Evaluation of the Beneficial Re-Use of Produced Water: A Review of Relevant Guidelines and Produced Water Toxicity.

by

Oluwadamilare Adebambo

Dr. David Hinton, Advisor
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Abstract

As global demand and production of fossil fuel (oil and gas) continues to increase, so do their associated environmental footprints. One example is produced water (PW), i.e. water used or extracted along with oil. Presently, over 5 billion gallons of PW is generated daily. In the past, produced water was simply re-injected into the empty oil well after extraction. As freshwater supply becomes increasingly scarce, PW can become an important water source after suitable treatment. This masters' project investigates the current beneficial reuse options of PW and the potential environmental risks that could result from this reuse

My literature review was conducted on PW generation during oil and gas extraction, and focused on significant constituents and their characteristics, treatment methods and current regulations guiding reuse. I concentrated on land-based oil and gas extraction since these activities use valuable freshwater. Peer-reviewed publications were used when available but industry and consultant reports were also used when necessary. Researchers at Clemson University with ongoing projects on PW treatment were interviewed for more up to date information.

A large body of literature confirms that toxicity of PW varies with age of the oil well and between different operations. However, salinity, dissolved oil and aromatics were often the constituents of concern. Salinity limits also confound PW toxicity assessment as current regulatory test organisms are salt intolerant. Therefore there is great need to develop cost-effective technology for desalination and to include more salt tolerant toxicity test species. Based on these findings, a decision framework was developed to better guide the beneficial reuse of PW in such a way that environmental risks are considered and minimized.

Chapter 1 - Introduction

1.1 Introduction

Communities across the world face water challenges due to increasing demand, drought, depletion and contamination of groundwater, and dependence on single sources of supply (Miller, 2006). There has been a push in recent times towards water reclamation, recycling and reuse (Miller, 2006) to address these challenges. Reusing water, that would otherwise be wasted, could potentially provide a wide range of opportunities for communities to meet freshwater needs and eventually create significant value for participating communities, the general public and the environment. Large regulatory institutions such as the World Bank and the US EPA have also endorsed wastewater reuse. The World bank recognizes that 'wastewater from point sources such as sewage treatment plants, industries and thermal power stations can provide an excellent source of reusable water because it is usually available on a reliable basis, can be accessed at a single point and has known quality' (World Bank, 2003). According to the US EPA, 'water reclamation and reuse offer an effective means of conserving our limited high-quality freshwater supplies while helping to meet the ever growing demands for water' (U.S. EPA, 2004). One of such types of wastewater considered for reuse is water generated during oil and gas extraction activities, known as 'produced water'.

Produced water (PW) is subsurface formation water coproduced during oil and gas production (Sauer et al, 1997) and has been described as the largest offshore discharge associated with fossil fuel extraction (Balaam et al, 2008). Over the economic life of a producing field, the volume of PW can be more than 10 times the volume of hydrocarbon produced (Stephenson, 1992). In many onshore areas of the world, PW is usually injected into underground formations or simply discharged in wetlands and offshore areas (Stephenson, 1992). However, declining freshwater resources have sparked a recent interest in the beneficial reuse of PW for a wide variety of uses ranging from agricultural to industrial, and under extreme situations as potable water. Miller (2006) suggests that 'one of the most significant benefits of water reuse is the value created by the inclusion of water reuse in integrated water resources planning and other aspects of water policy and the implementation of water projects resulting in the long-term sustainability of our water supplies'. To effectively carry out these integration projects, there is a need for inclusion of several relevant areas such as regulation, associated health impacts, public perception and effective government institutions (Miller, 2006). However, from these complex connections, arise the need to consider the associated potential human health and ecological risk from the reuse of PW.

Hence, this study aims to examine these potential risks by conducting an extensive review of literature on related areas. The review spans across the complex composition of PW and related toxicity studies, beneficial re-use options of PW as well as relevant guidelines guiding re-use. Conclusively, a generated framework is recommended for future use. This work is as a result of collaboration with a research lab at Clemson University currently conducting analysis on the potential for beneficial re-use options of PW.

1.2 Global Water Crisis

The United States Geological Survey (USGS) defines freshwater as water containing less than 1,000mg/L of total dissolved solids, mostly salts. Freshwater represents only about 3% of all water on earth, with easily accessible freshwater i.e. lakes, swamps and rivers, accounting for a mere 0.29% of the world's freshwater (USGS, 2005).

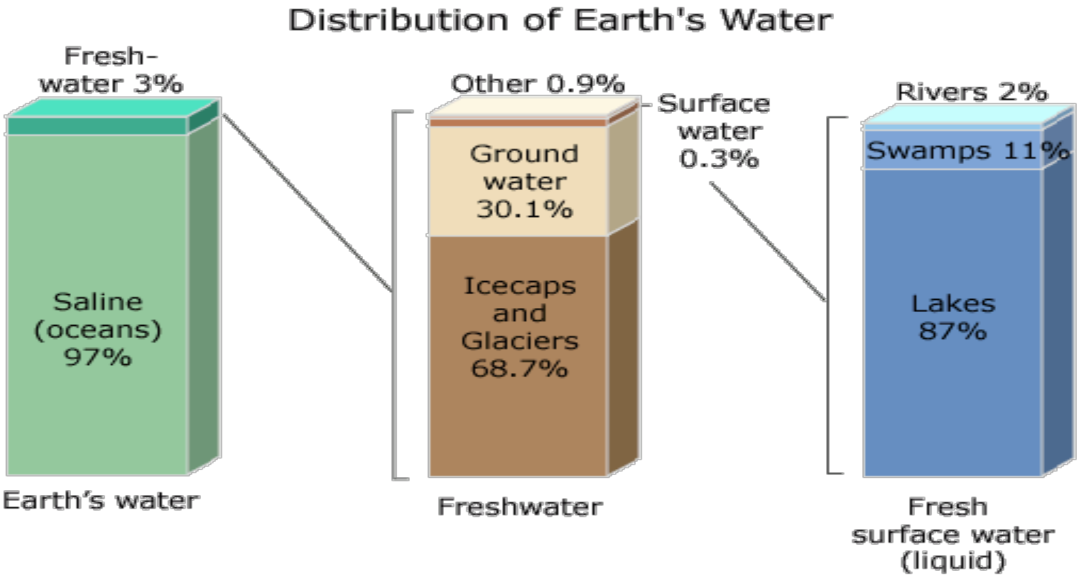

Fig 1: Distribution of Earth's Water (Source: Gleick, P. H., 1996)

According to the United Nations Environmental Program, approximately 70% of the worldwide freshwater resources are consumed by the agricultural sector, 20% by the industrial sector and 10% by the domestic sector. By 2025, agriculture is expected to increase its water requirements by 1.2 times, industry by 1.5 times and domestic consumption by 1.8 times (UNEP, 2002). However, as earlier mentioned, vast amounts of freshwater are utilized during the exploration and drilling of petroleum resources.

The challenge of PW is further compounded by water being a valuable resource especially in arid oil producing regions of the world. In dry climates, where easily accessible sources of freshwater are limited, large volumes of freshwater are being used for non- potable uses, such as by the agricultural and industrial sectors. There is also some correlation between the availability of freshwater supplies across the globe, and the location of oil and gas reserves. Regions of North Africa, the Middle East and America have scarce or stressed supplies of freshwater, 85-90% of which is being used for agriculture. These countries also have abundant reserves of oil or gas. Water reuse is accepted in principle in most industrialized and developing countries.

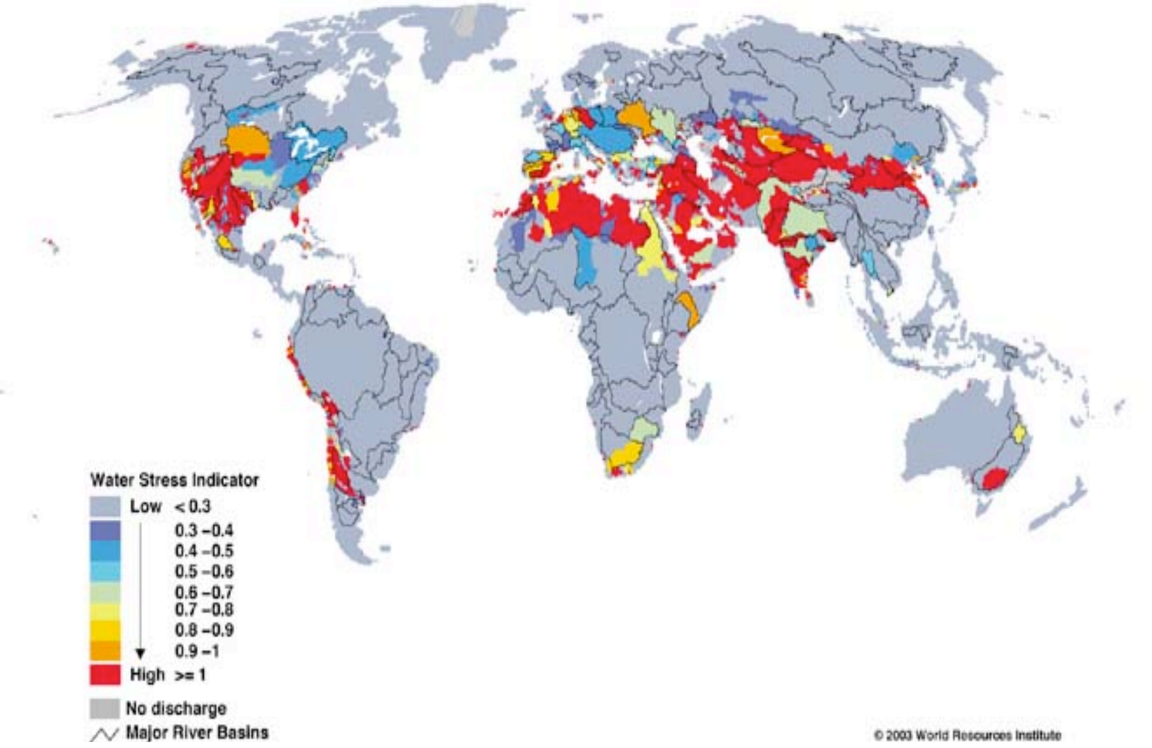

Figure 2: Projected Water Stress in 2025 (Source: World Resources Institute, 2003)

Chapter 2 – Objectives & Methods

2.1 - Objectives

The complex and variable composition of PW makes it difficult to assess which components have the potential to cause the most environmental harm. An optimal approach would be to determine the potential environmental risk by correlating toxicity and known contaminant concentration within PW to identify causes of observed effects. This approach is suitable when a group of substances can be clearly identified as having a detrimental effect or if the appropriate toxicity tests are utilized (Balaam et al, 2009). However, the physical and chemical properties of produced water vary significantly depending on the geographic location of the field, the geologic formation, and the type of hydrocarbon being produced. Based on the above, the main objectives for this project are:

1. Review current regulations for proposed re-use options.
2. Evaluate the potential for ecological and human health risk from the re-use of PW.
3. Make recommendations for future procedures

2.2 Methods

The methods used in conducting this research fall under 2 broad categories:

1. Literature review on the following subject areas:
    - Investigations on the assessment of toxicity of produced waters.
    - Current re-use options for treated produced water.
    - Regulations governing PW reuse and discharge

2. Interviews and Collaboration with relevant laboratories/investigators

- Consulting with laboratories performing aquatic toxicity studies with an emphasis on the organisms used and the endpoints of the tests.
- Collaboration with scientists/researchers who operate and design constructed wetlands.

Chapter 3 - Produced Water (PW)

3.1 Definition

According to the US Department of Energy (DOE), the term "produced water" (PW) has been assigned to water trapped in underground formations & brought to the surface along with oil or gas. The idea being that these are waters "produced” during operations or extraction of energy containing materials -fossil fuels- from the earth.

3.2 Origin of Produced Water (PW)

Naturally occurring rocks found in subsurface formations are generally permeated with fluids such as water and oil, or gas or mixtures of these substances. There is a hypothesis that the rocks that constitute most oil-bearing formations were completely filled with water prior to the deposit and accumulation of petroleum (Amyx et al. 1960). Gradually and over time, hydrocarbons migrated to cracks and trap locations, displacing some of the water from the formation in becoming hydrocarbon reservoirs. Hence, reservoir rocks normally contain both petroleum hydrocarbons (liquid and gas) and water. Sources of this water may include flow from above or below the hydrocarbon zone, flow from within the hydrocarbon zone, or flow from injected fluids and additives resulting from production activities (Fakhru’l-Razi et al, 2009). This water is frequently referred to as “connate water” or “formation water” and becomes produced water when the reservoir is produced and these fluids are brought to the surface (Veil et al, 2004).

Crude oil has a lower density (between 790 – 873kg/m^3) than water (1000kg/m^3) (Simetric, 2007) and as such, floats above the natural water layer/formation water.

In addition to the large volumes of water these reservoirs contain, more water is injected to help force the oil to the surface and achieve maximum oil recovery.

When hydrocarbons are extracted, they are brought to the surface as a mixture of produced fluids. The composition of this produced fluid is largely dependent on whether crude oil or natural gas is being extracted and generally includes a mixture of either liquid or gaseous hydrocarbons, produced water, dissolved or suspended solids, produced solids such as sand or silt, and injected fluids and additives that may have been placed in the formation as a result of exploration and production activities (Veil et al, 2004).

At the surface, PW is separated from the hydrocarbons, treated to remove as much oil as possible, and then either discharged into water bodies or injected back into the wells (Utvik, 1999). After treatment, PW still contains traces of oil, dissolved organics (including hydrocarbons), organic acids, phenols, production chemicals and inorganic compounds such as varying amounts of chlorides, sulfides, bicarbonates, ammonia, hydrocarbons, phenolic compounds, metals, and suspended solids (Ray & Engelhardt, 1992).

3.3 Global PW Production

Produced water is by far the largest volume byproduct or waste stream associated with oil and gas exploration and production. Approximately 21 billion bbl (barrels; 1 bbl = 42 U.S. gallons) of PW are generated each year in the United States from nearly a million wells. This represents about 57 million bbl/day, 2.4 billion gallons/day, or

913,000 m^3/day (Clark and Veil 2009). More than 50 billion bbl of PW are generated each year at thousands of wells in other countries with global PW production estimated at around 250 million barrels per day compared with around 80 million barrels per day of oil (Fakhru'l-Razi et al, 2009). It should be noted that PW volume varies primarily with age of the oil field and management methods employed during extraction.

3.4 Significant PW Constituents and Toxicity

This section describes constituents typically found in PW, and, to the extent that information is available, why they are of concern.

3.4.1 Dispersed & Dissolved Oil

This term refers to organic material that is either dispersed or dissolved in PW when discharged. Dispersed oil consists of small discrete droplets suspended in water while soluble oil is present in a dissolved state (Ray & Engelhardt, 1992).

3.4.1.1 Dispersed Oil

Oil is an important discharge contaminant, primarily because of potentially toxic effects around the discharge point. Dispersed oil consists of small droplets suspended in the aqueous phase. When discharged along with PW, dispersed oil may accumulate in the floor of the aquatic system, thereby resulting in contamination and accumulation of oil on aquatic sediments, which can potentially affect the benthic community negatively (Veil et al, 2004). Dispersed oils that do not reach the bottom may also rise to the surface and spread, causing sheening and increased biological oxygen demand near the mixing zone (Stephenson 1992), making hypoxic conditions likely. Volatile components may also evaporate with the more toxic compounds being the most volatile (Ray & Engelhardt, 1992). Factors that affect the concentration of dispersed oil in PW include oil density, interfacial tension between oil and water phases, type and efficiency of chemical treatment, and type, size, and efficiency of the physical separation equipment (Ali et al. 1999).

3.4.1.2 Dissolved or Soluble Organic Components

Soluble oil differs from dispersed oil in that it is not readily removed from PW and remains present even after treatment (Ray & Engelhardt, 1992). This can invariably increase the polar constitution of PW and subsequently, the amount of dissolved hydrocarbons (Veil et al, 2004). Hydrocarbons that are found predominantly in PW include organic acids, polycyclic aromatic hydrocarbons (PAHs) and phenols. It has been shown that these hydrocarbons are likely contributors to PW toxicity in that they are additively toxic even though individual toxicities may be insignificant (Glickman 1998).

Typically, the concentration of organic compounds in PW increases as the molecular weight of the compound decreases. However, even though these low molecular-weight compounds are present in large concentrations, it does not reflect in the oil and gas measurements because the organic solvent used in oil and grease analysis extracts virtually none of them due to their high solubility (Ali et al, 1999). Organic components that are very soluble in PW consist of low molecular weight (C2-C5) carboxylic acids (fatty acids), ketones, and alcohols. They include acetic and propionic acid, acetone, and methanol and in some PWs, their concentration may be greater than 5000ppm (Veil et al, 2004).

Partially soluble components include medium to higher molecular weight hydrocarbons (C6 to C15) such as aliphatic and aromatic carboxylic acids, phenols, and aliphatic and aromatic hydrocarbons (Veil et al, 2004). Aromatic hydrocarbons are structured around a benzene ring and made up primarily of carbon and hydrogen. PAHs are hydrocarbon molecules with several cyclic rings and are formed naturally from organic material under high pressure. Naphthalene is the most simple PAH, with two interconnected benzene rings and is normally present in higher concentrations than other PAHs (Veil et al, 2004). PAHs may vary based on their solubility from relatively "light" substances with average water solubility to "heavy" substances with high liposolubility and poor water solubility. While contributing to the formation of sheen, the major concern about these compounds centers on toxicity. They increase biological oxygen demand, are highly toxic to aquatic organisms, and can be carcinogenic to man and animals. Some may mutagenic and harmful to reproduction. Heavy PAHs bind strongly to organic matter (e.g., on the seabed) contributing to their persistency (EPA 2003). Aromatic hydrocarbons (including PAHs) and alkylated phenols are perhaps the most important contributors to toxicity (Frost et al. 1998). Alkylated phenols are considered to be endocrine disruptors, and hence have the potential for reproductive effects (Frost et al. 1998). However, phenols and alkyl phenols can be readily degraded by bacterial and photo-oxidation in seawater and marine sediments (Stephenson 1992).

3.4.2 Treatment Chemicals

Treatment chemicals include biocides, reverse emulsion breakers, and corrosion inhibitors and pose the greatest concerns for aquatic toxicity. The effects associated with the use of treating chemicals depend almost entirely on the particular chemical and quantity used as well as the treatment application method (Stephenson, 1992). Batch treatment involves the use of a greater volume of chemical than continuous treatment mode, and usually concentrations may exceed the toxic level for the chemical (Stephenson, 1992). However, some of these chemicals can be lethal at levels as low as 0.1 ppm even though these substances may undergo reactions that reduce their toxicities before they are discharged or injected (Glickman 1998). For example, biocides react chemically to lose their toxicity, and some corrosion inhibitors may partition into the oil phase so that they can never reach the final discharge stream (Glickman, 1998).

3.4.3 Heavy Metals

The concentration of metals in PW is field-specific and importantly related to the age and geology of rock formation from which the oil and gas are produced (Veil et al, 2003). Interestingly, there is no correlation between concentration in the crude and in the water produced with it (Utvik 2003). Metals commonly found in PWs include zinc, lead, manganese, iron, and barium. Metals concentrations in PW are often higher than those in seawater (Stephenson, 1992), although elevated levels of metals have been reported in sediments around producing locations (Neff, 1998). However studies suggest that potential impacts on aquatic organisms may be low, because dilution reduces the concentration and because the form of the metals adsorbed onto sediments is less bioavailable to aquatic animals than metal ions in solution (Stephenson 1992; Neff 1988).

3.4.4 Naturally Occurring Radioactive Material (NORM)

Like heavy metals, NORM originates in geological formations and can be brought to the surface with PW (Veil et al, 2003). The most abundant NORM compounds in PW are radium-226 and radium-228, which are derived from the radioactive decay of uranium and thorium associated with certain rocks and clays in the hydrocarbon reservoir (Utvik 2003). As the water approaches the surface, temperature changes cause radioactive elements to precipitate and the resulting scales and sludge may accumulate in water separation systems. In the North Sea, where ambient concentrations of Ra-226 are 0.027- 0.04 Bq/L, measured concentrations in PW range from 0.23 to 14.7 Bq/L (Utvik 2003). Radium contamination of PW has generated enough concern that some states have placed additional requirements on National Pollution Discharge Elimination System (NPDES) permits that limit the amount of radium that can be discharged. Compounding the NORM concern is that chemical constituents in many PWs can interfere with conventional analytical methods, and, as a result, radium components can be lost, leading to a false negative result for samples that may contain significant amounts of NORM (Demorest and Wallace 1992).

3.4.5 Salinity

The salinity of produced water can range from very low to high depending on geology and the production process (Stephenson, 1992). This constituent is discussed extensively in Section 4.4.1.

3.5 PW Treatment and Management

A three-tiered pollution prevention hierarchy is followed for managing PW, as follows:

1. Employing technologies to minimize volumes of PW produced,
2. Reuse (e.g. reinjection) and recycling PW where possible,
3. If neither of these tiers is practical, disposal is the final option (Veil, 2007)

Some of the options available to oil and gas operators for PW management proposed by Arthur et al. (2005) are as follows:

1. Injection: Re-injection of PW into the same formation from which the oil is produced or into another formation.
2. Discharge: treatment of PW to meet onshore or off- shore discharge regulations.
3. Reuse in oil and gas operation: treat the PW to meet the quality required for use in usual oil and gas fields operations.
4. Consume in beneficial use: PW treatment to meet to quality required for beneficial uses such as irrigation (Boysen et al, 2002), range-land restoration, cattle and animal consumption, and drinking water (Rao et al, 2005)

Treatment of PW is an effective option for PW handling. The general objectives for operators for treating PW are as follows (Arthur et al, 2005):

1. De-oiling: removing dispersed oil and grease;

2. Removal of soluble organics;

3. Disinfection: removal of microorganisms, predominantly bacteria;

4. Removal of suspended solids

5. Dissolved gas removal: removing of light hydrocarbon gases, carbon dioxide, and hydrogen sulfide,

6. Desalination: removing dissolved salts,

7. Softening: removing excess water hardness,

8. Miscellaneous: removing NORM.

3.6 Current Beneficial Reuse Options

3.6.1 Livestock Watering

The quality of water for livestock consumption is normally subjected to lower standards than that of human consumption. Livestock can tolerate a range of contaminants in their drinking water. However, at elevated contaminant concentrations, the animals though able to survive may begin to show some impairment (Veil et al, 2003).

Total dissolved solids (TDS) is the term used to describe the inorganic salts and small amounts of organic matter present in solution in water. The principal constituents are usually calcium, magnesium, sodium, and potassium cations and carbonate, hydroxy carbonate, chloride, sulfate, and nitrate anions (WHO, 1996). In general, animals can often tolerate a higher degree of TDS if they are gradually acclimated to the elevated levels. Water with TDS less than 1,000 ppm is considered to be excellent source water but water with TDS from 1,000 up to 7,000 ppm can be used for livestock but may cause some diarrhea (ALL 2003). Some coal-bed methane (CBM) projects on ranch land have created impoundments or watering stations to provide PW as a drinking water source for livestock (Veil et al, 2003).

3.6.2 Wildlife Watering and Habitat

Artificial PW-filled impoundments can be used to provide a source of drinking water for wildlife and offer habitat for fish and waterfowl in an otherwise arid environment Some Rocky Mountain area CBM projects have created impoundments that collect and retain large volumes of produced water (ALL, 2003). Some of these impoundments have surface areas of at least several acres. However, it is important to make sure that the quality of the impounded water will not create health problems for the wildlife. The impoundments can also provide additional recreational opportunities for hunting, fishing, boating, and bird watching.

3.6.3 Aquaculture and Hydroponic Vegetable Culture

Jackson and Myers (2002) report on greenhouse experiments to raise vegetables and fish using PW or potable water as the water source. The system used a combination of hydroponic plant cultivation (no soil) and aquaculture. Tomatoes grown with produced water were smaller than those grown in potable water. The produced water tank grew a larger weight of tilapia fish (Orechromis niuloticus/aureus), although some of the fish died. None of the fish in the potable water tank died. From the test results above, there is need to apply caution when using PW for such purposes.

3.6.4 Irrigation of Crops

Many parts of the United States and around the world have limited freshwater resources. Crop irrigation is the largest single use of freshwater in the United States, making up 39% of all freshwater withdrawn, or 150 billion gallons per day (USGS 1998). If produced water has low enough TDS and other characteristics, it can be a valuable resource for crop irrigation.

ALL (2003) summarizes crop irrigation water quality requirements, noting that the three most critical parameters are salinity (affects crops), sodicity (affects soil), and toxicity (affects crops). Salinity is expressed as electrical conductivity in units of mmhos/cm or more currently in microSiemens per cm (µS/cm). Crops have varying susceptibility to salinity; as salinity rises above a species-specific salinity threshold, crop yields decrease.

Excess sodium can damage soils. Higher SAR (Sodium Absorption Ratio) values lead to soil dispersion and a loss of soil infiltration capability. When sodic soils are wet, they become sticky, and when dry, they form a crusty layer that is nearly impermeable. Paetz and Maloney (2002) describe an approach for treating CBM water to mitigate its salinity and sodicity problems so it can be used in a managed irrigation program.

Some trace elements in produced water can cause harmful effects to plants when present in sufficient quantities. ALL (2003) suggests that the most common sources of plant toxicity are chloride, sodium, and boron.

Another source of information on the effects of applying produced water to soils is a manual developed for the American Petroleum Institute on remediation of soils that had experienced produced water spills (API 1997). The authors of that manual have subsequently taught a series of workshops on the same subject. The manual is a detailed guide with much useful technical information on the impacts of salinity and sodium on soils and vegetation.

Texas A&M University established a program to develop a portable produced water treatment system that can be moved into oil fields to convert produced water to potable or irrigation water. The goal is to produce water suitable for agricultural use (less than 500 mg/L of total dissolved solids and less than 0.05 mg/L of hydrocarbons). Such a system not only augments scarce water supplies in arid regions, but also provides an economic payback to operators that could allow the well to produce longer (Burnett et al. 2002; Burnett and Veil 2004).

3.6.6 Industrial Uses

PW may be substituted in various industrial practices in areas where traditional surface and groundwater resources are scarce. This may be subject to treatment before use and in some cases, PW may be used without treatment depending on what it’s being used for in the industrial process and if no risk/harm is posed to workers or surrounding ecosystem.

3.6.6.1 Dust Control

In most oil fields, the lease roads are unpaved and can create substantial dust. Some oil and gas regulatory agencies allow operators to spray produced water on dirt roads to control the dust. This practice is generally controlled so that produced water is not applied beyond the road boundaries or within buffer zones around stream crossings and near buildings.

CBM produced water may be generated in areas with active surface coal mining. Surface mining, processing, and hauling are inherently dusty activities. PW can be used for dust suppression at those locations, too, if regulators allow the practice (Murphree 2002).

3.6.6.2 Vehicle and Equipment Washing

ALL (2003) notes that some state and federal agencies recommend that vehicles and equipment leaving production sites be washed to control the possibility of distributing seeds of undesirable weed species.

3.6.6.3 Oil Field Use

Peacock (2002) describes a program in New Mexico through which produced water is treated to remove hydrogen sulfide and then is used in drilling operations. This beneficial reuse saves more than 4 million bbl per year of local groundwater.

3.6.6.4 Use for Power Generation

In at least one case, produced water is used to supply water to make steam. About 360,000 bpd of produced water from a ChevronTexaco facility in central California is softened and sent to a cogeneration plant as a source of boiler feed water (Brost

2002).

Another potential use of produced water is cooling water. The electric power industry is the second largest user of freshwater in the United States, making up 38% of all freshwater withdrawn, or 150 billion gallons per day (USGS 1998). Conventional surface and ground water sources are no longer sufficient to meet increasing power plant needs in many parts of the country. Produced water represents a large-volume source of water that could potentially serve as make-up water for a power plant. In August 2003, DOE/NETL announced that it had awarded a contract to a group of researchers led by the Electric Power Research Institute to study the feasibility of using water produced from CBM production to meet up to 25% of the cooling water needs at the San Juan Generating Station in northwestern New Mexico. The researchers will evaluate the quality, quantity, and location of the produced water. They will also evaluate the existing produced water collection, transportation, and treatment systems for possible use in delivering cooling water to the generating station. The results are expected in about two years. Argonne National Laboratory recently completed a study that evaluates the use of another alternative type of water supply for power plant cooling (Veil et al. 2003). Although that study considers underground pools formed in abandoned coal mines, many of the report's discussions concerning water quality, water quantity, and mode of operation are relevant for using produced water as a cooling source.

3.7 Fire Control

Fires often break out during the driest portions of the year and in areas experiencing drought conditions. In many cases, only limited surface and ground water resources are available for fire fighting in these areas. Although application of large volumes of saline produced water can have an impact on soils, this impact is far less devastating than a large fire (Veil et al, 2003). ALL (2003) reports that firefighters near Durango, Colorado, used CBM produced water impoundments as sources of water to fill air tankers (helicopters that spray water onto fires) during the summer of 2002.

Chapter 4 - PW Regulations and Toxicity Tests

The discharge of PW into surface waters has been regulated since the late 1960's (EPA 1993). Increased concern over the potential impacts of produced water in the aquatic environment has led to the development of regulatory requirements in some jurisdictions and a number of methodologies for the management of production chemicals (Scholten, 1997). The regulations prohibit discharge of any water that would cause permanent harm to the environment and sets limits on waters that are discharged based on best available technology for removing regulated contaminants.

Significant amongst these regulatory requirements include the ecotoxicological assessment of effluents by NPDES (National Pollutant Discharge Elimination System), as part of the Clean Water Act in the USA and the selection (notification) of environmentally harmless chemicals together with a strict regulatory control of the use of chemicals with a potential impact by HOCNF (Harmonized Offshore Chemical Notification Format) adopted by OSPAR in the PARCOM decision 96/3 for the northwestern European Region.

Generally, a main distinction can be made between the European approach, which is directed towards the control of chemical use (potential environmental toxicity of chemicals), and the American approach, which is directed towards the control of the final emissions (actual environmental toxicity of effluents) (Scholten et al, 2000). In the European approach, ecotoxicological risk modeling is being used to extrapolate chemical hazard information into environmental risk assessment of resultant emissions (CHARM). In the American approach however, a TIE (Toxicity Identification Evaluation) method is used to identify chemicals responsible for observed toxicity in effluents.

4.1 United States National Pollutant Discharge Elimination System (NPDES)

The US is subdivided into categories under United States Environmental Protection Agency (EPA) regulations. Discharge limits in the subcategories range from no discharge to surface waters to discharges limited by available technology for controlling toxicity and oil and grease. These subcategories as recognized by the EPA are:

- The onshore subcategory
- The stripper well subcategory
- The ‘beneficial use’ subcategory
- The coastal subcategory
- The territorial seas subcategory, and
- The outer continental shelf subcategory.

Discharge Operations — The Clean Water Act (CWA) requires that a permit issued under the NPDES program must authorize all discharges of pollutants to surface waters (streams, rivers, lakes, bays, and oceans). The 2 basic types of NPDES permits issued are individual and general permits. Individual NPDES permits are specifically tailored to individual facilities. General NPDES permits cover multiple facilities within a certain category located in a specific geographical area.

4.1.1 Calculation of Effluent Limits

In order to meet the goals and requirements of the CWA, the EPA advises permit writers to consider two types of effluent limits when identifying effluent limits for PW discharges: technology-based effluent limits and water quality-based effluent limits. Specifically, Federal regulations require NPDES permit writers to identify for each permitted wastewater discharge any applicable technology-based effluent limits (EPA, 1996; 2008). The permit writer is required to base the effluent limits in the permit on the more stringent of these two approaches.

4.1.2 Toxicity Identification Evaluation (TIE) of PW Effluents

In the past, the approaches to identifying causes of PW toxicity have involved direct chemical analysis of the whole composition of the PW with inference of toxicity made directly from the chemical composition of the effluent (Boelter et al, 1992, Johnsen et al, 1994; Rikseim et al, 1994; Gulley et al, 1992; Schiff et al, 1992; Tibbetts et al, 1992). A more recent approach to determining the toxic components in effluent has involved a toxicity-based concept called a toxicity identification evaluation (Burkhard & Ankley, 1989).

The following is a summary of EPA's aquatic toxicity tests as documented in "Toxicity Identification Evaluation: Characterization of Chronically Toxic Effluents, Phase I, II & III (EPA, 1992; 1993a; 1993b).

There are 3 phases in the TIE tests as follows:

Phase I is also known as the toxicity characterization phase, in that the tests characterize the physical/chemical properties of the effluent toxicant(s) using effluent manipulations and accompanying toxicity tests. Each characterization test in the Phase I series is designed to alter or render biologically unavailable a group of toxicants such as oxidants, cationic metals, volatiles, non- polar organics or chelatable metals. The effluent is chemically treated and processed in various ways, and the toxicities of the resulting test samples are compared to that of the untreated effluent to see if toxicity is reduced by the treatments. “Small” test organisms are used, such as daphnids and newly hatched fish (flathead minnows) are used (Reimer, 2003).

Aquatic toxicity tests performed on the effluent before and after the individual characterization treatment indicate the effectiveness of the treatment and provide information on the nature of the toxicant(s). By repeating the toxicity characterization tests using samples of a particular effluent collected over time, these screening tests will provide information on whether the characteristics of the compounds causing toxicity remain consistent (EPA, 1992).

With successful completion of Phase I, the toxicants can be tentatively categorized as cationic metals, non-polar organics, oxidants, substances whose toxicity is pH dependent, and others. Information on physical/chemical characteristics of the toxicants will indicate filterability, degradability, volatility, and solubility. Either of two choices is available in the second phase of testing, i.e. toxicant treatability or toxicant identification studies’ (EPA, 1992).

Phase II involves several steps, all of which rely on tracking the toxicity of the effluent throughout the analytical procedure. Although effluent toxicants are partially isolated in the first phase of the study, further separation from other compounds present in the effluent is usually necessary (EPA, 1993a). Techniques are available to reduce the number of compounds associated with the toxicants. Unlike Phase I procedures, Phase II methods will be toxicant-specific (EPA, 1993a). Once the toxicants have been adequately isolated from other compounds in the effluent and tentatively identified as the causative agents, final confirmation (Phase III) can begin.

Like Phase I, Phase III contains methods generic to all toxicants. No single test provides irrefutable proof that a certain chemical is causing effluent toxicity. Rather, the combined results of the confirmation tests are used to provide the "weight of evidence" that the toxicant has been identified (EPA, 1993b). Once the toxicant has been identified, it can be tracked through the process collection system using chemical analyses (EPA, 1993b).

4.2 Chemical Hazard Assessment and Risk Management (CHARM)

This section is a review of the CHARM Implementation Network Report of 2004 (CIN, 2004) on 'The evaluation of chemicals used and discharged offshore' and a review paper by Scholten et al (2000) on 'Ecotoxicological risk assessment related to chemicals and pollutants in off-shore oil production'

The basic principle of the environmental risk evaluation in CHARM is to compare the predicted environmental concentration (PEC) of chemicals in the ambient aquatic environment, with the ecotoxicological threshold for the chemical (predicted no effect concentration, PNEC) (Scholten et al, 2000). The PEC is an estimate of the expected concentration in the environment during and after the discharge of that chemical. The actual exposure depends upon the intrinsic properties of the chemical (such as its partition coefficient and degradation rate), the concentration in the waste stream, and amount of dilution in the receiving environmental compartment (Scholten et al, 2000). The PNEC is an estimate of the highest concentration of a chemical in a particular environmental compartment at which no adverse effects are expected. It is, thus, an estimate of the sensitivity of the ecosystem to a certain chemical (Scholten et al, 2000). In general the PNEC represents a toxicity threshold, derived from standard toxicity data (NOECs, LC50s, EC50s). A PNEC value is then extrapolated from toxicity data using the OECD method, which is accepted by most OSPAR Countries. In this method, the PNEC for a certain ecosystem is determined by applying an empirical extrapolation factor to the lowest available toxicity value. The magnitude of the extrapolation factor depends upon the suitability of the available ecotoxicological data (Scholten et al, 2000).

The CHARM model contains 3 significant modules/steps as follows:

Hazard assessment – This step aims to rank individual chemicals according to their predicted environmental impact, in order to facilitate the selection of the least environmentally harmful alternative. The hazard of a chemical is quantified as a

PEC:PNEC ratio, calculated on the basis of the intrinsic properties and toxicity of the chemical under ‘realistic worst case standard conditions’ during drilling or production in the aquatic environment (Scholten et al, 2000) . A ‘hazard quotient’ (HQ) is calculated for the water- phase (plankton, and related food-chain) and sediment-phase (benthos, and related food-chain). The higher of the two represents the HQ for the ecosystem.

Risk analysis - The ‘risk analysis’ module is based on the same calculation principles as the ‘hazard assessment’. module. However the default values for the ‘standard conditions’ are replaced by data on the actual conditions of the drilling and production processes and the actual ecological conditions around the platform environment (Karman and Reerink, 1998). The ‘risk quotient’ (RQ), therefore, gives an indication of the likelihood of actual adverse ecological effects occurring due to the use and discharge of the chemical at a specific platform.

Risk management - The ‘risk management’-module offers the possibility of comparing various risk-reducing measures on the basis of a combination of RQs of individual components of the effluents including ‘natural pollution’ with oil and other formation chemicals. The RQ of each chemical is converted to a ‘probability that aquatic biota are adversely affected’ P(x) (Schobben and Scholten, 1993). The combined risk of a mixture of chemicals is than calculated according the rule:

$P(A+B)=P(A)+P(B)-P(A)*P(B)$ (Scholten et al, 2000).

This approach to estimating combination toxicology in offshore E&P effluents has been validated by comprising observed whole effluent toxicity of produced water with the calculated combined toxicity on the basis of measured chemical composition of these effluents (Karman et al., 1996). The risk management analysis is completed by assessing the cost-effectiveness of certain options for including new environmental practices in off- shore oil and gas activities. Finally, the achievable environmental risk reduction of a particular option is then compared its associated costs (Scholten et al, 2000).

4.3 Dose-related Risk and Effect Assessment Model (DREAM)

The DREAM is a self-imposed method of assessment of chemicals also acting like a regulation. This model was developed by the Norwegian Oil Industry Association (OLF) in reaction to the Norwegian government requiring the oil industry operating in their sector to develop a strategy for reaching “zero environmental harmful discharges” of produced water before the end of 2005 (Payne, 2005).

The model uses the environmental impact factor (EIF) based on the combined environmental risk and hazard assessment of produced water discharges, accounting for both the composition and amount of the discharge. Operators can rank the available technologies for produced water discharge reduction based on cost and environmental benefit.

The DREAM model was initially developed for the naturally occurring substances in produced water, for which substantial environmental data were available. Added production chemicals with fewer datasets available, cannot be easily assessed by the DREAM model. This model is based on chronic data for the Predicted No Effect Concentration (PNEC) calculation compared with acute data that are acceptable for other risk assessment models, such as Chemical Hazard Assessment and Risk Management (CHARM), which is endorsed by OSPAR. This leads to high assessment factors, resulting in a much higher contribution to the EIF. Using chronic toxicity testing, which takes considerably longer to obtain results and is significantly more expensive than acute toxicity testing, might give significant reductions in EIF values, but there is no actual change to the environmental impact of the discharge.

4.4 Limitations of PW Regulatory Tests

4.4.1 Effects of Salinity and Ion toxicity

It has been shown that salinity contributes directly to the toxicity of PW samples with very high salinities (Sauer et al, 1997). Because of the usually low salinity tolerance of test species, high-salinity samples usually require dilution to concentrations no higher than 10-15% effluent to avoid salinity-stress toxicity. This process of dilution usually leads to a masking of the actual toxicity of the sample through dilution.

None of the commonly used TIE methods are targeted to detect toxicity from the salinity, hardness, or ionic imbalance that may be found in produced waters. Toxicity identification and evaluation methods are designed specifically to identify toxicants such as organics, metals, ammonia, and hydrogen sulfide. In addition to these toxicants, however, PWs often contain elevated concentrations and/or unusual ratios of common inorganic ions that may create toxicity risks in aquatic organisms (Ho & Caudle, 1997). When PWs have low enough total dissolved solids

(TDS) to be discharged to onshore surface waters, ion toxicity can contribute to the toxicity of the PW within discharge limits. For offshore operations, the degree of dilution and dispersion required under current US regulations makes it unlikely that ion toxicity would cause produced waters to exceed the discharge limitations. (Ho & Caudle, 1997). However, the following concerns remain about the ionic content of PW and their contribution to toxicity in offshore discharges:

1. Ion toxicity may mask or complicate the determination of the actual toxicant in TIE studies undertaken when compliance failures occur;
2. Changes in offshore discharge regulations may result in new compliance tests that will be impacted by regulation;
3. Residual produced water may contribute ions and therefore affect the toxicity of refinery effluents discharged subsequently.

Additionally, from the late 1960s until recently, the standard procedures for determining the ionic constituents of produced water for scale control stated that the 'sodium calculation is a "catch-all" in that it includes Na and K and is used to balance the cations with the anions for the dissolved-solids calculation' (API, 1968). This means that the Na concentration is inaccurate because it includes K, and the k concentrations are ignored altogether. While this situation is acceptable for scale control because Na and K do not enter into the calculations except as components of salinity, it is unacceptable for determining biologically meaningful ratios of ion toxicity.

4.4.2 Sporadic and Unpredictable Toxicity

In a geographically broad set of PW samples, potential causes of toxicity can be different for each PW. In a study carried out by Sauer et al (1997), no single fraction was consistently toxic among the 14 tested PW samples. For most samples, the entire PW toxicity could not be totally attributed to toxicities associated with the individual fractions. Also, in many PWs in which toxicities were low (high LC50s), toxicities decreased from day 1 to day 2. The cause of this loss was not evident from the toxicity identification evaluation (TIE) analysis carried out, except when it indicated potential toxicant was a volatile component or one that precipitated from solution after the sample containers were opened.

4.4.3 Suitability of Test Species

The EPA only has published procedures for freshwater species (Ceriodaphna and Pimephalas) for TIE studies because most effluents of interest to the EPA are low in salinity (US EPA, 1993). Freshwater toxicity tests would be inappropriate for high-salinity PWs. Hence, there is need to consider the use of marine species such as Mysidopsis and Cyprinodon) (Sauer et al, 1997) that have greater salt tolerance.

4.4.4 Presence of non-regulated Toxic Compounds

The conventional approach of determining the environmental risk by correlating toxicity and known contaminant concentration within PW to suggest toxicity, used in DREAM and CHARM, are only suitable when a group of contaminants have been described as having detrimental effects. Recent studies have demonstrated that PW effluent contains compounds that exert sublethal toxic effects (Balaam et al, 2004). Also, effluents from certain oil and gas production platforms are known to contain in vitro estrogen receptors (ER) (Balaam et al, 2004) as well as aryl hydrocarbon receptors (AhR) agonists and androgen receptor agonists (Tollefsen et al, 2007). These compounds identified in PW effluents in these studies are not currently listed as those to be analyzed by oil and gas operators. Hence, this may result in undetected toxicity even after the required tests are carried out.

Chapter 5 – Recommendations

5.1 Recommendations

Based on the above evaluation of issues relating to toxicity of PW and their potential beneficial re-use options, the following recommendations were made:

There is an ultimate need to move away from fossil fuels, however this may not take place for some time. In the interim, reuse of water used in extraction of such fuels is important in order to get the optimal use of freshwater. In light of this therefore, there is a need for relevant stakeholders and major players in the O&G industry to explore more appropriate and cost-efficient technologies for treatment of PW considering water quality desired for local beneficial reuse. To better guide this effort, the development of an integrated framework that links the composition of PW to beneficial use applications by identifying the most cost-efficient, environmentally sound, and most beneficial strategies for management and treatment of PW is highly recommended. Finally, the results obtained should be tested to provide validation of the integrated framework.

The framework recommended below is an improvement on a framework developed by the United States Dept. of Energy (US DOE, 2010). The Technology Identification Module follows the philosophy of a. three-tiered water management/pollution prevention hierarchy (i.e., minimization, recycle/reuse, and disposal). My proposed framework below goes a step further in introducing a toxicity-testing component in the form of focused toxicity tests to help speed up the process of testing and associated costs.

5.1.1 Proposed Framework

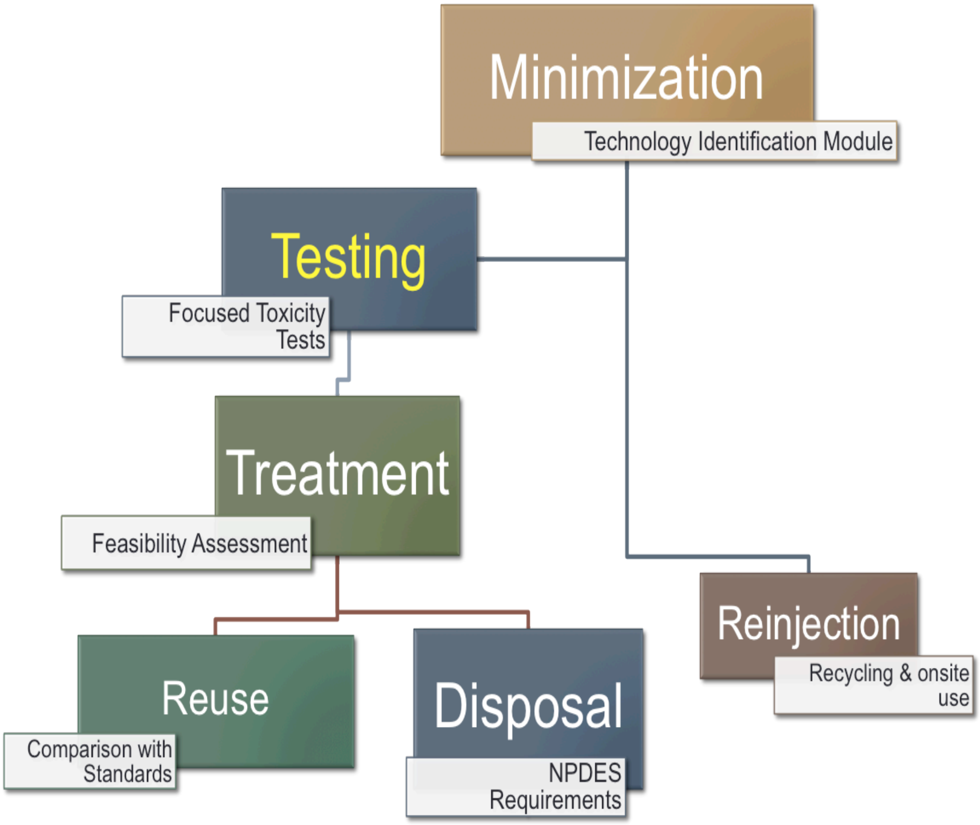

Figure 3: Recommended framework to guide re-use of Produced Water

Concept of the Framework – The main aim of the framework is to promote the use of options with the lowest environmental impacts before those with more significant environmental impacts. Hence, the first strategy proposed is to reduce, to the greatest extent possible, the amount of PW generated during oil and gas extraction. Where minimization is not possible or not entirely successful, and huge volumes of PW are still brought to the surface, the next step proposed is toxicity testing to determine the level and source(s) of contamination. The test results should invariably determine the appropriate treatment methods to be selected. It is however necessary, at this point, to conduct economic and feasibility assessments to determine the higher of the cost of treatment and transportation to reuse site/location **versus** cost of recycling in the form of reinjection into reservoirs. Where treatment and transportation costs are low enough, 2 reuse options exist. PW may either be discharged, in accordance with NPDES standards, to augment natural supplies or reused in agriculture, livestock watering or industrially depending on the need and water quality standards. The different steps are further explained below.

5.1.1 Minimization

This involves the adoption of technologies to minimize the production of PW during the extraction process. Some technologies used in this process include options for keeping water from getting into the wells and options for preventing water from getting to the surface. Mechanical blocking devices and water shut-off chemicals are the 2 principal methods used to prevent water from getting into the wells (Veil et al, 2004). Options that exist for preventing PW from reaching the surface include dual completion wells, down-hole oil/water and gas/water separators etc. (Veil et al, 2004).

5.1.2 Testing

The potential causes of toxicity differ for each PW, however the predominant source of toxicity is consistently expected to be organic compounds. The major contributors to the acute toxicity of PW according to Johnsen et al. (1984) are the aromatic and phenolic fractions. Hence, in the event that total reduction or elimination of PW waste is not possible, there is need to subject samples to toxicity tests to identify potential sources of toxicity before identifying potential beneficial reuse option. Focused toxicity tests may be beneficial in the event that the toxic substances identified in the samples are fairly constant over a period of time. Hence, instead of going through the entire process again from scratch, focused tests can be carried out to immediately identify the presence/absence of a particular compound or group of compounds.

5.1.3 Treatment

After toxicity testing to identify the constituents of concern or potential risk, different treatment methods or options should be considered based on eventual reuse or disposal option. The treatment methods available for PW have been reviewed in section 3.5 above.

5.1.4 Reuse

For effective and safe reuse, proper treatment methods should have already been identified in the previous step to bring the PW to meet standards specific for the reuse purpose. National and state regulatory authorities have set criteria for water to be used in different kinds of activities and could be used as standards of water required for each specific beneficial reuse option. Also, a feasibility assessment based on proximity to site of reuse, financial justifications or profitability, transportation etc. need to be considered in order to determine whether PW should be reused or just disposed to augment natural supplies.

5.1.5 Disposal

Disposal (i.e. discharge into natural waters, with or without treatment) is usually the preferred option for most oil and gas producers due to the fact that it involves minimal transportation and treatment. However, there is need to take more caution than is being done currently because environmental impacts of discharge are more far-reaching because of the large volume of discharge involved and large area potentially impacted. Also, there are specific requirements that must be met before discharge and in the United States; this is controlled by the National Pollutant Discharge Elimination System (NPDES). Strict monitoring should be in place to make sure that the discharge is not harmful to the environment.

5.1.6 Reinjection

Reinjection involves the reuse of PW in the oil and gas extraction process. Most PW is injected to maintain reservoir pressure and hydraulically drive oil toward a producing well. This practice can be referred to as enhanced oil recovery (EOR), water flooding, or, if the water is heated to make steam, as steam flooding. In the context of improving oil recovery, produced water becomes a reusable resource rather than a waste product (US DOE, 2010). In the absence of PW, operators would need to use other surface or groundwater supplies to conduct the water or steam flood, hence recycling PW may help to conserve fresh and better sources of water.

Conclusion

This review paper examines produced water sources, its constituents and potential toxicity as well as current beneficial re-use options with the aim of understanding how to best re-use PW while also considering the impact on the environment. Even though oil spills have been the major headline grabbers, there is need for concern over PW due to the great volumes produced daily during land-based oil and gas activities. Most researchers have dismissed the suggestion that PW constituents may pose a contamination problem with the explanation these constituents are present at low concentrations and will be diluted upon discharge. However, if PW production is in billions of barrels worldwide daily, there is a great possibility that these contaminants may accumulate over time or even be additively toxic. Another source for concern is that increasing use of PW in agriculture, livestock and wildlife watering may create potential ecologic risk, if not properly treated. This review shows that current tests and regulation may not necessarily be adequate to accommodate this new dimension of usage. Therefore, it is proposed that a combination of a selection of accurate toxicity testing and treatment methods may help in determining the best PW re-use option while also minimizing risk. Also, there is need to pay more attention to PW reuse and further research is strongly encouraged.

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