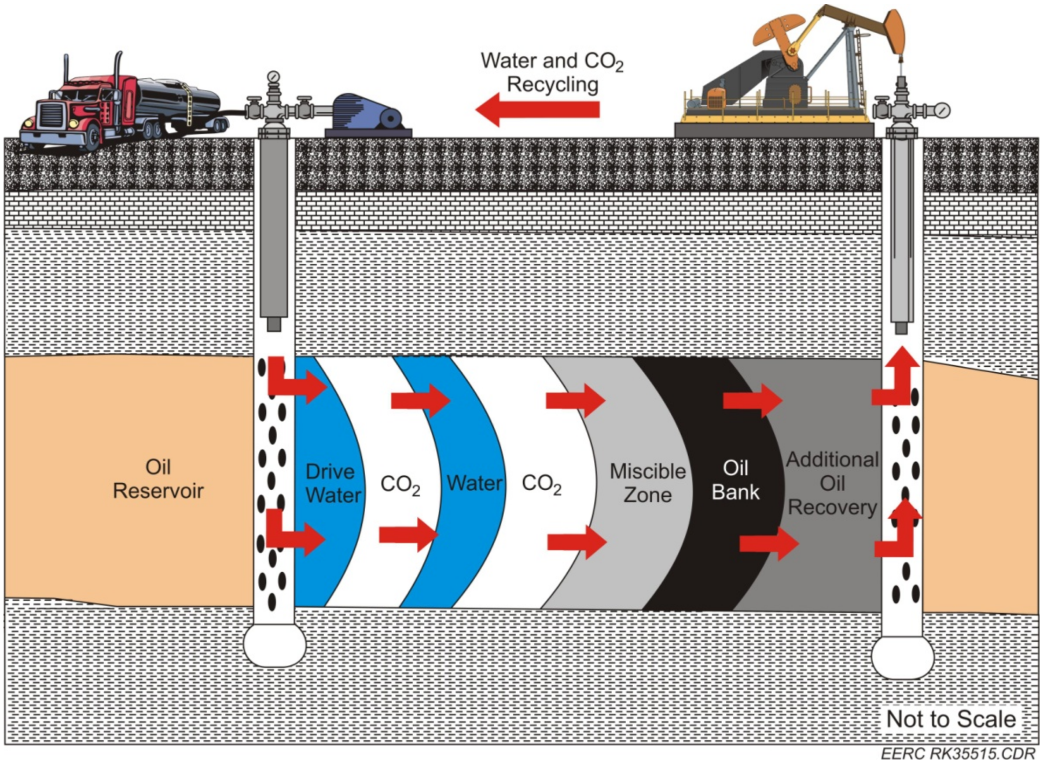


Figure 2. The WAG method liberates additional oil from the pore space of a reservoir by injecting CO_2 at a pressure greater than the minimum miscibility pressure, allowing the CO_2 to lower the oil's viscosity and increase its volume. Water or CO_2 recovered from the pumping well is recycled back into the injection well.

practice of ECBM is not expected to increase water production significantly above these volumes. When used independently of traditional methods, ECBM production may reduce the total volume of produced water, although physical and chemical reactions such as the swelling of the coal may reduce the effectiveness of this method without careful management. ECBM has been tested extensively in the United States and elsewhere.

Overview of CCS

CCS is a promising set of technologies with the potential to prevent large quantities of anthropogenic greenhouse gases from reaching the atmosphere. The CCS process begins at large stationary sources such as power generation facilities, which produce roughly one-third of U.S. emissions (U.S. Department of Energy, 2009b). The captured gas is dehydrated, compressed, and transported to a suitable target formation where it is injected into depleting/depleted oil or gas reservoirs, deep saline formations, or unminable coal seams.

A suitable target formation is a rock unit that possesses the necessary formation properties of porosity, volume, permeability, injectivity, pressure, temperature, and mechanical integrity to safely accept and contain the expected amount of injected CO_2. The formation must possess a sealing unit (of sufficient thickness, mechanical integrity, and sufficiently low permeability) that will limit or prevent upward migration of the injected CO_2. Thirdly, the formation or its fluids must not be otherwise protected or regulated from CCS activities. In oil and gas reservoirs and saline formations, it is strongly recommended that the chosen formation is at a sufficient depth so that the temperature and pressure are high enough to ensure the injected CO_2 remains in a dense liquid or supercritical state. This greatly increases the storage efficiency and, therefore, the capacity of the formation.

Hydrocarbon reservoirs in particular are highlighted for their potential storage resource because of their proven ability to store oil and gas for millions of years, as well as the possible economic incentives offered through EOR and ECBM. Injected CO_2 may be miscible in oil, which increases the fluid volume and reduces the viscosity, both of which aid in oil production. Deep saline formations do not offer similar traditional economic incentives; however, they are more widespread, which can reduce the cost of transportation. Deep saline formations also possess the highest potential capacity because of their size and prevalence. The development of carbon credit-trading markets will likely provide an economic incentive for storage in deep saline formations.

Saline formations are underground rock units that contain saltwater or brine as the primary pore fluid: a mixture of water and various salts. Brines can exist with TDS exceeding 300,000 mg/L or ppm; this is almost ten times saltier than ocean water, which is typically 35,000 ppm. The minimum TDS of a saline formation for CO_2 storage is 10,000 ppm in order to protect potentially usable USDW (U.S. Environmental Protection Agency, 2008d). Storing CO_2 in saline formations does not require the production of brine, although it may become an option in certain cases where site-specific variables favor brine production to reduce reservoir pressure or to control CO_2 plume movement. If brine production is required, proper disposal or treatment represents an additional cost to the project. In the United States, brine disposal is extensively regulated by the EPA Underground Injection Control (UIC) Program and is a well-known process in the oil industry, where currently over 144,000 wells inject approximately 2 billion gallons of brine daily (U.S. Environmental Protection Agency, 2008a).

Unminable coal seams have the ability to store CO_2 using different mechanisms, relying on the adsorption of CO_2 molecules onto the surface of the coal rather than storage in pore space as in hydrocarbon reservoirs and saline formations. Total storage estimates of unminable coal seams have lower capacities when compared to hydrocarbon reservoirs and saline formations but may offer economic incentive by using CO_2 for ECBM production. In ECBM, methane is liberated from productive coal when exposed to CO_2 as a result of preferential adsorption. If ECBM activities are initiated early in production, efficiency of the well may increase, potentially decreasing the amount of produced water over the life of the well.

Currently, 100 CO_2 EOR projects are operating in the United States and Canada (Moritis, 2008). Among the largest CO_2 EOR efforts currently operating are those in the Permian Basin oil fields of West Texas, the Weyburn and Midale Fields in Saskatchewan, Canada, and the more recent projects along the U.S. Gulf Coast. While total volumes of CO_2 injected into the Permian Basin oil fields may be larger, EnCana's Weyburn project remains the world's largest project that has been optimized for long-term geological storage of CO_2 (Shell Media, 2008). A majority of produced water in oil production is reinjected, including waterflood recycling. A smaller percentage of oil and gas produced water is being put to various beneficial uses and will be discussed later in this document. CO_2 is also injected into saline formations in commercial and demonstration projects, most notably the Sleipner project in the Norwegian portion of the North Sea, which has been injecting 1 MT of CO_2 per year from natural gas processing since 1996 (Arts and others, 2008). To date, no saline formation injection project has required water production.

Water Issues Associated with CCS

The water issues associated with CCS revolve primarily around water usage at CO_2 sources and water production at CO_2 storage sites (Figure 3). The capture phase of CCS requires water for the cooling of equipment used during the separation and compression processes, as well as for the regeneration of chemical and physical solvents/sorbents and related processes. Depending on the type of compressor chosen, water may also be used for interstage cooling. These water requirements are in addition to the already large amount of water typically needed for power generation. The amount of additional water and energy required for CCS depends greatly on the design and size of the system.

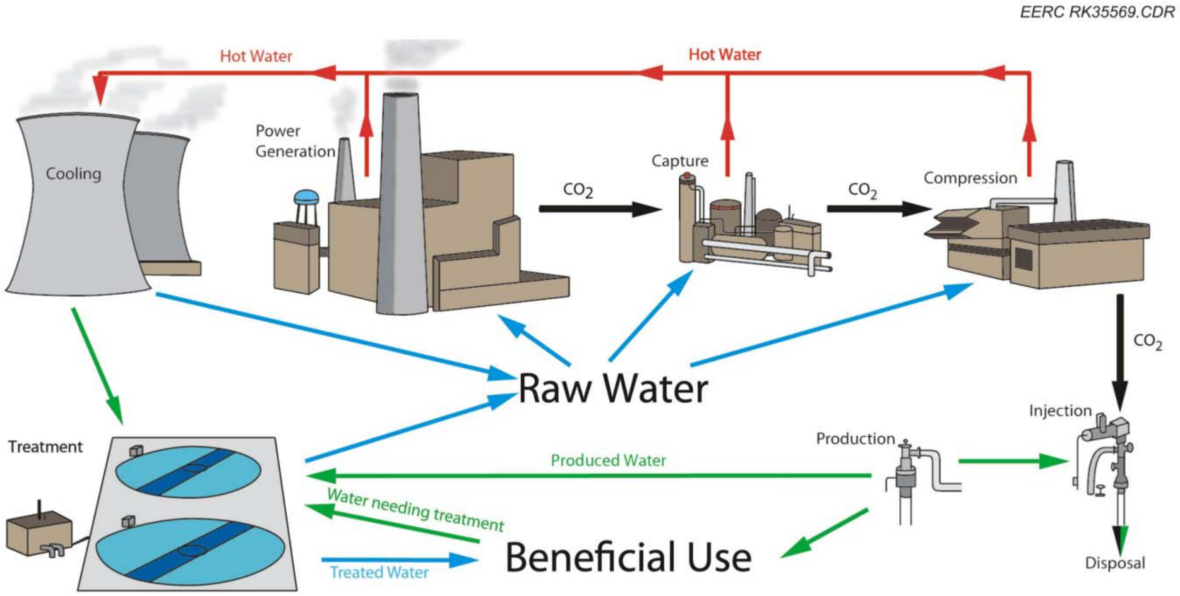


Figure 3. The nexus of CO_2 and water results in water usage at carbon sources and potential production and beneficial use near storage sites. Blue arrows represent water withdrawn from surface water or groundwater sources. Blue arrows also represent water which may be returned to the original or related source. Red arrows represent hot water sent to cooling facilities. Black arrows represent the flow of CO_2 through the system. Green arrows represent water requiring some management strategy.

During the storage phase of CCS, the primary water concern is the volume and quality of water produced, if any, from storage activities. Presently, large amounts of water are produced by the oil and gas industry in the form of formation water that coexists with the hydrocarbons in the reservoir. Valuable hydrocarbons are separated out, and the remaining water is reinjected into the reservoir or into a separate saline formation. If economically viable, the produced water can be used directly or treated to remove salt and hydrocarbon residues and put to various uses such as agriculture, power generation, steam generation, industrial processing, or human consumption (Hum and others, 2006). Water injected for EOR or for disposal of oil field produced water is regulated as Class II injection wells by EPA's UIC Program. Injection of oil field produced water is often necessary, since the dissolved substances in brine are a potential hazard to surface water and shallow groundwater resources (U.S. Environmental Protection Agency, 2008a). Reinjection is the most commonly employed disposal method for produced water, which involves pumping the fluids back into the formation from which they originated or into a formation with similar reservoir characteristics and water quality (U.S. Environmental Protection Agency, 2008a). This maximizes the rate at which produced liquid can be disposed of while simultaneously minimizing aboveground interaction and potential for accidental release. UIC regulations for injection wells require strict adherence to standards for construction, monitoring, and inspection.

THE CONNECTION BETWEEN WATER AND CAPTURE, COMPRESSION, TRANSPORTATION, AND INJECTION

Large Stationary Point Sources of CO_2 Emissions

Stationary sources of CO_2, such as power generation and industrial plants, account for roughly 60% of total global CO_2 emissions (Metz and others, 2005) and 62% of total U.S. emissions in 2007 (U.S. Environmental Protection Agency, 2009a). Near-term opportunities are likely to focus on facilities that produce relatively pure CO_2 streams, such as ethanol plants, ammonia plants, and gas-processing facilities. The facilities that produce the largest quantities of CO_2 (electricity-generating stations and some industrial plants) typically produce it as a high-volume but relatively dilute stream. Flue gas typically contains high amounts of nitrogen and other atmospheric gases, resulting in the need for bulk CO_2 separation (Metz and others, 2005). The resources needed for CO_2 separation, compression, and transportation require an initial investment in equipment and infrastructure that makes the capture of small sources of CO_2 uneconomical and inefficient. Numerous capture technologies are in the commercial or demonstration phase. New facilities can be constructed including a capture technology, but most are of capture-ready design, most notably in the power generation sector. Capture-ready means that the facility has included the footprint and piping, wiring, and water needs of a capture plant in its design but has not constructed it. These additions will significantly impact the cooling water requirements and associated water consumption of point sources and must be matched with the appropriate cooling processes.

Power Generation

Coal-Fired Power Stations

Pulverized Coal (pc) Steam Plants

The most common form of power generation is the pc boiler, which produces a subcritical, supercritical, or ultrasupercritical supply of steam that, in turn, runs a turbine. Atmospheric air is used in the combustion process, which produces a flue gas with 3%–15% CO_2 (Metz and others, 2005). These plants are candidates for postcombustion separation, where the CO_2 is separated from the flue gas at low pressures. On average, pc steam plants consume the highest volume of water per megawatt of electricity produced among all fossil fuel-based power plants (Gerdes and Nichols, 2009). The additions of carbon capture (CC) systems could potentially double this water consumption, as the additional equipment will also require large amounts of water for cooling (Gerdes and Nichols, 2009). The increase in cooling needs comes from the need for replacement generation of power used for the capture and compression processes as well as cooling both the capture and compression processes themselves. Additional water will also be directly consumed in the capture process (Figure 4).

Integrated Gas Combined Cycle (IGCC)

The IGCC plant utilizes precombustion separation, where the carbon-rich fuel is processed into CO_2 and hydrogen gas using high-pressure steam. Hydrogen serves as the carbon-free energy medium and is combusted in a primary gas turbine. Heat is recovered from this combustion and is then used to power a secondary steam turbine (hence, combined cycle). The pressurization needed for the gasification process has the ability to produce pressurized CO_2 at concentrations of 15%–60%, eliminating some of the energy burden of compression (Metz and others, 2005). Water consumption of an IGCC plant is roughly 60% of pc plants, but the addition of CC systems will still increase water consumption by 35%–45% (Gerdes and Nichols, 2009) (Figure 4). This savings is largely the result of the ability to use a physical absorbent to capture CO_2 that requires less energy (and, therefore, water) to regenerate (Gerdes and Nichols, 2009).

Oxyfuel

An emerging technology, oxyfuel power plants separate oxygen from the air by cryogenic distillation or other means and, in turn, burn coal in a stream that is void of nitrogen, resulting in a flue gas with greater than 80% CO_2. Secondary separation activities, including removal of water vapor and minor amounts of sulfur and nitrogen oxides, yield a stream of 95%–99% pure CO_2 (Metz and others, 2005) (Figure 4). As a result of the high CO_2 stream purity, the overall water consumption penalties of CC are relatively low in this case (Rao, 2007).

Gas-Fired Power Stations

Natural gas combined-cycle plants also produce electricity directly via a gas turbine and then harvest the heat from combustion to run a secondary steam turbine. This process is highly

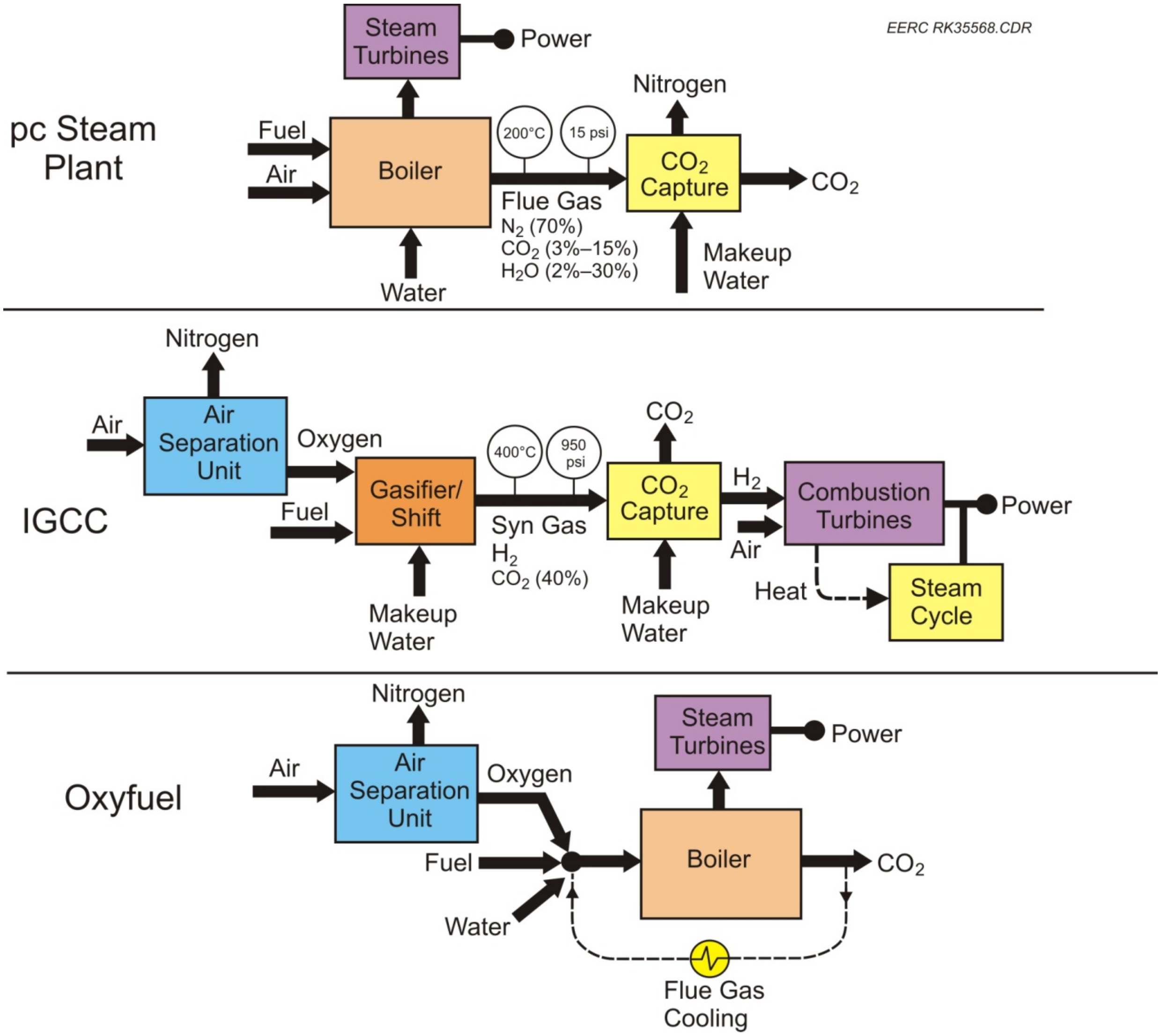


Figure 4. Generalized process schematics of the three common coal-burning power plant configurations. The largest water-consuming processes are cooling makeup water (including the cooling needed for replacement power generation as a result of the parasitic load at the capture systems, which is not pictured), boiler feedwater, gasifier feedwater, and CO_2 capture makeup water.

efficient overall, consuming the least amount of water per kilowatt (Klara, 2007), but it produces a low-concentration CO_2 stream, typically only 3%–4%. Because of the low pressure and concentration of the CO_2, chemical absorption is the most likely capture technology. New plants with CCS technology may increase water consumption by 80% or more over a similar plant without such technology because of decreases in efficiency of the plant and the increased water demand of the process equipment (Gerdes and Nichols, 2009).

Oil-Fired Power Stations

Oil-fired power stations typically generate electricity in a similar fashion to a coal plant via a boiler and steam turbine, or the combustion gases turn the turbine directly. An oil-fired plant may also utilize a gasification process that would allow for precombustion separation (Metz and others, 2005). In any case, these plants represent approximately 1% of U.S. power generation (Energy Information Administration, 2009) and can generally be assumed to have similar CO_2 output to and water consumption characteristics of a similarly sized coal-fired counterpart.

Non-Power-Generating Sources

Outside the power generation industry, several sources of CO_2 emissions have been identified by either the bulk amount of CO_2 they generate or the purity of their CO_2 stream. These tend to be on a different scale of CO_2 production than power generation but remain under the definition of large point sources of emissions with the ability to capture CO_2. Currently, oil refineries and natural gas-processing plants provide a large portion of the CO_2 used for EOR or saline formation demonstration projects, including the Sleipner, In-Salah, Snohvit, Gorgon, Weyburn–Midale, Rangely, and Salt Creek projects.

Additional sources of CO_2 include cement kilns, paper and pulp mills, iron and steel plants, and petrochemical facilities that consume fossil fuels as feedstock, specifically ammonia, ethylene, ethylene oxide, and hydrogen production facilities (Metz and others, 2005). In most cases, the output CO_2 stream is relatively dilute. Ethanol, ammonia, and ethylene oxide producers, which generate a pure CO_2 waste stream, account for a small fraction of total CO_2 emissions (Metz and others, 2005). Water consumption is also high in some of these processes. For example, ethanol plants consume approximately 2 to 6 gallons of water for each gallon of ethanol produced, depending on the type of ethanol (cellulosic or corn) and production method. The majority of process water is recycled, so most of the water consumption is a result of water makeup for cooling towers and boilers (Aden, 2007). This is in addition to any water used to irrigate the corn crop, which can consume from 5 to over 2000 gallons of water per gallon of ethanol produced, depending on the region of the country in which the corn is produced (Chiu and others, 2009). For comparison, petroleum refining, which also recycles the vast majority of its process water, consumes approximately 2–2.5 gallons of water per gallon of gasoline produced, although this ratio is lower if it includes all refined products (Aden, 2007). The addition of CCS technology will increase the overall water demand of these facilities. Nevertheless, the implementation of emission limits may eventually dictate CC utilization at these point sources.

CC Technologies Matched to CO_2 Sources

CC technology applications can be divided into three types: those that are amenable to application on postcombustion, precombustion, and oxycombustion CO_2 sources. Postcombustion CO_2 capture applies mainly to conventional coal-fired power generation but may also be applied to combustion turbines fueled by natural gas. Precombustion technology is a process whereby fossil fuel is gasified, producing a CO_2 waste stream that can be readily captured prior to combustion of the gasified fuel. With oxycombustion, coal is burned in pure oxygen instead of in air, with resulting exhaust containing essentially only CO_2 and water vapor. Because it yields a nearly pure CO_2 stream that is readily transportable, the process has strong potential; however, it remains energy-intensive because of the need for on-site oxygen separation processes (Rao, 2007).

Chemical Absorption

Postcombustion capture of CO_2 occurs predominantly through the use of chemical absorbents, typically monethanolamine (MEA)- or methyl-diethanolamine (MDEA)-based solvents or ammonia. A variety of amine-based scrubbing technologies are presently available on the commercial market. These processes typically consist of an absorber in which CO_2 is scrubbed out using a chemical absorbent. The CO_2-rich fluid flows to a stripper where heat is used to break the bonds between the CO_2 and the absorbent. The regenerated solvent is then fed back into the absorber (Reddy and others, 2003). Proprietary additives and techniques provide a range of process efficiency and flexibility.

Chemical absorption requires cooling of the flue gases prior to entering the absorber as well as heating of the CO_2-rich amine stream during stripping and subsequent cooling of the CO_2-lean amine stream after the stripping phase. These latter two steps are accomplished more efficiently by passing the hot CO_2-lean amine stream and the cool CO_2-rich amine through a heat exchanger (Rao, 2007). Additionally, some fresh solvent (generally about 70%–80% water) is required as makeup in the regenerated fluid. The process results in a CO_2 stream that is nearly pure (>95%) and typically is able to remove 85%–95% of the CO_2 from the flue gas (Chapel and others, 1999). Advantages of chemical absorption processes include the following (Rao, 2007):

- The ability to treat exhaust streams with CO_2 concentrations of only a few percent
- The relative ease of retrofitting existing facilities since it is an “end-of-the-pipe” application
- The ability to operate at low temperature and ambient pressure
- The production of a high-purity product
- The commercial availability of processes and associated equipment

Development continues on the processes that promise higher efficiencies and lower energy costs for stripping and regeneration (Reddy and others, 2003). SO_x and NO_x levels within the flue gas also need to be controlled as they both irreversibly react with these chemical absorbents. Corrosion is also a concern, as CO_2 forms carbonic acid when exposed to water and oxygen, although existing corrosion inhibitors may be successful in preventing or reducing the effect (Reddy and others, 2003). The increased water use of the system is also an important factor. Subprocesses that require a significant amount of water include the cooling of flue gas, water wash, absorber, reflux condenser, reclaimer, and lean solvent. Some of this cooling requirement can be offset through the increased use of heat exchangers within the plant. Generally, the amine-based capture process will decrease a plant's water use efficiency by 15%–30% (Gerdes and Nichols, 2009).

Physical Absorption

Precombustion processes are predominantly utilized in plants that practice gasification, where a solid fuel such as coal is converted into a cleaner gaseous synthetic fuel. By-products of the gasification process are high-pressure hydrogen (H_2), methane (CH_4), carbon monoxide (CO), and CO_2 as well as other minor compounds. The concentration of CO_2 can be increased by converting the CO to CO_2 through the use of a water–gas shift reactor which uses steam and a catalyst to carry out the conversion of CO and water to H_2 and CO_2, which can also increase plant efficiency (Gerdes and Nichols, 2009). Because of the higher CO_2 concentration and pressure, a physical absorption process may be used to remove the CO_2 from the gas stream and the remaining H_2, unreacted CO, and CH_4 may then be treated and sent to the gas turbine. The two-stage Selexol™ process is commonly recognized as the preferred physical sorption process, utilizing a dimethyl ether of polyethylene glycol as the absorbent. The process also has the added advantage of being able to remove hydrogen sulfide (H_2S) in a separate stream. Since this is a physical process, rather than chemical, the overall energy required to regenerate the physical solvent in the stripper is lower than for the chemical absorption processes (Ciferno and others, 2009). The advantages of the gasification and physical absorption process include the following (Rao, 2007):

- The nearly complete removal of CO_2 from the flue gas
- A significant reduction in sulfurous oxide (SO_x) and nitrous oxide (NO_x) emissions
- A reduced energy penalty relative to other capture processes
- The production of valuable by-products such as CO_2, H_2, and nearly all the sulfur present in the original stream
- The ability to operate at pressures of a few hundred pounds per square inch

Despite these advantages, the IGCC process is relatively complex and only recently introduced, resulting in high capital costs and higher initial operating costs per kilowatt. Furthermore, the term "capture-ready" carries a significant amount of ambiguity, resulting in a difficult absorption process retrofit in many cases. Increased water usage results predominantly from the demands of the water–gas shift reactor (Rao, 2007). Cooling demands are also increased as a result of the use of an air separator unit and the various gas-processing stages (cooling, humidifying, etc.). The addition of this process will decrease a gasification plant's efficiency by approximately 15%–22% (Gerdes and Nichols, 2009).

There is a wide range of additional solvents and sorbents that are currently under development. These include physical solvents composed of organic or inorganic liquids, a category of salt known as ionic liquids, and solid sorbents such as potassium oxides, zeolites, and metal–organic frameworks. These emerging technologies promise lower energy and water costs over a wider range of conditions (Ciferno and others, 2009). Another emerging technology is the use of membrane absorption (atomic sieve) systems, which have both pre- and postcombustion applications (Shelly, 2009).

Oxycombustion

As previously discussed, oxycombustion is a developing technology in which a relatively pure stream of oxygen is used to combust coal (predominantly carbon) and thus produces a relatively pure stream of CO_2. Oxycombustion was first proposed in the early 1980s, although without penalties for CO_2 emission, the process is not competitive for the purposes of power generation (Rao, 2007). The largest singular advantage of the oxycombustion process is that it drastically reduces the energy and equipment necessary for CC. Further efficiencies may be realized in reduced boiler sizes and the possible elimination of certain flue gas cleanup processes. Since nitrogen is not introduced to the system, it has the additional benefit of eliminating NO_x pollutants. Other pollutants are expected to be reduced dramatically as well (Ciferno and others, 2009). Finally, since the process utilizes existing boiler technology, albeit with certain improvements, and does not use complicated physical or chemical processes, oxycombustion is a viable retrofit candidate (Rao, 2007).

The largest barrier to implementation is a cost-effective oxygen source. Current technologies are energy-intensive and very expensive to implement and operate; therefore, several organizations are currently developing technologies to resolve these problems (Ciferno and others, 2009). Other technical challenges include boiler designs capable of higher temperatures and optimal flow streams and include the capture and disposal of other pollutants such as sulfates. The added demands of oxygen separation and CO_2 compression will likely lead to an overall increase in water consumption, despite the elimination of other processes (Tigges and others, 2008). Pilot-scale tests such as Total’s 30-MW Lacq project are currently ongoing and have provided encouraging results, although full-scale implementation is still only in the planning stages (Ciferno and others, 2009).

Water Needs for Capture Technologies

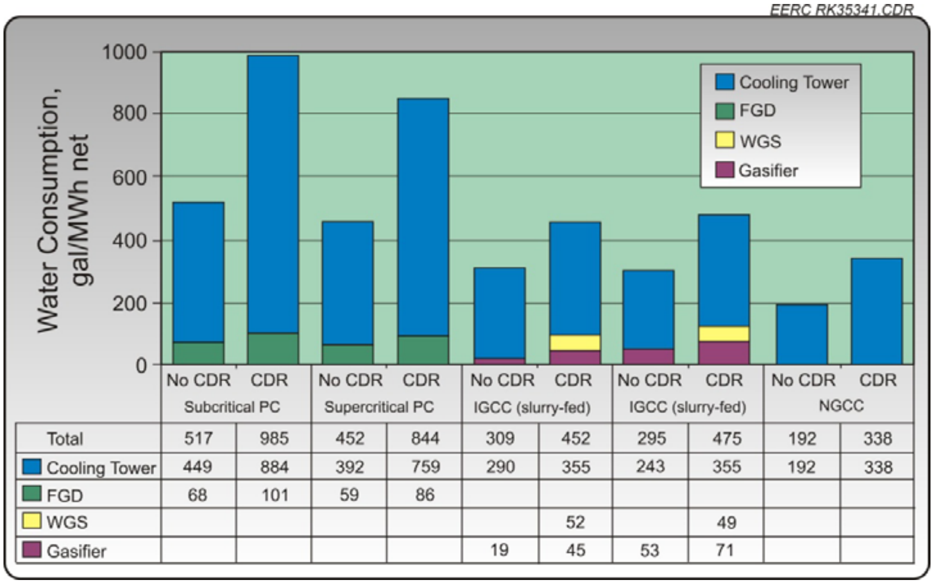
Water Quantity

Thermoelectric (fossil fuel-based and nuclear) power generation already accounts for 136 billion gallons of freshwater withdrawal daily (38% of total withdrawals) (U.S. Geological Survey, 2004) and 3 billion gallons per day of freshwater consumption (3% of total consumption), which is primarily a result of evaporative losses (U.S. Geological Survey, 1998). Water use for irrigation ranks first in both of these categories ahead of the power generation industry. However, while irrigation accounts for 40% of total withdrawals (U.S. Geological Survey, 2004), it accounts for 81% of total water consumption in the United States, as very little irrigation returns to its original source through runoff, infiltration, or other measurable means (U.S. Geological Survey, 1998). Under the wide-scale implementation of CC technology, the freshwater withdrawals and consumption of the power industry are likely to increase. As mentioned previously, the addition of CC facilities will increase the water demand of most fossil fuel-based facilities to accommodate the additional cooling loads due to parasitic energy use, as well as several major and minor subprocesses associated with the various CC methods. For example, it has been estimated that water consumption at new subcritical and supercritical pc plants would be 90% higher with the addition of amine-based capture systems than the same new plant without CC technology (Gerdes and Nichols, 2009). Natural gas combined-cycle plants, which could also utilize amine-based capture, would experience an increase of 76% over those plants without CC processes (Gerdes and Nichols, 2009). Similar increases of 95% and 81% have been reported by Klara (2007). Gasification systems would also experience a significant increase in water consumption with the addition of the two-stage Selexol process. Gerdes and Nichols (2009) estimate the increase for new IGCC plants is 45%, with more than half of this resulting from the needs of the water–gas shift reactor (Figure 5). These figures are not necessarily the same for existing plants that retrofit with new CC technology, as the overall power output of the plant will be reduced, resulting in a smaller ratio of water consumption per power produced (Gerdes and Nichols, 2009).

The impact of these water withdrawl and consumptive increases may be managed or reduced through a variety of strategies. Efficiency may be increased through updated equipment or process flow. Water use could be reduced through a change in cooling strategy at a given source, such as adding or including a dry cooling (air cooling) or hybrid (air and recirculating), or perhaps by updating the cooling systems themselves. Further reductions may be possible through the inclusion of degraded (secondary) water sources in the cooling strategy. One possible source of degraded water may be produced water from CCS storage projects.

Water Quality

The quality of water required for cooling purposes is relatively high and variable. This variability is largely the result of diverse combinations of cooling processes and equipment. In



	No CDR	CDR	No CDR	CDR	No CDR	CDR	No CDR	CDR	No CDR	CDR
	Subcritical PC		Supercritical PC		IGCC (slurry-fed)		IGCC (slurry-fed)		NGCC	
Total	517	985	452	844	309	452	295	475	192	338
🟦 Cooling Tower	449	884	392	759	290	355	243	355	192	338
🟩 FGD	68	101	59	86						
🟨 WGS						52		49		
🟪 Gasifier					19	45	53	71		

Figure 5. Comparison of water consumption per net power with and without CCS for typical plant configurations using wet recirculation towers (from Gerdes and Nichols, 2009).

general, there are two main cooling systems: once-through and recirculating. Once-through systems take in water from a nearby source (typically surface water), pass it through a condenser, and return it to the original source (the water may be allowed to cool in a holding pond before being returned to the source). As a result, water withdrawals are high but consumptive use in this system is relatively low. Recirculating (closed-loop) cooling systems are designed to minimize water withdrawal and utilize cooling towers to recycle the cooling water within the system. Many cooling towers utilize evaporation to cool the water so the volume of water evaporated must be made up. Therefore, consumptive use in recirculating systems is much higher than once-through systems, while overall withdrawals are lower. Furthermore, recirculating systems are more sensitive to makeup water quality since the water is recycled and there is an opportunity for water constituents to be concentrated in the evaporative step.

The most common problems associated with poor water quality include scale formation, corrosion, and microbiological fouling, any of which can significantly impact the system's efficiency or lifespan. Dissolved species that are commonly associated with scale formation include calcium carbonate, calcium sulfate, calcium phosphate, and magnesium silicate. Carbonate concentration is commonly monitored along with other factors such as pH, temperature, and alkalinity with computer programs that are able to calculate the relative saturation indices of these species within the cooling water stream to help prevent scaling of equipment and pipelines. The presence of any scale-forming species (beyond what is typically found in freshwater) used for makeup water may limit the effectiveness of common scale control technologies and will likely require treatment prior to use (Nalco Company, 2006).

Corrosion is also a concern related to levels of TDS, particularly levels of chloride and sulfate. High concentrations of these ions can cause corrosion to the copper alloys and stainless steel that is often used in condenser tubing and tube sheets. Excessive levels of nitrogen, phosphate, and organic compounds and favorable pH conditions can provide an environment where "biofilms" will form on system surfaces that often must be controlled through chemical biocides such as chlorine or hydrogen peroxide (Daniels, 2002). A variety of cooling water quality requirements are available, depending on the type of cooling system employed and the specific technology brought to bear on the system. Table 1 summarizes general recommendations for cooling water quality for recirculating cooling systems. For example, cooling water systems may be designed to utilize highly impaired waters (TDS in excess of 70,000 ppm) through the use of special metal alloys and scaling and corrosion control inhibitors. The designs of the vast majority of existing plants are much more restrictive and may be incapable of accepting water with TDS levels in excess of 500 ppm (Electric Power Research Institute, 2003).

Compression and Transportation

Another significant water and energy consumer present in all CCS technologies is the equipment used to compress CO_2 from atmospheric pressure (except in gasification plants, which have a higher starting point) to supercritical pressure above 72.8 atm or 1071 psia (T_c 88°F) (Midwest Geological Sequestration Consortium, 2004) (Figure 6). The increased water consumption due to cooling and associated plant efficiency decrease (because of the increased

Table 1. General Water Chemistry Parameters and Limiting Concentrations for Common Constituents of Recirculating Cooling Tower Water (Electric Power Research Institute, 2003) (Note: some of the footnotes refer to sections in the original EPRI document.)

Parameter	Units	Basic Parameters
Ca	mg/L $CaCO_3$	900 (max.)[1]
Ca × SO_4	$(mg/L)^2$	500,000
Mg × SiO_2	mg/L $CaCO_3$ × mg/L SiO_2	35,000[3] 75,000[2]
HCO_3 + CO_3	mg/L $CaCO_3$	30–50[3] 200–250[2]
SO_4	mg/L	500,000[1]
SiO_2	mg/L	150
Fe (total)	mg/L	< 0.5
Mn	mg/L	< 0.5
Cu	mg/L	<0.1
Al	mg/L	<1
S	mg/L	5
NH_3	mg/L	<2[7]
pH		6.8–7.2[1] 7.8–8.4[2]
pH with PO_4 present	mg/L	7.0–7.5[4]
TDS	mg/L	70,000
TSS (total suspended solids)	mg/L	<100[5]–<300[6]
BOD (biological oxygen demand)	mg/L	<100[4]
COD (chemical oxygen demand)	mg/L	<100[4]
Langelier SI		<0
Rysnar SI		>6

[1] Refer to the $CaSO_4$ limit.
[2] Assumes scale inhibitor is present.
[3] Without scale inhibitor.
[4] Consult with specialty chemical provider before finalizing control parameters.
[5] <100 mg/L TSS with film fill.
[6] <300 mg/L TSS with open fill.
[7] <2 mg/L NH_3 applies when copper-bearing alloys are present in the cooling system. This does not apply to 70–30 or 90–10 copper nickel.

electrical load of the compressors) was included in the quoted figures of Gerdes and Nichols (2009). Typically, pressures of approximately 2200 psia are utilized, which allow for transport via pipeline over distances up to 50 miles without the need for recompression at booster stations. Longer distances are possible at higher compression levels. For example, the Dakota Gasification Company plant near Beulah, North Dakota, compresses captured CO_2 to 2700 psia and transports it via a 205-mile pipeline to a storage site in Saskatchewan (Perry and Eliason, 2004).

Compression is usually accomplished using a multistage, intercooled centrifugal compressor (Klara, 2007). As many as ten stages of compression may be used, depending on the pressure of the supply stream and final output pressure, with intercoolers placed between each stage to maintain the efficiency of the compressor (Perry and Eliason, 2004). Intercoolers may be either air- or water-cooled, depending on local climate and water availability. In the case of the

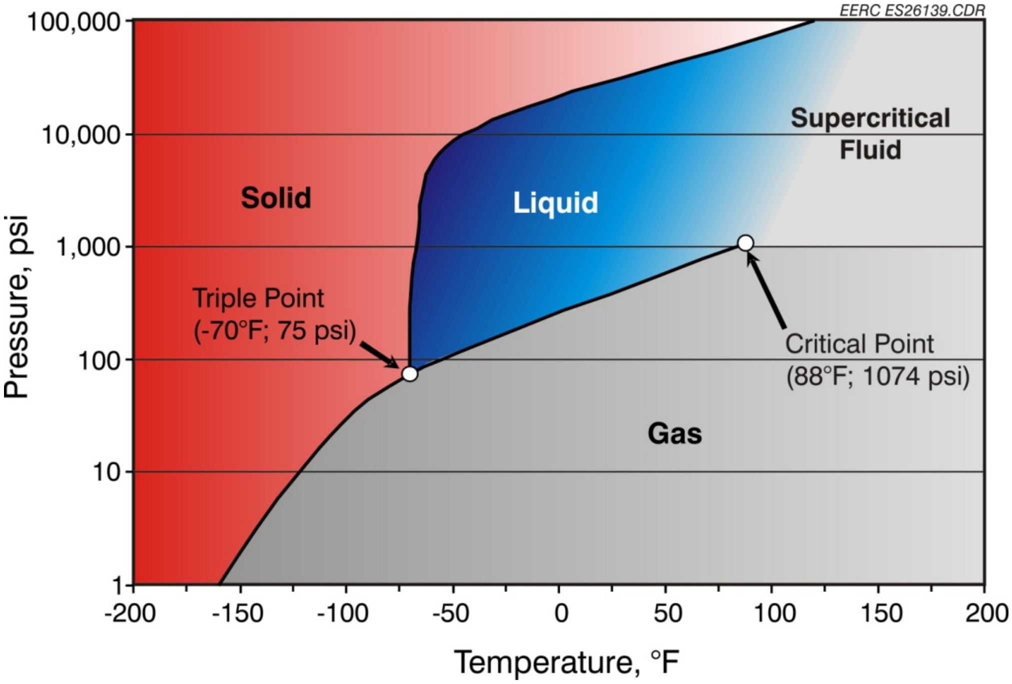


Figure 6. Pressure–temperature phase diagram of CO_2 showing the triple point and the critical point of 1071 psia and 88°F.

Dakota Gasification Plant, all interstage cooling is accomplished through air-cooling (dry cooling) which results in zero water consumption (Perry and Eliason, 2004). Presently, there are no published data for compressor interstage cooling water consumption.

The discharge pressures of each stage are balanced (Table 2), and the CO_2 is dehydrated during the compression process, leaving the stream almost completely moisture-free. This is necessary to prevent corrosion of pipeline components during the transportation phase (Klara, 2007). If CO_2 is transported over longer distances (>50 mi), booster compressor units and their associated cooling and power load will need to be assessed in any cost–benefit analysis.

Emerging technologies hold the potential of dramatically reducing the costs associated with CO_2 compression. As one example, through the use of “shock compression technology,”

Table 2. CO_2 Compressor Interstage Pressure (adapted from Klara, 2007)

Stage	Outlet Pressure, psia
1	52
2	113
3	248
4	545
5	1200
6	2215

new compressor design may be capable of compressing CO_2 to a supercritical state in as little as two stages. These compressors would be able to achieve 10:1–12:1 compression ratios, which eclipses the 1.7:1–2:1 ratios achievable in centrifugal compressors at a cost savings of 40%–60% (Ramgen, 2009). In addition to the increased compressor efficiency, interstage heat output would be 250% greater (450° to 500°F), allowing for effective heat recovery that may be reused for other plant processes (Ramgen, 2009). Other dramatic cost reductions could be realized in the reduced size and associated cost of these units. Water consumption, on the other hand, would remain similar to other compressors as the overall cooling need would not change.

Geologic Storage of CO_2

Injected CO_2 Pressure Behavior

The effects of CO_2 injection extend far beyond those immediately encountered at the borehole site. The injection of CO_2 results in an increase of reservoir pressure as in situ formation fluids are displaced. As injection continues, this increased pressure field quickly propagates through the underground formation far beyond the physical extent of the CO_2 plume. It has been estimated that pressure buildup could extend more than 100 km away from the injection zone (Birkholzer and others, 2009). Depending on well spacing and reservoir characteristics, the increased reservoir pressure has the potential to both enhance local production activities and at the same time hinder other local injection activities, whether they are water or gas injectors. It will be the responsibility of field managers and regulators to ensure all parties' interests are served during the injection phase of a storage project. Once injection is completed, the overall reservoir pressure field is expected to stabilize, but a return to preinjection conditions is expected to take much longer than the original injection activities. For example, Birkholzer and others (2009) were able to estimate a growing sphere of pressure influence 70 years after the completion of injection activities (100 years since the start of injection). Continued monitoring, verification, and accounting (MVA) will likely be required until the system can be shown to have stabilized.

EPA and UIC Regulations for Injection Well Design

EPA's UIC Program regulates the injection of all hazardous and nonhazardous materials into the subsurface. The UIC Program defines CO_2 injection wells for EOR as Class II injectors (U.S. Environmental Protection Agency, 2008a) requiring that all injection occur below the lowest USDW.

EPA is proposing federal guidelines specific to CCS requirements under the SDWA for underground injection of CO_2. The new EPA proposal for regulations pertaining to CO_2 injection well design applies to owners or operators of wells that will be used to inject CO_2 into the subsurface for the purpose of long-term storage (U.S. Environmental Protection Agency, 2008d). It proposes a new class of injection well and standard technical criteria for the geologic site characterization, fluid movement, area of review (AoR) and corrective action, well construction, operation, mechanical integrity testing, monitoring, well plugging, postinjection site care, and site closure for the purposes of protecting USDW (U.S. Environmental Protection Agency, 2008d). The elements of this proposal are based on the existing UIC regulatory framework, with modifications to address the unique nature of CO_2 injection for geologic storage. If finalized, this proposal would help ensure consistency in permitting underground injection of CO_2 at geological storage operations across the United States and provide requirements to prevent endangerment of USDW in anticipation of the eventual use of geologic storage to reduce CO_2 emissions (U.S. Environmental Protection Agency, 2008d).

THE CONNECTION BETWEEN WATER AND GEOLOGIC STORAGE OF CO_2

Geologic Storage Targets

For geologic storage of CO_2 to be successful in any situation, a few basic requirements must be met. A potential storage target should have sufficient capacity (porosity and thickness) and injectivity (permeability) as well as a competent confining unit or sealing cap rock. The level of “competence” required is largely a site-specific question and is also an area of ongoing research. Potential targets also need to be located in geologically stable environments, such as in midcontinental basins or near stable continental plate boundaries to minimize structural or tectonic leakage risks. Targets deep enough to maintain CO_2 in a supercritical state (>800 m) are also largely preferred, as this maximizes the density of the CO_2 stream and the associated storage potential (Cooperative Research Centre for Greenhouse Gas Technologies, 2008) and makes pipeline transport much more efficient. Another important consideration for any storage project is the proximity of CO_2 sources, as any effort requiring the transportation of CO_2 over long distances may prove to be economically impractical.

Depleting/Depleted Oil and Gas Reservoirs

A potential target for geologic storage of CO_2 is in depleting/depleted oil and gas reservoirs. These formations have a proven ability to trap liquid or gaseous hydrocarbons for long periods of time and tend to be much better characterized by information uncovered during exploration and production activities. Depleted reservoirs also possess infrastructure, including access roads, utilities, and wells, that in many cases may be retrofitted for injection or will suffice for monitoring and verification. Additionally, in some reservoirs, CO_2 can be used for the dual purpose of storage and EOR.

The optimal depth of EOR operations has been suggested by several authors and is generally agreed to be >800 m to maintain CO_2 in a supercritical state (Bachu, 2003; Metz and others, 2005) Generally, reservoir pressures high enough to maintain supercritical CO_2 are required. Other important criteria may include reservoir temperature, oil weight and viscosity, and remaining oil content (Gozalpour and others, 2005). Oil weight and viscosity can also determine whether miscible or immiscible flooding techniques are applied. Reservoir pressures may need to be higher for miscible floods and are also dependent upon the purity of the CO_2 stream (Metz and others, 2005) and the oil composition.

Miscible floods aim to inject a fluid or gas that will dissolve into the oil, increasing its volume and decreasing its viscosity, allowing greater drainage and mobility. CO_2 is the primary fluid used today, but historically, various liquid petroleum gases, nitrogen, and flue gases have been used (Green and Willhite, 2003). Typically between 5000 and 8000 mcf of CO_2 is required per barrel of incremental oil recovered, but much of the CO_2 is produced and is then recycled (Jarrell and others, 2002).

The reservoir must also meet general storage criteria described previously. The optimal reservoir has low heterogeneity, with relatively few vertical fractures. In certain scenarios, low vertical permeability, high reservoir angle, absence of natural flow, and low formation thickness may also be advantageous. The type of injection scheme is typically optimized to specific field conditions.

Formation fluids in depleting/depleted oil and gas reservoirs can be composed of a variety of phases which will vary considerably, depending on the geography and geology of the field and the type of hydrocarbon being produced. These reservoirs are often a mixture of high-saline waters or brines, dispersed oil, soluble organic components, volatile hydrocarbons, and metals such as Zn, Pb, Mn, and Fe. Depending on the production history of the field, excessive volumes of water (from waterflooding) or a variety of treatment chemicals (biocides, emulsion breakers, corrosion inhibitors, etc.) may also be present (Veil and others, 2004).

Dispersed oil consists of small suspended droplets of oil. Often the microscopic droplet size (4–6 µm) can pose considerable treatment challenges. Dispersed oil may be associated with or even agitated by the presence of soluble organic compounds such as carboxylic acids, ketones, and alcohols. A variety of heavier-weight hydrocarbons, such as phenols and aliphatic and aromatic carboxylic acid and hydrocarbons may also be partially dissolved within formation fluids. If the formation is primarily a gas reservoir, volatile hydrocarbons are likely to be present (Veil and others, 2004), including increased amounts of BTEX (benzene, toulene, ethyl-benzene, and xylene). Aside from organic contaminants, these formation waters are often highly saline. TDS can range from as low as 37 ppm to greater than 300,000 ppm (Petroleum Technology Alliance Canada, 2007). The dissolved constituents often consist of ions of Na^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, and HCO_3^-. The pH of these waters may also be reduced, which increases the likelihood of dissolved mineral and metal species. Using similar techniques to those employed by the oil and gas industry, a careful analysis of formation fluids, particularly of soluble compounds, is expected to be conducted prior to CO_2 storage operations to minimize the effects of produced waters and associated fluids on equipment and the environment (Jarrell and others, 2002).

A variety of physical and chemical processes are likely to occur in a formation following the injection of supercritical CO_2. Residual oil and gas present in the reservoir under miscible conditions reduces CO_2 breakthrough time and the rate of pressure buildup (Kharaka and others, 2009). Injected supercritical CO_2 is less dense and less viscous than the surrounding oil and water and will tend to float on top or "finger" through formation fluids if not properly managed, resulting in early CO_2 breakthroughs and poor oil recovery (Figure 7). Ideally, the supercritical CO_2 will quickly reach miscibility composition with the formation fluids, mobilizing the hydrocarbons and producing a miscibility front which "sweeps" through the formation. One of the most effective methods to minimize early breakthrough is the use of the WAG process (Figure 2). During this process, well over 50% of the injected fluids return with the production stream. Once CO_2 reaches the producer well, the pH of the produced water can be expected to

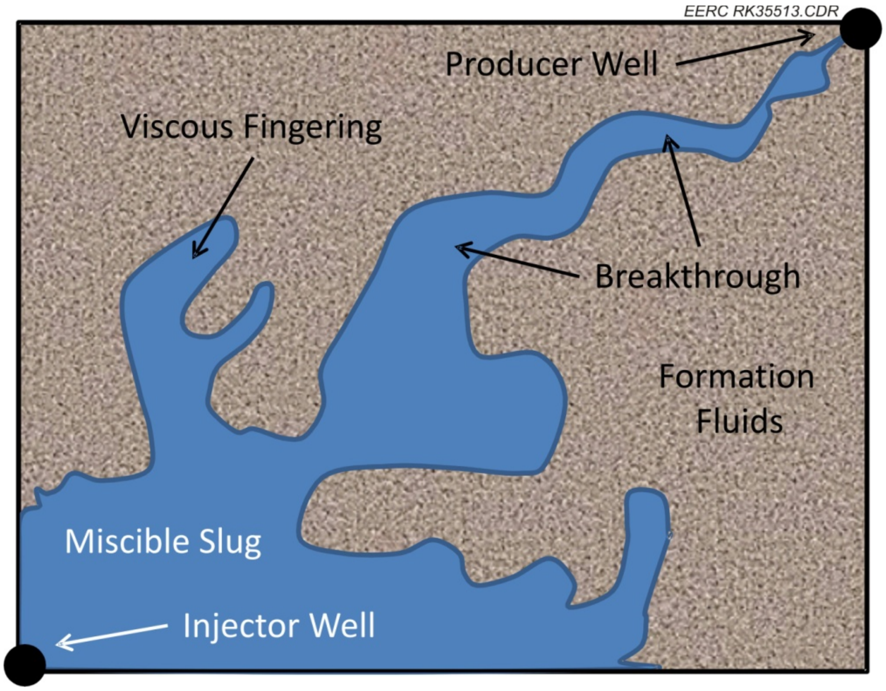


Figure 7. Schematic (a real view) of breakthrough, a common problem in EOR where the miscible slug moves rapidly through higher-permeability zones and bypasses much of the pore space that was to be treated. Once breakthrough occurs, it is very difficult to treat those areas that have been bypassed. One goal of the WAG method is to avoid the occurrence of breakthrough by alternating the applied fluid slugs.

drop considerably (Kharaka and others, 2009). The produced oil, water, and CO_2 can be separated at the surface, and the CO_2 and water may be reinjected until EOR operations are completed, at which point much of the injected CO_2 remains trapped within the reservoir.

Over time, residual gas trapping, dissolution into both the remaining formation oil and water, and mineral trapping stabilize and remove the free-phase CO_2 (Metz and others, 2005). It is possible to categorize all these reactions and provide approximate time frames for all described processes (Figure 8). All chemical reactions tend toward thermodynamic equilibrium, but they do so at highly different rates. At low temperatures, low pressures, and neutral pH conditions, most reactions in water–rock systems are very slow. Moreover, at pressures and temperatures of storage (below 800 m with variable temperature gradients from 20°C/km to 50°C/km) in deep saline formations or depleting/depleted oil or natural gas reservoirs, the system water–rock is stabilized at conditions approaching equilibrium. With injected fluids, such as water for stimulation or supercritical CO_2 for storage, the equilibrium is disturbed, and the system is “seeking” a new equilibrium point. At this stage, the rates of reactions can increase; however, they tend to stay within time frames described in Figure 8.

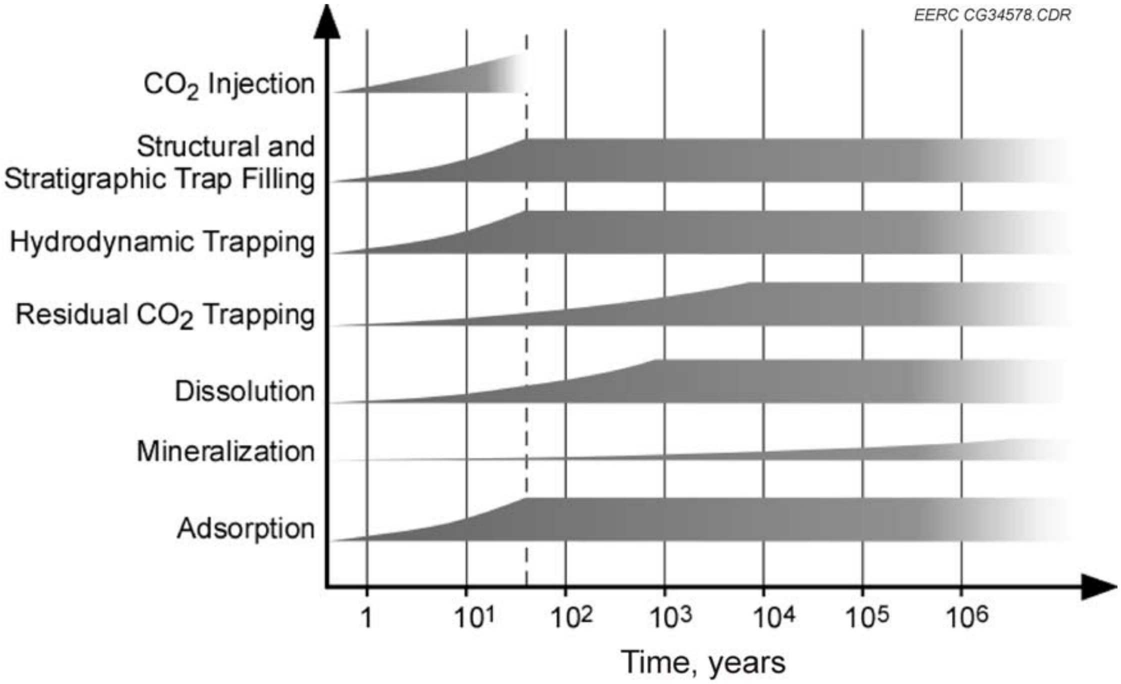


Figure 8. The working time of the physical and geochemical processes that trap CO_2 in geologic formations (Metz and others, 2005).

Unminable Coal Seams

The primary process of CO_2 storage in unminable coal seams is adsorption of the CO_2 onto the coal surface. CO_2 naturally bonds to the surface of any coal or organic carbon through a process known as adsorption. Coal’s affinity to adsorb CO_2 is higher than it is for methane, and thus injected CO_2 may liberate CH_4 as an economical by-product. Any unit considered for ECBM should be screened for a variety of characteristics that will impact its ability to produce methane and store CO_2. These include but are not limited to coal geology and stratigraphy (coal rank, physical characteristics, and structure), hydrodynamics and hydrogeology, as well as the coal’s gas content and sorption capacity (Pashin and others, 2001). Ideally, the coal bed will be structurally simple with a few thick seams (as opposed to many thin seams), be confined vertically and laterally, have adequate gas content, and be able to be dewatered (Metz and others, 2005). Although many coal beds may be unminable at depths of greater than 300 m, future efforts focused on maximizing CO_2 storage may use supercritical CO_2 and thus require depths of greater than 800 m (Mazzotti and others, 2009).

ECBM production is still a developing technology, and as such, many process properties are not fully understood. Issues such as coal heterogeneity, coal and gas impurities, and the effect of water on storage capacity remain areas of continuing research (Mazzotti and others, 2009). The fact that the physical and chemical properties of coal may change during gas production and exchange only complicates this uncertainty (White and others, 2005). Currently, the production of water from CBM extraction is greatest in the early stages of reservoir development as water is drawn off to reduce formation pressure, allowing methane to desorb from the coal surfaces. The rate at which water is produced decreases with time as the coal bed is dewatered. Produced water from CBM can be of such quality that it may be disposed of at the surface. In the Powder River Basin in Wyoming, for example, produced water is typically discharged at the surface into catchment ponds since this water often has TDS levels at less than 2000 ppm (Benko and Drewes, 2008). These ponds provide drinking water for livestock and indigenous fauna (U.S. Geological Survey, 2000). Lower-quality waters are typically reinjected into deeper wells. In all cases, disposal must be permitted according to both state and federal regulations.

As with the other geologic media for CO_2 storage, salinity is an important parameter in coalbed water. However, coalbed water in certain regions may commonly fall below the lower limit of 10,000 ppm TDS for saltwater and thus be classified as protected water. In these situations, these fields will not be approved for CO_2 injection without acquiring a special aquifer exemption. Other important constituents of coalbed waters include sodicity (the amount of sodium ions) and the concentration of metals, such as Fe or Mn (Veil and others, 2004). These constituents can significantly impact the potential for surface use of ECBM waters that are produced.

Despite CO_2's affinity for coal, it may still dissolve into formation waters and be transported away. Dissolved CO_2 species such as bicarbonate or carbonic acid may then flow to areas of lower pressure, exsolve from the fluid, and migrate toward the surface or into shallower aquifers. Dissolved CO_2 will increase the acidity of the formation waters and can increase the concentration of Ca^{2+}, Fe^{2+}, and Mg^{2+} in the formation fluid as more carbonate and iron-bearing minerals are able to dissolve. The concentration of dissolved organics may also increase, a problem not typically associated with standard CBM-dewatering practices (White and others, 2005). Proper adherence to the guidelines described in DOE's MVA Best Practices Manual (2009a) as well as EPA's UIC Class II or Class VI regulations (U.S. Environmental Protection Agency, 2008d) will ensure that CO_2 plumes will be monitored and controlled.

Deep Saline Formations

Deep saline formations are those that exist at depths of greater than 800 m and contain formation waters or brines with TDS concentrations of greater than 10,000 ppm. These waters are generally considered unsuitable for treatment, even for agricultural use, and as a result, there is little demand for the water resources they contain (U.S. Environmental Protection Agency, 2008e). Ideal storage targets should have sufficient capacity and injectivity to allow for efficient injection of supercritical CO_2 (Hovorka and others, 2000). A competent confining unit should also be present to prevent leakage of the CO_2 into overlying strata or further toward the surface. Supercritical CO_2 has a lower density than saline formation waters and will migrate upwards. The CO_2 that is not trapped will migrate along the base of the cap rock until it is either trapped through residual gas-trapping mechanisms, in structural traps, or dissolves into solution, where it eventually reacts with the rock matrix and is transformed into stable minerals (mineral trapping). Thus deep saline formations with very long residence times or structural traps (or a combination of the two) are preferable, as they will enhance the effects of solubility and mineral trapping (Hovorka, 1999).

Formation water in deep saline formations typically contains high levels of TDS composed primarily of HCO_3^-, Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, K^+, and Na^+ ions (Tibbetts and others, 1992). Generally, salinity increases with depth because of natural processes related to compaction and diagenesis of the formation rock which slowly forces a portion of the formation water out of the rock's pore space. In many cases, this upward vertically migrating water passes through shale units, whose low permeability and high clay content act as natural filters, concentrating salts in the formation water of deep units (Interstate Oil and Gas Compact Commission and ALL Consulting, 2006). The overall expression of this salinity gradient can be impacted by local factors such as the original salinity of the formation water during deposition or recharge by meteoric water migrating down-dip into deep formations. Shale units undergoing diagenesis may also release large volumes of water that may be notably different than surrounding pore water as clay minerals dewater and alter. This process occurs at similar pressure and temperature conditions as when hydrocarbon generation occurs. As a result, deep saline formations may contain a variety of soluble or insoluble organic fluids or gases that may not be economical but have the potential to impact CO_2 plume dynamics or produced water quality (Interstate Oil and Gas Compact Commission and ALL Consulting, 2006).

Initially, CO_2 will become trapped in a process known as residual gas trapping, a process whereby the free-phase CO_2 becomes physically trapped in the pore spaces through relative permeability hysteresis. Hysteresis occurs when the higher pressure of injected CO_2 displaces formation fluid from the pore space (a process known as drainage). Then, once injection is completed and the plume moves away from the injection site, the formation fluid is able to move back into the drained pore space (known as imbibition) which traps a portion of the retreating CO_2 (known as residual gas) within the pore space (Jarrell and others, 2002). The remaining CO_2 that is trapped in the pore space is known as residual gas. These processes occur as long as the injected CO_2 plume is moving away from the injection point and will continue at the trailing edge of the plume until the movement stabilizes.

Physical and solubility trapping will become the dominant trapping mechanisms as the plume migrates and stabilizes. Since the free-phase CO_2 will be less dense than the surrounding saline formation water, it will tend to rise to the top of the formation and accumulate in localized pockets or traps along the bottom of the cap rock or confining unit. Plume movement will either cease because of a structural trap or become so slow as to be considered stable (known as hydrodynamic trapping). Over a timescale of hundreds to thousands of years, the CO_2 will dissolve into the formation fluid, resulting in a solution that is denser than the original CO_2 plume or formation fluid (Cooperative Research Centre for Greenhouse Gas Technologies, 2008). This higher-density solution will tend to sink within the formation, possibly setting up a convection current that will enhance the dissolution of CO_2 (Ennis-King and Paterson, 2007). This process has the added benefit of reducing the likelihood of CO_2 release as it accumulates in the lower portions of the formation. In most cases, this reaction will proceed until the entire plume has dissolved. Local heterogeneity will play a significant role in the rate of dissolution as it will strongly influence the fluid's ability to mix and flow horizontally or vertically. Careful study will be required to establish if site heterogeneity has an added benefit or impediment to the storage process.

Additional geochemical reactions may occur within the saline formation, with the potential to impact the injectivity and operations efficiency, cap rock or other sealing structure integrity, and long-term storage processes. The injection of dry supercritical CO_2 into saline formations has the potential to dry saline formation waters as a result of evaporation effects (Spycher and others, 2003), leading to severe increases in salinity and salt precipitation (Muller and others, 2009; Zeidouni and others, 2009). This can significantly impair injection rates, as has been noted in gas storage reservoirs (Kleinitz and others, 2001). This effect may be mitigated by first "flushing" the area with very low-salinity or fresh water, reducing the salinity of the waters near the well bore, thereby preventing or reducing the amount of salt precipitation.

Other CO_2–water–rock interactions include mineral dissolution or mobilization, precipitation and, consequently, mechanical alteration, porosity and permeability changes, etc. Careful analysis and modeling of formation water chemistry, petrology, and pressure–temperature regimes will be necessary to assess the impact of these processes, as they have the potential to enhance or impede injection rates and mineral-trapping mechanisms (Cooperative Research Centre for Greenhouse Gas Technologies, 2008), alter sealing unit integrity, and alter the mobility of the CO_2 plume. For instance, early results from the Frio-I project, a DOE-funded test of CO_2 storage in a deep saline formation in Texas, show significant changes in pH and alkalinity, as well as increased concentrations of Fe, Mn, and Ca in the produced waters from the formation, occurring as a result of CO_2 injection. Kharaka and others (2009) indicate that the rapid rate of these and other observed changes could have significant effects not only on the environmental impact of these produced waters but also on the integrity of the well bores, casing, and reservoir itself. This remains an area of ongoing research, and new regulations are being designed with this and other issues in mind (U.S. Environmental Protection Agency, 2008d).

Injection Management

The operations of CO_2 storage projects are to be managed in an effort to accomplish the goal of stable, long-term storage of CO_2, while introducing minimal environmental impact and simultaneously optimizing the type of storage strategy employed. Currently, all U.S. underground injections are monitored through the EPA UIC Program (U.S. Environmental Protection Agency, 2002). Wells are designed to be drilled to depths below USDW and contain a variety of protective measures such as casing, cementation, and tubing that separate the well fluids from other fluids present below the surface (U.S. Environmental Protection Agency, 2002). Furthermore, all injection activities are only permitted to occur beneath sealing formations, such as shale, which further separate injection activities from USDW zones.

The type of storage process determines which production variable is optimized over the lifetime of the project. In the case of enhanced methane and oil recovery, the production of methane gas and oil is optimized through a variety of CO_2 injection processes and designs. When CO_2 is stored directly in a saline formation, the distribution and rates of CO_2 injection are optimized to maximize plume control and CO_2 injection volume.

Injection Management for ECBM

The use of high-pressure CO_2 for ECBM recovery has been demonstrated effectively (Metz and others, 2005). ECBM has the potential to release up 95% of the original gas in place, while standard depressurization practices recover only approximately 50% of the original gas (Metz and others, 2005). The Allison Unit CO_2–ECBM Recovery Pilot Project in northern New Mexico found that approximately one volume of methane was produced for every three volumes of CO_2 injected (Reeves and others, 2004). For lower-rank coals, considerably higher unit volumes of CO_2 are required to produce a single unit volume of methane gas.

When CO_2 storage is combined with ECBM production, the injection well distribution and injection pressure should be optimized to provide for maximum methane production while minimizing the production of other fluids. A reported problem associated with ECBM production can be the swelling of coal as CO_2 is injected and adsorbed (Metz and others, 2005). This can reduce the coal's permeability and, hence, the coal's storage capacity. Careful consideration of the geology of the target coal formation, in addition to careful injection design, can minimize these impacts. The quality of water produced from ECBM production will determine how it is handled, but in many circumstances, it will likely be reinjected into other suitable formations. Any water reused aboveground will be subject to federal and state regulations such as the Clean Water Act, the SDWA, and the Resource Conservation and Recovery Act. Currently, some water produced from CBM operations is treated for agricultural use or reused for waterflood and hydrofracturing activities in Texas (Burnett and Vavra, 2006). In Wyoming, water from CBM is typically of near-potable quality and often is discharged to surface ponds that provide water to livestock, storage, and irrigation (ALL Consulting, 2003).

Injection Management for EOR

In most EOR operations that utilize CO_2, a WAG process is utilized (Jarrell and others, 2002). In addition to the ability to recycle produced fluids and minimize breakthrough, WAG has the advantage of extensive field experience in the West Texas oil fields, Wyoming's Salt Creek Fields, and the Weyburn and Midale Fields, Saskatchewan, Canada. Costs associated with the addition of a storage project may be reduced, as many units and the associated fluid behaviors are already characterized in this area. Other optimizations of oil production will determine the design of the injection field and the injection pressure(s). Site-specific characteristics will help determine the appropriate production methods, and when necessary, specialized well equipment and treatment chemicals may be used to limit the production of water from a given well (Hyne, 2001). Long-term monitoring of the size, shape, and movement of the CO_2 plume will also be required.

Injection Management for Deep Saline Formations

Deep saline formations are typically considered excellent storage targets because of their widespread distribution, large potential storage volume, and high potential injectivity (Metz and others, 2005). Furthermore, these formations are ideal storage targets because of their proximity to CO_2 point sources and the fact that the formation pore fluid typically has little economic value. Target storage formations will be prioritized by their proximity to point sources and other factors that affect their overall storage potential, such as salinity, reservoir pressure, and capacity. Unlike enhanced hydrocarbon recovery operations, no fluids need to be produced; however, there may be circumstances where the production of water from the target formation is favorable or even necessary in order to optimize the storage process. These circumstances relate to managing the reservoir pressure of the storage formation and controlling plume movement during and after CO_2 injection. For example, producing water from a saline formation at some distance from the injection well will reduce the reservoir pressure in the vicinity of the well and, to a lesser extent, the overall reservoir pressure. This pressure decrease may allow for an additional CO_2 injection rate or even a larger total storage volume. Pressure reductions may also prevent portions of a storage formation from exceeding maximum allowable pressures, reducing any possible risk of damaging the integrity of the storage formation or the overlying cap rock. In other instances, the use of water production from the storage formation may enhance the movement of the CO_2 plume toward structural traps or impede movement toward the boundaries of the leased zone. In most storage reservoirs, the production of water will be avoided whenever possible. If a need is found for this produced water, such as power plant cooling water, the production of water may become part of the overall CO_2 storage design, but in most circumstances where water is produced, it will be reinjected into the storage formation or another suitable saline formation.

THE CONNECTION BETWEEN POTABLE WATER AND GEOLOGIC STORAGE OF CO_2

The primary public concern challenging the CCS industry is that of assuring the injected CO_2 will remain underground and will not leak toward the surface or migrate into underground sources of drinking water or protected waters. Industry experts, however, point to the current capacity of existing oil and gas reservoirs to prevent the migration of buoyant fluids or gases for millions of years (Metz and others, 2005). There certainly are risks involved with CO_2 leakage, specifically dealing with the protection of USDW, but regulations and methodologies are adapting or have already been put in place to minimize the danger involved with deep injection of CO_2 and other fluids. Furthermore, careful implementation of all appropriate environmental regulations is paramount to the overall vision and ultimate success of CCS programs.

Possibility of Direct Interaction

In order to understand the risks involved in CCS, knowledge is required of the physical and chemical processes involved in the deep injection of CO_2. CCS projects will typically target formations in which CO_2 will exist as either a supercritical or dense fluid phase. A common guideline for the depth required to produce supercritical conditions is approximately 800 m, although the depth will vary depending on the unique pressure and temperature gradient of the surrounding basin as well as on site-specific formation or reservoir characteristics. Once CO_2 is injected, buoyant forces cause it to rise vertically through permeable formations until it reaches a cap rock, which by a combination of high capillary entry pressure and very low permeability halts upward migration. Meanwhile, CO_2 will begin to migrate laterally along the base of the cap rock. CO_2 is demobilized by containment in a physical trap that prevents both upward and lateral migration (such as a dome), encountering hydrodynamic flow regimes that oppose or prevent plume movement, dissolving into the pore fluids, or adsorbing onto the surface of organic material such as coal. Additionally, CO_2 is removed from the mobile phase by becoming residually trapped in small pore spaces following migration during the imbibition phase or by reactions that precipitate stable minerals.

Great care should be taken when characterizing, designing, and implementing a site to identify and prevent potential pathways for leakage (Figure 9). In the event of small-scale leakage, it is expected that the other trapping mechanisms including secondary physical traps will demobilize CO_2. Several processes are enhanced by CO_2 migration (specifically dissolution and residual trapping) and distance (hydrodynamic trapping), so small-scale leakages, while still an issue, are of only a minor risk to USDW.

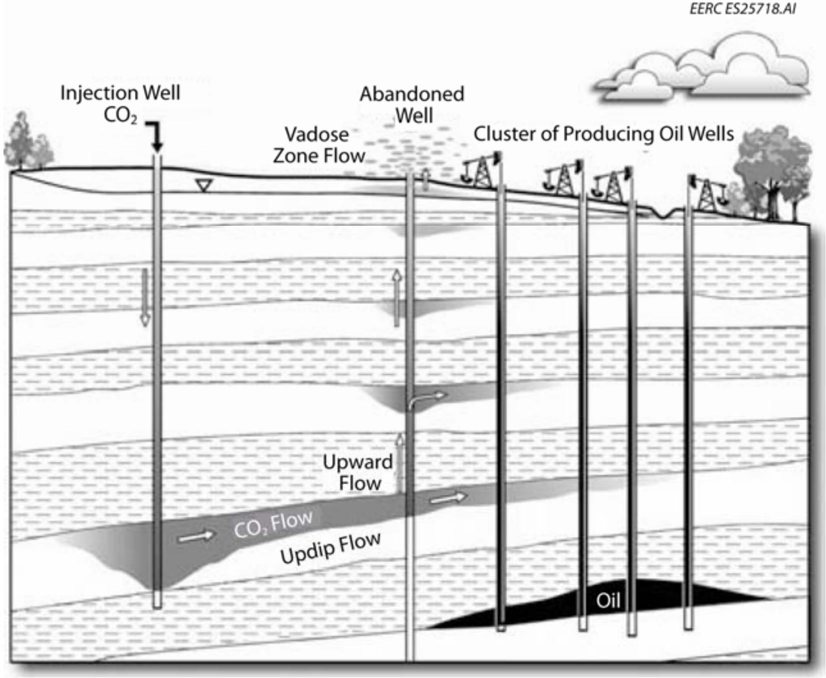


Figure 9. Schematic of CO_2 injection, migration, and leakage along abandoned wells (Celia and others, 2004).

Effects of Direct Interaction

Although substantial regulations are in place to prevent exposure of USDW to CO_2, experimentation has been done to assess the effects of direct water and CO_2 interactions. CO_2 will dissolve into water at a varying rate, optimized when (Hangx, 2005):

- There is a large contact area between the two fluids.
- The water temperature is cool (under 100°C).
- The formation pressure is high.
- The water has low salinity.

Since any contact between injected CO_2 and potable water will be the result of leakage and migration, surface areas between the two fluids are likely to be high. Shallow potable water is largely cool and, by definition, has low salinity, albeit at lower pressures than normal injection targets. This combination nonetheless suggests that dissolution rates in potable water supplies could be high. As CO_2 dissolves in water, a portion converts into carbonic acid by the reaction (Benson and others, 2002):

$$CO_2 + H_2O \leftrightarrows H_2CO_3 \leftrightarrows HCO_3^- + H^+$$

$$\text{(carbon dioxide)} + \text{(water)} \leftrightarrows \text{(carbonic acid)} \leftrightarrows \text{(bicarbonate)} + \text{(hydrogen ion)}$$

Carbonic acid contributes to a rise in pH of the water potentially to dissolve existing carbonate minerals and liberate heavy metals from within the formation, which may adversely affect the overall water quality (Metz and others, 2005). The ability of the aquifer and formation to buffer or otherwise resist the change in pH will be a site-specific characteristic.

Preventive Measures and Regulations

The key to successful geologic storage of CO_2 is appropriate characterization of local geology prior to CO_2 injection and the establishment of long-term monitoring and verification activities. The design phase of a project should follow all UIC permit regulations as administered by the local permitting body. Proposed EPA UIC regulations to prevent unnecessary risk to USDW define an adequate receiving and confining system for a CO_2 injection site as (Dougherty and McLean, 2007):

- A receiving zone of sufficient depth, areal extent, thickness, porosity, and permeability.
- A trapping mechanism that is free of major nonsealing faults.
- A confining system of sufficient regional thickness and competency.
- A secondary containment system that could include buffer formations and/or thick, impermeable confining rock layers.

A target formation possessing these attributes should be able to minimize migration of fluids into USDW, even in the event of leakage from the intended reservoir. In the end, there is no evidence that CO_2 may be stored underground any less effectively than other gases, such as methane and other hydrocarbons (Benson and others, 2002).

In order to standardize the permitting of these activities, EPA has proposed a new class of injection wells for the UIC Program, Class VI. These wells are those specifically designed for the purpose of geologic storage and are separate from those utilized for enhanced hydrocarbon recovery (U.S. Environmental Protection Agency, 2008d). The new Class VI wells will employ similar design and construction standards to those already enforced for Class I (wells for deep injection of hazardous and nonhazardous wastes) and Class II wells. New regulations alter requirements for AoR assessment, testing for mechanical integrity, and well plugging and ensure long-term postinjection monitoring and financial responsibility for geologic storage sites (U.S.

Environmental Protection Agency, 2008d). Also included in the new proposed regulations is the flexibility of certain permit criteria, which will allow permitting authorities to adapt these regulations to site-specific conditions. EPA hopes these new regulations will provide consistency and transparency for all stakeholders as the practice of geologic storage of CO_2 continues to grow (U.S. Environmental Protection Agency, 2008d). While some states are waiting for EPA to finalize its rules, many states, including Kansas, Montana, North Dakota, Oklahoma, Texas, Washington, West Virginia, and Wyoming, are moving forward with their own rules and regulations to accommodate CCS projects. A model statute and associated regulations were released in 2007 by the Interstate Oil and Gas Compact Commission to provide guidance to states as they undertake the effort of developing their own statutes and regulations covering the geologic storage of CO_2.

Mobilization of Brine

Possibility of Brine Mobilization

Many oil and gas reservoirs and all deep saline formations contain either saltwater or brine as the primary pore fluid. As CO_2 is injected into a reservoir, the local pressure increases and the formation fluids are displaced. In closed systems (a reservoir surrounded laterally, above and below by low-permeability units), the fluids cannot escape the reservoir and a combination of pressure increase, fluid compression, matrix compression, and/or reservoir expansion takes place. In open systems (units that are not laterally contained by impermeable units) and semiclosed systems (units with one or more low-permeability boundaries), brine may be mobilized and migrate away from the injection site. If an injection project (or multiple projects injecting into a single unit) are not properly managed, the potential exists for brine to migrate out of the unit. Unlike the trapping mechanisms that exist with CO_2, brine and lower-salinity waters are miscible fluids, so the dominant force preventing brine movement is the low-permeability units and the finite distance that an increase in pressure may affect brine movement.

Effects of Brine Mobilization

If brine were to migrate out of a deep saline formation into another formation, the brine would disperse the dissolved salt into the potable water unit. The primary effect within a formation experiencing brine contamination is an overall increase in saltiness and reduction of water quality. It has been theorized that large volumes of injected CO_2 may increase water table levels within hydraulically connected potable water formations. Furthermore, outflow from the formation into surface water may also increase (Nicot, 2008; Nicot and others, 2008). It is expected that the overall impact will be minimal and remain only in localized areas or may be avoided altogether through AoR and characterization activities.

Preventive Measures and Regulations

Displacement of brine fluids from saline formations in response to pressurization of the reservoir is a potential pathway for mobilizing impurities such as minerals or salt into USDW if not properly managed (Dougherty and McLean, 2007). The sealing units that prevent CO_2 migration from the reservoir must also play a role to prevent pressure-related fluid migration

(Birkholzer and others, 2008). Capillary entry pressure and relative permeability effects do not prevent brine migration either, so the cap rock unit must possess sufficiently low permeability to prevent fluid migration as well as CO_2 migration. All potential risks to USDW are subject to regulation under the SDWA, so risks associated with brine movement are subject to the same regulations described above. All risks to USDW associated with geologic storage of CO_2 will be described in the Class VI permitting process (U.S. Environmental Protection Agency, 2008d). State regulations may further determine how permitting is processed.

THE CONNECTION BETWEEN WATER PRODUCTION AND CCS

Description of CCS Produced Water

The quality of currently produced water varies widely from near-potable to that of potential environmental concern (Table 3). Oil and gas produced water quality depends on a variety of factors, including the reservoir geology of the producing formation, the regional geology, the type of (any) hydrocarbon produced, and the production history of the well and associated field. As a result, the qualities of produced water and the associated management strategies vary as much as the geologic conditions from which they originate.

Oil and gas produced water is generally considered a by-product of oil and gas operation; however, if improperly handled, it can cause damage, especially to surface and shallow groundwater resources, so treatment and/or safe disposal may be necessary. Produced water may contain a number of constituents that could prohibit its usefulness at the surface, mainly high concentrations of salts, trace metals, hydrocarbons, and dissolved organic compounds (Veil and others, 2004). Dissolved organics and dispersed hydrocarbons are of particular interest since they are difficult to remove (Stephenson, 1992). Oil and gas produced water may also contain a variety of treatment chemicals and/or proppants, solid particles, often sieved sand, which are

Table 3. Range of Common Water Quality Constituents in Produced Water Calculated from the U.S. Geological Survey Produced Water Database (All units [except for pH] are in mg/L, and the data represent 49,138 individual samples [U.S. Geological Survey, 2002]).

Constituent	Avg.	Min.	Max.
pH	7.08	5.00	8.98
Bicarb	639	0	14,700
Calcium	5056	0	74,185
Chloride	55,606	2	254,923
Magnesium	1048	0	46,656
Potassium	80	0	14,840
Sodium	25,083	0	149,836
Sulfate	1127	0	15,000
TDS	92,467	1000	399,943

injected into a well to hold hydraulically induced fractures open once the fracture pressure is released. These chemicals and proppants often require removal prior to disposal. Furthermore, produced water is warm or hot, often around 50°F near the surface in very shallow wells to over 300°F in deep wells or in areas possessing a high geothermal gradient. Recent advances in geothermal technology have turned this hot produced water into a potential form of renewable energy (Gosnold, 2009).

Water Management Strategies

Water management is a complex subject surrounding enhanced hydrocarbon recovery and underground storage. Water management is crucial because of the high volume of produced water (EOR operations average 7 bbl of water per bbl of oil in the United States [Veil and others, 2004]) and the high costs that can be encountered in its treatment and/or disposal. Ideally, minimization of produced water through proper well design, installation, and maintenance would be the primary management strategy. In the event that water is produced, the most direct form of management is reinjection into the reservoir. Currently, EPA Class II wells inject over 2 billion gallons of brine daily into saline formations and oil and gas reservoirs in the United States (U.S. Environmental Protection Agency Office of Water Management, 2004). Injection minimizes the environmental impact at the surface (Hum and others, 2006) and typically has a significantly lower cost than other options involving treatment. However, there are options for CCS produced water that may provide some economic benefit depending on the water quality. In the end, site-specific variables will determine the appropriate water management strategies.

Reinjection

The most straightforward method of any CCS produced water disposal will likely be through reinjection into underground formations. These formations are typically deep saline formations and are not otherwise suitable for drinking water. This method minimizes interaction with or processing of the produced fluid. As mentioned earlier, the EPA UIC Program and a variety of state agencies have established regulations and guidelines for injection wells that protect USDW. These include regulations that control the permitting, construction, operation, monitoring, and abandonment of these wells (New Mexico Energy, Minerals, and Natural Resources Department, 2006). In most cases, injection wells are drilled thousands of feet deep into target formations that are isolated from USDW by at least one and often several confining formations such as shale. Confining formations serve as seals or barriers to the migration of fluids into or out of the target formations. In addition, these deep target formations must meet geologic criteria that will allow for the injection of fluids such as appropriate formation and fracture pressures.

Proper well construction emphasizes isolation to prevent the migration of fluids from deeper formations into shallower formations. In general, shallower intervals that contain USDW are isolated from the well with well casing and cement. Within the casing, tubing is run from the top of the well to the bottom, where a packer is installed that isolates the upper sections of the well from the lower injection zone (U.S. Environmental Protection Agency, 2002). All injected fluids or CO_2 are carried by the tubing, providing further isolation from contamination. The permitting process allows for adjustment of this basic design, enabling the safe and effective installation of injection wells in a wide variety of geographic and geologic circumstances (New Mexico Energy, Minerals, and Natural Resources Department, 2006). To this point, the oil and gas industry has practiced underground injection for decades under these regulations.

If water is produced during CO_2 storage activities, reinjection of this water may also aid in the overall reservoir management strategy. Water injection can be effectively used to control plume migration in the subsurface by altering the reservoir pressures in specific areas. Additionally, the agitation of water in the subsurface will increase the contact area of CO_2 and undersaturated brine, greatly accelerating the dissolution process (Leonenko and Keith, 2008).

Alternatively, CCS produced fluids may be used as an active carrier of CO_2 to the storage formation. This is accomplished through the carbonation of water or brine at the surface followed by injection of the CO_2-enriched water into the formation. Ordinarily, CO_2 will dissolve in formation fluids over long time periods (on the order of centuries); however, this can be expedited on the surface by mechanically increasing the contact between the two phases (Bachu and others, 2007). This method minimizes the risks of CO_2 migration and leakage and potentially hastens mineral-trapping mechanisms. Effective use of these strategies can minimize the surface impact of any produced waters while maximizing the storage rate and capacity of a CO_2 storage operation.

Potential Use of CCS Produced Waters

In oil production, the sale of the incremental oil helps defer the costs associated with the treatment or disposal of produced water. Storage projects may not have the same economic benefits available; however, produced water can have several uses that may prove cost-effective over the option of simple disposal by reinjection, depending on the quality of the produced water. It is expected that, in most cases, when water is produced in a CCS project, it will have TDS levels in excess of 10,000 ppm and, as a result, would need to be treated for most common uses. The level of treatment required varies greatly on the effluent water quality and the application of the treated water (Hum and others, 2006). When allowed by permitting authorities, there may be circumstances where CO_2 storage associated with EOR and ECBM results in the production of water with TDS loads less than 10,000 ppm, which increases the opportunity for beneficial use of the water.

Use in Oil and Gas Operations

The recycling of oil and gas produced water for other oil and gas operations is a common practice in today’s oil fields, in particular those in areas where water resources are limited. These uses include water for the practice of waterflooding, hydraulic fracturing, and enhanced recovery through steam injection. Prior to use for most processes, the produced water must go through a certain amount of treatment to remove suspended and dissolved hydrocarbons, solids such as clays and other fine particles, treatment chemicals (if present) and, depending on the application, salinity may need to be addressed (Hum and others, 2006). In most cases, treatment will produce a waste stream that will also require disposal, such as through injection.

Waterflooding is a technique used to stimulate an oil reservoir once the pressure has subsided to the point where the wells no longer produce naturally. The injection of water in a waterflood operation pushes, or "drives," the oil toward the production well. A large amount of water is required for this process, so it is not uncommon for produced waters to be mixed with other water sources to increase injection volumes. Typically, injected water must be "compatible" with the formation water; that is, its water quality must be similar to the formation water to prevent the development of precipitates or other reactions within the formation that could result in decreased permeability. Additional treatment may also be required to prevent corrosion or other problems. This includes treatment with biocides to prevent bacterial contamination and removal of oxygen from the water to prevent scaling and/or corrosion (Hyne, 2001).

Oil and gas produced water has also been successfully used in hydraulic fracturing activities in Canada (Rieb and others, 2009). In hydraulic fracturing, large volumes of water, along with proppants, are pumped into a well at pressures high enough to fracture a formation in an effort to increase oil or gas production. Much of the water used in hydraulic fracturing returns to the surface when the well returns to production and becomes a new source of produced water, subject to the same treatment and disposal options as other produced waters. It is possible that a portion of the water generated through CO_2 storage may be reused several times for several hydraulic fracturing operations in areas where water resources are otherwise stressed.

Another potential use of water in oil fields is through thermal recovery (Hum and others, 2006). There are two common thermal recovery processes "cyclic steam injection," known in the industry as "huff 'n' puff," and "steamflooding." In either case, treated produced water is fed to steam generators which produce high-pressure steam that is injected into an oil well. In the huff 'n' puff method, the well is sealed for a period of days, allowing the steam to heat the oil in place, reducing its viscosity. The well is then reopened, and oil is pumped out. This process may be repeated 20 times or more until recovery is no longer economical. The steamflooding procedure is much like waterflooding except that the heat of the steam helps to reduce the oil's viscosity and further enhance production (Hyne, 2001). Aside from solids and hydrocarbons, produced water will need to be treated for water hardness prior to steam generation. If the TDS are below 8000 to 10,000 ppm, the water may be used to generate steam without treatment (Hum and others, 2006).

Industrial Use

Power generation is one of the largest users of water in the United States, ranking second in total withdrawals to irrigation in the year 2000 (U.S. Geological Survey, 2004). There are several power plant processes that utilize water, both physical and chemical, many of which have been described in the section on water, capture, and storage. The single largest water need is process and equipment cooling, a need that is shared by all fossil fuel-based plant operations. As previously mentioned, water used for cooling has limitations on its various constituents to prevent corrosion, scaling, or biofouling of tubing and equipment. Thus produced water will likely only be considered for power plant cooling if the water is of relatively good quality (low-TDS and impurities content) or only requiring basic treatment, and the source is close enough to the power plant to allow for economical transport of the water resource. Because of these restrictions, it is likely that the use of CCS produced waters as part of a cooling stream will be utilized first in regions where water resources are limited. This is also an area of current research.

Other industries currently use “degraded” water sources (such as gray wastewater) for a variety of uses. Some of these industries may benefit from the availability of CCS produced water in their regions. While some industrial processes require very high-quality water, others have lower standards. Some industries or processes that may benefit from produced water include paper and pulp production, the textile and tanning industry, certain chemical-manufacturing processes, cement production (U.S. Environmental Protection Agency, 2004), and a variety of municipal facilities that consume large amounts of water for washing or flushing toilets. These facilities include restaurants, hospitals, schools, and universities (Hum and others, 2006). In all cases, feasibility studies must identify the specific requirements of each potential reuse process as well as the expected produced water quality.

Transportation

In most cases, oil fields are remote sites with numerous unpaved roads that can create substantial dust (Veil and others, 2004). During dry times or times of heavy traffic, some regulatory agencies allow produced water to be sprayed on the roads to prevent the dust from mobilizing. Regulators may also limit the application in certain areas, such as near streams or other surface waters. In frigid regions, saline produced waters have been successfully (albeit controversially) used on roads to prevent ice and snow buildup at considerable cost savings over traditional road salt (Associated Press, 2009).

Geothermal Energy from Produced Brines

New power generation technology that utilizes a hot-water heat exchanger to warm a fluid with a low vapor pressure (known as a binary system) has been recently introduced and commercialized by several companies (Gosnold, 2009). This technology has greatly reduced the temperatures required to produce geothermal energy, in some cases qualifying produced water as the heat source. These systems have the potential to produce electricity from produced water (Gosnold, 2009). The generation and sale of this electricity could help offset the costs associated with the implementation of CCS technology at existing power plant and storage sites.

Typically, geothermal electricity generation requires high-temperature (>150°C) fluids that either decompress to high-pressure steam at surface conditions or produce a combination of water and steam that runs a turbine (Institute of Management and Technologies, 2007). A typical commercial geothermal well can generate between 5 and 8 MW of electricity (Duffield and Sass, 2003).

A more recent technology utilizes a binary system (also known as organic Rankine cycle, [ORC]), enabling “moderate geothermal resources,” meaning 85° to 170°C water, to be harnessed for electric generation. This range of temperatures is often observed in produced water. The water is run through a heat exchanger with a low-boiling-point “working” fluid, such as isopentane or various varieties of halogenated hydrocarbons (freons) that boil to a vapor, run the turbine, then are condensed and recycled (Bleim and Mines, 1991; Institute of Management and Technologies, 2007). Currently, U.S. binary geothermal power generation capacity is 2000 MW (Duffield and Sass, 2003). The systems use much smaller turbines than traditional geothermal power, from several kW up to 1 MW per unit; however, because of their modular design, several turbines can be easily linked to service one site. Geothermal power generation has long been at a disadvantage to fossil fuel power plants because of the greater cost (Bleim and Mines, 1991), despite the plentiful resource and zero-emission operation. As energy demand rises, the beneficial reuse of binary power generation may be highlighted, as it is estimated that oil field produced water has thousands of megawatts of untapped electric potential (Slack, 2009).

An additional geothermal need for water comes from enhanced geothermal systems (EGS), a process where hot, but not water-producing, rock is stimulated with injected water (Slack, 2009). The injected fluid is allowed to heat at the temperature and pressure of the formation, then the heated fluid is withdrawn, and its thermal energy is harnessed in a traditional or binary system. CCS produced water is potentially usable for EGS source and makeup water, as water quality requirements for this application are low, and resources are nearly always deep enough to inhibit USDW contamination (Slack, 2009).

Agricultural Uses

Since livestock are more tolerant of water impurities, produced water is used as a source of drinking water for animals where it is of appropriate quality and availability. EPA recommends TDS in drinking water for humans to be less than 500 ppm, but water with TDS less than 1000 ppm is considered excellent for livestock, with levels up to 7000 ppm being potentially usable (Veil and others, 2004). Metals such as cadmium, copper, molybdenum, nickel, and zinc are also a concern when watering animals, and each constituent should be analyzed independently when considering its use.

Agricultural irrigation is the largest use of freshwater in the United States, making up 39% of freshwater withdrawn (U.S. Geological Survey, 2004), and also accounts for over 80% of water consumed annually (U.S. Geological Survey, 2004). Because of concerns over water scarcity as a result of overpumping of groundwater resources (i.e., saline intrusion, subsidence, etc.), some states have already begun utilizing water reuse programs as an irrigation source (U.S. Environmental Protection Agency, 2004). Produced water may be used directly for irrigation in some cases if the salinity, sodicity, and toxicity (in the form of trace elements, excess chlorine, and residual hydrocarbons) are below a limit that will affect the crops or the soil. The requirements of water quality will vary according to the crop and soil type to which it is applied, and as such, the source of produced water and treatment will have to be matched to its application (U.S. Environmental Protection Agency, 2004).

Surface and Subsurface Uses

Freshwater, or produced water that has been suitably treated, can be injected into aquifers for future use (Veil and others, 2004). This activity also takes advantage of the natural filtration and biodegradation that occurs in the subsurface, allowing for some in situ treatment. Recharge can be accomplished through three major means: surface spreading, vadose zone injection, or direct injection. Surface spreading utilizes traditional treatment methods, such as lagoons, and requires the least amount of pretreatment, while direct injection requires the injected water be compatible with the formation water of the aquifer, thus requiring pretreatment (U.S. Environmental Protection Agency, 2004). The process of aquifer storage and recovery is in use in several places in the United States, but very few, if any, inject produced water at this time. Recently, a feasibility study of CBM produced water from the Powder River Basin in Wyoming was conducted by ALL Consulting (2006), which described the potential for injection of high-quality produced waters into shallow aquifers for later urban or agricultural use. Nevertheless, reinjection for recharge remains an area of continuing research.

A related use of any fresh CCS produced water would be surface discharge for the purpose of augmenting flow in stream or river systems. This could be particularly beneficial in water-stressed portions of the country where during normal or low-flow events all available water is already allocated or, in some instances, overallocated. Under the Clean Water Act, all surface discharges are subject to permits issued under the National Pollutant Discharge Elimination System (U.S. Environmental Protection Agency, 2009b). This program, as well as state and local permitting programs, will ensure that water used for augmentation will only contain constituents that are compatible with the surface system. This will protect the rights of downstream users and the environmental health of the system. As a result, in many instances, CCS produced water utilized for this use will require treatment.

CCS produced water may also be used in coastal areas to control saline water intrusion into aquifers that provide drinking water through the use of saltwater intrusion barrier wells. Wells in aquifers hydraulically connected to saline water bodies may become contaminated with saline water if the aquifer is overpumped (Argonne National Laboratory, 2007). This allows saline–freshwater interface to move onshore, potentially interfering with freshwater supplies. Coastal areas in California, Washington, Florida, and New York have had success controlling saline water intrusion with Class V injection wells. These wells inject water into the aquifer to be protected, raising the local pressure head, and either halt saline water advance or push saline water back toward the saline water body (Argonne National Laboratory, 2007). A variety of fluids have been injected in these wells including surface water, groundwater, treated drinking water, treated municipal wastewater, or mixtures of these sources (U.S. Environmental Protection Agency, 1999). Since these fluids are injected into freshwater supplies, the fluid must be treated to meet drinking water standards subject to the regulation of the local permitting body (U.S. Environmental Protection Agency, 1999). Treated produced water may provide an additional cost-effective source of water for these injection operations.

The potential also exists to generate potable water from produced water sources. Several processes exist for desalinization of saline waters to generate water fit for human consumption. The processes, cost, and amount of waste salt all depend on the salinity of the input water. In some, direct use of produced water for human consumption may encounter areas of social and political barriers and may only be a viable option when the need for water exceeds that of locally available supplies.

Water Treatment Technology for CCS Produced Water

The level of treatment required for a given water source depends on the quality of the water being treated and on the proposed use of the treated water. The quality of produced water is not only variable on a regional basis but may also vary significantly on a local basis, depending on the production history of a given well, the geology of the producing formation, and the type(s) of well (hydrocarbon vs. nonhydrocarbon) being produced. As described earlier, the addition of CO_2 for EOR or ECBM recovery may also influence the quality of water produced. As such, the quality of produced water designated for reuse needs to be adequately described. Furthermore, some consideration must be given for the quantity of water to be produced, in particular the minimum production rate. Most treatment technologies are optimized for specific flow rates, and flow streams that are too high will require storage, while lower flow rates will likely result in uneconomical treatment. Thus minimum expected production rates can be used as a basis for determining the size of a given treatment process, and allowances can be made for storage of excess production.

Treatment options for produced water range from routine to complex. Research and development is an ongoing process in the field of water treatment, with process improvements and innovations occurring regularly. Most treatment processes target a specific group of contaminants, so the water quality of the input stream and the desired output stream will dictate the type of treatment utilized. In most cases, the use of oil or gas produced water will require the removal of some, if not all, of the organic constituents (both soluble and insoluble) and dissolved solids and ionic species. As mentioned previously, most treatment begins with the basic separation of any insoluble hydrocarbons, water, and solids (such as clay or silt) through the use of settling tanks. Once any hydrocarbons are recovered, several conventional and innovative treatment processes may be utilized.

Conventional Water Treatment Processes

Conventional methods of water treatment remove particulates and unwanted chemicals from wastewater through a variety of physical and chemical processes. Physical processes include coagulation, flocculation, sedimentation, thermal desalination filtration, and active carbon adsorption. The chemical processes include ion exchange softening, lime softening, and disinfection.

A variety of filtration processes are capable of removing the vast majority of constituents, both inorganic and organic. Reverse osmosis is perhaps the most universal of filtration processes in terms of its ability to remove a wide variety of constituents from water, although other forms of filtration such as microfiltration, ultrafiltration, and nanofiltration may be preferred, depending on the end use (Crittenden and others, 2005). All forms of filtration are susceptible to fouling of the membrane surfaces and must be properly managed and maintained to perform at maximum efficiency. Large-scale reverse osmosis plants (capable of treating >100 mgd) have been built, although these large systems do not necessarily become cheaper with increased size (Yun and others, 2006). Some organic constituents may also be removed through activated carbon which preferentially absorbs these constituents from the water. Activated carbon may be incorporated as a filter bed or added to the treatment stream as a granulated powder and later removed through filtration (Crittenden and others, 2005). Activated carbon absorption also requires occasional regeneration or replacement.

Another common treatment for saline water is thermal desalination. Thermal desalinization is most commonly practiced in areas with abundant fossil fuels to capitalize on the cogeneration of power and water, such as in the Middle East. Rarely are thermal processes used to desalinate water with less than 10,000 ppm of TDS, and indeed the vast majority of these applications use seawater as the feed source, which typically has a TDS concentration of 35,000 ppm TDS. Thermal technologies are generally not cost-effective for low-TDS waters. The most common thermal technology is multistage flash (MSF) distillation, which employs thermal heating and reduced pressure zones to flash liquid water to vapor in a series of stages, each of which is at a lower pressure. This process is commonly coupled with power generation or oil and gas-processing facilities to make use of their waste heat and is capable of treating millions of gallons of water per day.

A variant of thermal desalinization is mechanical vapor recompression (MVR). The MVR system includes a boiler, multiple heat exchangers, and a vapor compressor. MVR is a very efficient water recovery process that extracts heat from the compressed vapor and transfers it to the liquid in the boiler. MVR requires compression, which increases the pressure of the steam produced. Since the pressure increase of the steam also generates an increase in the steam temperature, the steam can be used as a heat source for the remaining distillate. This cycle can be repeated many times, making the evaporation method very energy-efficient. Potentially, the system may only use the equivalent of 1/30th to 1/40th of the energy typically required to evaporate water by simple evaporation.

CCS produced water with high levels of dissolved calcium or magnesium may also be treated with a water-softening process such as lime softening or ion exchange softening. This process produces a sludge composed of calcium carbonate and magnesium hydroxide through a series of chemical reactions (Crittenden and others, 2005). This sludge is typically sent to landfills. Ion exchange-softening systems utilize ion exchange resins, which replace calcium and magnesium ions with sodium ions. The excess calcium and magnesium ions collect on the resin; thus it requires periodic regeneration by the application of a sodium-rich brine solution (Skipton and others, 2008). Disinfection of water, typically through chlorination, at the conclusion of the treatment phase may also be required depending on the end use.

Innovative Treatment Processes

Innovative treatment processes often use technology or engineering to enhance naturally occurring processes that may be applied to water treatment. These processes have been shown to be effective at a variety of scales, but their overall implementation is limited. Innovative processes discussed here include forward osmosis, freeze–thaw/evaporation (FTE®), and constructed wetland water treatment.

In reverse osmosis, high fluid pressure drives water molecules through a semipermeable membrane, an effective but expensive process. The innovative method of forward osmosis accomplishes similar filtration standards through the use of an osmotic pressure gradient, instead of a hydraulic pressure gradient, eliminating the need for high-pressure pumps and lowering the occurrence of membrane fouling (Cath and others, 2006). This process utilizes a draw solution to pull water molecules across a semipermeable membrane. The draw solution has a higher total dissolved concentration and, thus, a lower osmotic pressure than the treatment stream and induces a flow of water molecules from the treatment stream to the draw solution. This effectively separates the water in the treatment stream from its constituents. The design of the draw solution is optimized for the final application of the water and enables it to be utilized immediately after it has been freshened by the treatment stream or after a simplified treatment process such as filtration (Cath and others, 2006).

The innovative process known as FTE is applicable in areas where seasonal temperatures drop below freezing. In this process, commercialized by the Energy & Environmental Research Center, Gas Research Institute, and B.C. Technologies, water is sprayed onto a freezing pad during times when the air temperature is low enough to promote freezing. The ice that forms is composed of relatively pure ice crystals, while the remaining concentrated brine, which has a lower freezing point, is drained off into a separate holding tank for reuse or disposal (Sorensen and others, 2002). Once seasonal temperatures increase, the relatively pure meltwater is collected for reuse in other applications. The system operates as a traditional evaporative purification facility during warm months (Sorensen and others, 2002). This process is simple, easily automated, and readily scalable. Recent applications of these processes in Wyoming are treating more than 40,000 gallons/day.

Constructed wetlands designed for water treatment utilize biogeochemical transfer and transformation processes such as oxidation, reduction, and sorption, which take place in the sediments of wetland environments. These specifically designed systems can provide effective treatment by reducing the quantity of metals, dissolved oil and grease, suspended solids, organic matter, and nutrients at a lower energy cost than traditional treatment facilities (Verhoeven and Meuleman, 1999; Mooney and Murray-Gulde, 2008; Nelson and Gladden, 2008; Rodgers and Castle, 2008). Constructed wetland treatment systems have proven effective for treating both organics and metals in oil field produced waters (Myers and others, 2001; Al Mahruki and others, 2006; Ji and others, 2007). Some constructed wetland treatment systems require increased water residence time and increased acreage needed for the facility (Kadlec and Knight, 1996). Currently, the city of Arcata in northern California treats its wastewater with a constructed wetland system capable of processing nearly 6 million gallons per day of wastewater through the combination of conventional settling and mechanical separation with constructed ponds and wetlands (U.S. Environmental Protection Agency, 1993). Some water constituents, such as high TDS, require hybrid wetland treatment systems, which incorporate components to handle the conservative elements (Kadlec and Knight, 1996; Murray-Gulde and others, 2003; Johnson and others, 2008). As such, constructed wetland systems can be used in combination with other processes for the treatment of produced water and may be part of an efficient, effective, and environmentally beneficial treatment suite.

SUMMARY AND CONCLUSIONS

CCS comprises a promising set of technologies with the ability to significantly reduce anthropogenic CO_2 emissions into the atmosphere. The WWG was formed to address concerns and challenges pertaining to CCS and the utilization of water resources. The focus is on addressing the interactions of water with the implementation of large-scale CCS from a regional perspective, as the related benefits and complications will vary on a regional scale. The process involves capture from stationary point sources, compression, transportation and, finally, injection into unminable coal seams, depleting/depleted oil or gas reservoirs, or deep saline formations. Fossil fuel-based power plants are among the likely stationary sources of CO_2 to be affected. Water will be required for any new CCS processes and equipment and will increase the already large water demand of most power generation facilities because of the increased water demand of capture technologies and their high parasitic power requirements.

Water use in power generation varies greatly depending on the design of the plant, the most common using pc to produce steam. Newer plants may also utilize coal gasification or oxyfuel combustion to generate electricity. Water is required for cooling equipment in all three designs; however, the greatest amount needed per kilowatt produced is in pc plants, which also require a greater amount of water for flue gas desulfurization—a product removed from the fuel prior to combustion in the other two designs.

Each plant design has different options for carbon capture, each with attendant water demands. Fossil fuel utilization platforms include postcombustion, precombustion, and flue gas refinement (oxyfuel). Postcombustion, developed for gas refinement or pc plant retrofit, likely necessitates the use of a chemical solvent that absorbs CO_2 from the flue gas stream and then separates the CO_2 during a stripping and solvent regeneration phase. Precombustion occurs in gasification plants where CO_2 can be separated from the fuel prior to combustion. Flue gas refinement occurs in oxyfuel combustion, where nonoxygen species in the intake gas stream, primarily nitrogen, are removed prior to combustion, resulting in a flue gas highly enriched in CO_2.

After capture, compression, and transportation, CO_2 is injected into an unminable coal seam, oil or gas reservoir, or deep saline formation. Upon introduction to the formation, the CO_2 will begin to migrate through formation fluids where it adsorbs (in coals), mixes (in oil and gas), or dissolves (in brine). For the purposes of storage in saline formations, water production is not required, although the practice may add to the effective capacity or be used to control CO_2 plume movement. For EOR and ECBM objectives, CO_2 and hydrocarbons will be produced along with formation water; however, the hydrocarbons, gas, and water can typically be separated, and the CO_2 and water can be reinjected and eventually left in the formation indefinitely.

In most cases, the processes pertaining to CCS should be optimized to minimize water production. To date, no non-EOR CCS projects have produced water. If water production is necessary, it will likely be disposed of through reinjection, unless a beneficial use is found to be economically viable. Beneficial use is much more likely in the case of CBM produced water, which tends to be of higher quality (in the fresh and treatable range). In EOR projects, recycling of produced water is likely the most viable management technique. Water produced in water-stressed regions where minimal treatment can be employed for other beneficial uses may be attractive.

Fresh or treated water has been used to recharge aquifers, livestock watering, industrial and power generation cooling, crop irrigation, human consumption, and for various industrial tasks. Several treatment options have been developed to remove constituents from water, each suited to a variety of input water qualities. The treated water may be fit for various tasks, depending on the level it was treated to, and the waste stream (concentrates or crystallized) properly disposed of. Lower-quality water and saline water have a reduced set of uses; however, the heat present in some CCS produced water may be put to use. Typically, geothermal waters have been used for heating or electrical generation if temperatures were sufficient. Recent technology has reduced the minimum temperature for power generation within the bottomhole range of some oil and gas produced water.

EPA has established a regulatory framework that protects all surface water and USDW from potential pollution according to the SDWA. All CCS activity will be required to operate within this framework, as careful implementation of all environmental regulations is paramount to the overall vision and ultimate success of CCS programs. For instance, wells are typically designed to be drilled to depths below USDW and contain a variety of protective measures such as casing, cementation, and tubing that separate the well fluids from other fluids present below the surface. Also, all injection activities will be only permitted to occur beneath sealing formations, such as shale, which further separate injection activities from USDW zones. A new set of regulations has been proposed by EPA to address injection related to wide-scale implementation of CCS which includes further protection of USDW as well as providing consistency regarding regulation. Some states are also moving ahead with their own rules and regulations to accommodate CCS.

Water issues will almost certainly increase through implementation of CCS technology by an amount highly dependent on the design of the point source and the method of capture. Injection of CO_2 should be optimized to minimize produced water to the extent possible through careful management and proper site selection. In the instance that water must be produced, beneficial uses should be explored. Should no beneficial use be found, standard practices exist for the safe disposal of produced waters, primarily through reinjection into a suitable formation.

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