Comparative Analysis of Long-term Environmental effects of Produced water on Human health and Eco-system. Management Practices in the US & Pakistan.

THESIS

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PRESENTED BY

Sayed Murtaza Hussain

Department of Environmental, Land and Infrastructure Engineering

Relatore:	Candidato:
Adriano Fiorucci	Sayed Murtaza Hussain

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Abstract:

Produced water, a inevitable byproduct of oil and gas production, that contain complex mixture of contaminants, including hydrocarbons, heavy metals, and naturally occurring radioactive materials (NORM). Despite treatment measures, a significant portion of produced water is discharged into the environment, posing potential risks to human health and ecosystems. This thesis aims to provide a comprehensive analysis of the long-term environmental effects of produced water on human health and ecosystems, focusing on potentially impact caused by Norms thought accumulation , bioaccumulation in food chains, direct , indirect ingestion by human/animals and potential environmental impacts. Through an in-depth review of existing literature, case studies, and environmental monitoring data, this study will elucidate the mechanisms through which produced water contamination affects ecosystems and human populations over time. The findings of this research will contribute to a better understanding of the long-term implications of produced water discharge and inform strategies for mitigating its environmental and health impacts.

The thesis concludes with recommendations for stricter regulations, advanced treatment technologies, and increased monitoring to mitigate the adverse impacts of produced water discharge. By addressing these challenges, the research aims to contribute to a better understanding of the long-term implications of produced water and inform strategies for safeguarding human health and the environment.

1. Introduction

Introduction of Produced water (saline/brain/formation water):

As global population increases, there is a corresponding rise in energy demand. This has driven significant industrial expansion over the decades to meet these growing needs. An inevitable consequence of this expansion is the production of large volumes of produced water, a saline byproduct of oil and gas extraction. Despite its prevalence, produced water is often overlooked, though it carries significant environmental and health implications. This water, a mixture of underground formation water, injection water, and various chemical additives used in hydrocarbon extraction, demands careful management and attention.

Globally, the production of produced water is estimated at around 250 million barrels per day, compared to approximately 80 million barrels per day of oil, resulting in a water-to-oil ratio of about 3:1, or a water cut of 70%. Oil fields account for more than 60% of the produced water generated worldwide. Effective treatment of produced water is crucial as it contains various toxic substances. Once treated, produced water can be repurposed for numerous applications, including underground injection to enhance oil recovery, irrigation, livestock and wildlife watering, industrial uses such as dust control, vehicle washing, power plant water makeup, and fire control. [1,2].

In hydrocarbon-bearing reservoirs, saline water typically exists beneath oil and gas zones due to its higher density. Produced water may originate from saline water and formation water, which enter the hydrocarbon zone from various sources. There are three primary sources of saline water: flow from above or below the hydrocarbon zone, flow within the hydrocarbon zone, and flow from injection fluids and additives used during production activities. Connate water, or formation water, becomes produced water when mixed with hydrocarbons and brought to the surface. [2,3].

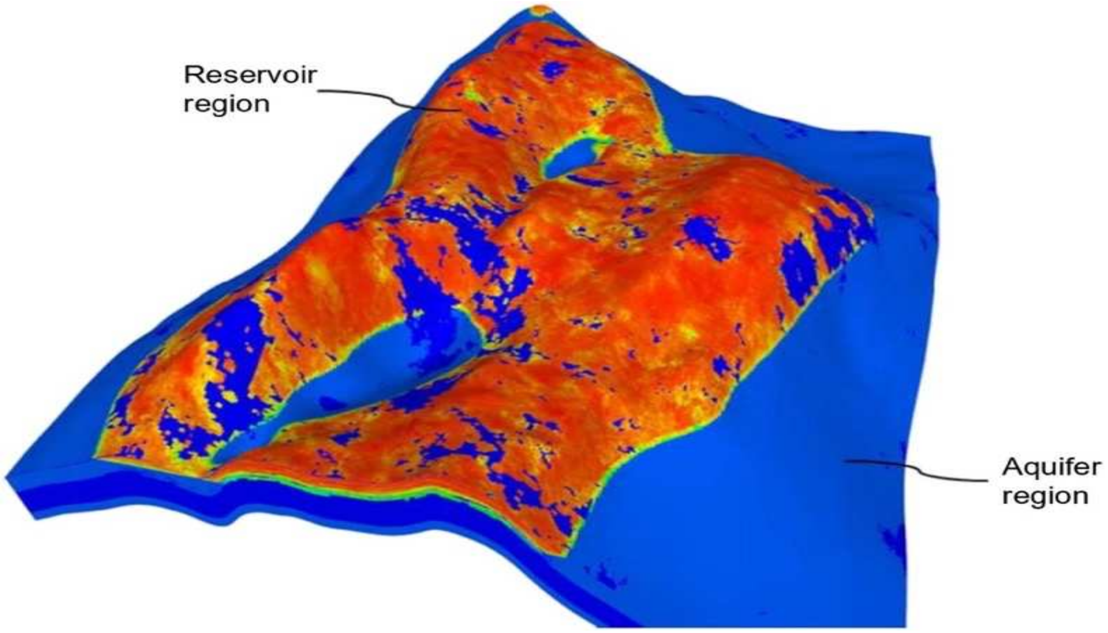


Figure 1 A typical case of formation water (Aquifer) in a reservoir. Hydrocarbon (reservoir region) besides above formation water (aquifer region). (4)

The volume of water in a reservoir increases over time and may eventually exceed the volume of hydrocarbons, especially with the use of secondary or tertiary recovery techniques. Figure 1 conceptually depicts a reservoir with formation water (aquifer) and hydrocarbons (reservoir region).

Water scarcity is a significant global challenge, affecting various industries, including oil and gas. The industry consumes large amounts of water for operations such as drilling, hydraulic fracturing, and enhanced oil recovery techniques. The production of produced water, also known as brine, formation water, or saline water, presents a significant concern. Over time, oil and gas production decreases as water production increases, making it less economical to produce hydrocarbons with large amounts of associated water. Produced water is the largest waste product generated by oil and gas production activities and must be managed effectively to mitigate environmental and health risks. (1,82)

Produced water is a complex mixture of hydrocarbons, chemicals, and naturally occurring compounds. On average, 3 to 7 barrels of produced water are generated for every barrel of oil extracted, highlighting the need for stringent management practices. The composition and characteristics of produced water vary widely, depending on factors such as the geographic location of the field, the geological formation, and the type of hydrocarbon being produced. It may include dispersed oil, aromatic hydrocarbons, alkylphenols, heavy metals, and naturally occurring radioactive materials (NORMs).

The toxicity and composition of produced water vary significantly due to differences in geological environments and formation characteristics. Factors influencing this variability include the geological composition of the reservoir, the age and depth of the reservoir, and the production techniques used.

Additionally, the presence of NORMs, microbial activity, and external contamination sources contribute to the complexity of produced water composition. Understanding and managing this variability are crucial for effective treatment and disposal strategies in the oil and gas industry, aimed at reducing potential environmental and health risks.

Produced water, the largest waste byproduct of the oil and gas industry, contains hazardous pollutants, including organic and inorganic materials that are more toxic than oil itself. Therefore, it cannot be discharged directly into the environment. Uncontrolled discharge can cause significant environmental damage, harm aquatic life, and pose serious health risks to humans. It is essential to treat produced water to meet quality standards before discharge or reuse to ensure environmental sustainability and safety in the energy sector.

1.Primary Production:

In the initial stages of oil and gas extraction, the hydrocarbon is produced from the natural energy of reservoir's pressure. This primary production phase reveals the inherent geological dynamics that have shaped the hydrocarbon-bearing zones over millions of years.

Produced water during primary production primarily consists of connate water — water naturally present in the reservoir since its formation. This water, having been in contact with hydrocarbons for extended periods, carries dissolved minerals, salts, and trace hydrocarbons. Its emergence is a testament to the reservoir's geological history.

The volume of produced water during primary production is relatively lower compared to later stages. However, its composition varies based on reservoir characteristics, with some primary-produced waters exhibiting high salinity or containing naturally occurring chemicals.

2. Secondary Production:

After producing certain amount of hydrocarbon, the oil fields production is going to decrease with time and natural reservoir pressure is going to decline, so the secondary production methods come into play. Water injection is one of a common technique, involves injecting water into the reservoir to maintain reservoir pressure at same time displace the remaining hydrocarbons (heavy oil) towards production wells and to enhances oil recovery, it significantly alters the nature of produced water. Some can be some chemical added to increase the viscosity of water in order to displaced the heavy oil.

The injected water blends with the connate water, introducing new elements to the produced water composition. This may include chemicals from the injection process, additional dissolved minerals, and, in some cases, a higher volume of water compared to primary production.

Produced water volumes increase during secondary production, reflecting the injected water's contribution and the contribution of aquifer starting to enter hydrocarbon zone and we produced more water. The composition becomes more complex, with a wider range of contaminants. Understanding and managing this produced water is crucial for both environmental stewardship and efficient resource recovery.

3.Characterization of (Complex Composition) Produced Water:

The characterization of produced water is a multidimensional endeavor, requiring a combination of chemical, physical, and biological analyses. From unraveling its molecular complexity to assessing its environmental impact, each facet of produced water characterization contributes to a nuanced understanding. As we delve into subsequent chapters, the focus will shift to the practical applications of this characterization knowledge, addressing environmental management strategies, treatment methodologies, and regulatory considerations.

3.1 Produced water from oilfield

The produced water from the oil field may contain groundwater or seawater which is injected into the reservoir to mobilities and maintain the reservoir pressure and the content of solid particles and bacteria. Most of the produced water contains more saline water than sea water and fluids (chemicals) used in drilling and production processes.The chemical compounds for processing are usually the complex mixture of many molecular compounds. The mixture may contain:

a. Corrosion inhibitor and oxygen remover: These chemicals help reduce the risk of corrosion and separation processes.
b. Scale/Crust inhibitor: these compounds limit mineral crust (scale) deposits in pipes and other equipment's.
c. Biocides: used to reduce bacterial growth that can cause fouling and other issues in equipment.
d. Emulsion Breakers: Helps to separation of oil from water by breaking down emulsions and vice versa.
e. Coagulants, flocculants, and purifiers: these substances help remove solid by causing them to clump together for easier removal.
f. Solvents: used to dissolve and reduce paraffin deposits in equipment and pipelines.

Table 1. Summary of oilfield-produced water parameters in world. A range of produced water characteristics in different oilfields in the world. The data show ranges of pollutants and constituents that are present in produced water.[2, 9].
(a)-Analyzed by atomic absorption. (b)-Value should be regarded as a minimum due to poor solubilities.

Parameter	Values	Heavy metal	Values (mg/L)
Density (kg/m^3)	1014–1141	Calcium	13–25801
Surface Tension (dynes/cm)	43–79	Sodium	132–97001
TOC (mg/L)	0–1501	Potassium	24–4301
COD (mg/L)	1221	Magnesium	8–6001
TSS (mg/L)	1.2–1001	Iron	<0.1–101
pH	4.3–11	Aluminum	310–411
Total oil (IR; mg/L)	2–566	Boron	5–96
Volatile (BTX; mg/L)	0.39–36	Barium	1.3–651
Base/neutrals (mg/L)	<141	Cadmium[a]	<0.005–0.3
(Total non-volatile oil and grease by GLC/MS) base	276	Chromium	0.02–1.2
Chloride (mg/L)	80–200,001	Copper	<0.002–1.6
Bicarbonate (mg/L)	77–3991	Lithium	3–51
Sulfate (mg/L)	<2–1651	Manganese	<0.004–176
Ammonia nitrogen (mg/L)	10–301	Lead[a]	0.002–8.9
Sulfite (mg/L)	11	Strontium	0.02–1001
Total polar (mg/L)	9.7–601	Titanium	<0.01 –0.8
Higher acids (mg/L)	<1–63	Zinc[a]	0.01–36
Phenols (mg/L)	0.009–23	Arsenic[a]	<0.005–0.4
VFA"s (volatile fatty acids) (mg/L)	2–4900	Mercury	<0.001–0.003
		Silver[a,b]	<0.001–0.16
		Beryllium	<0.001–0.005

In the Produced water these chemical compounds can affect the coefficients of partition, toxicity, bioavailability, and biodegradability. In line either the development of the oil fields, these compounds are needed in large quantities to ensure flow in the underwater piping system [8].

3.2 Produced water from gas fields

In gas fields, particularly unconventional gas fields such as shale gas or tight gas , water injection is not used to main reservoir pressure because usually gas is produced by their won energy, so therefore, the produced waters are mixture of formation water and condensed water. Their chloride content varies from almost those of fresh water to salty formation water with chloride concentration about 14 times more then sea-water and the acidity of gas-field is greater than that of produced water from oilfields [2,10]

Father more Pw from gas production have higher contects of low molecular weight aromatic hydrocarbon such as benzene, toluene, ethylbenzene and xylene (Btex) than oil production so the pw discharge from gas/condensater platorms are about 10 time more toxic then pw discharge then oil Platform.[11]

Generally, the volume of PW from gas field is less than in oilfields. A wide range of gas treatment chemicals is used in gas fields including methanol, ethylene glycol, and triethylene glycol. About one-third of these chemicals are discharged in produced water [1,12]. Volatile components concentrations in produced water from gas fields are higher than those in produced water from oilfields [1,13].

Table 2. Constituents (mg/L) in natural gas produced waters (pH is presented in standard units) [1,2] shows concentrations of constituents in produced water from Gas fields.

Parameter	Minimum	Maximum	Parameter	Minimum value	Maximum value
pH	4.5	7.1	Iron		
pH[b]	3.1	6.47	Iron[b]	39	681
Conductivity[a] (umhos/cm)	4200	180,000	Lead[b]	<0.2	10.3
Conductivity[b] (umhos/cm)	136,000	586,000	Lithium[b]	18.6	235
Alkalinity[b]	0	285	Magnesium[a]	0.9	4301
TDS[a]	2600	310,000	Magnesium[b]	1300	3901
TDS[b]	139,000	360,000	Manganese[a]	0.045	6.6
TSS[a]	14	800	Manganese[b]	3.59	63
TSS[b]	8	5484	Nickel[a]	N-D	0.03
BOD5[a]	75	2870	Nickel[b]	<0.08	9.3
COD[a]	2600	120,000	Potassium[b]	149	3871
Aluminum[a]	N-D	0.4	Silver[b]	0.047	7.0
Aluminum[b]	<0.50	83	Sodium[a]	520	45,001
Arsenic[a]	0.004	1	Sodium[b]	37,500	120,001
Arsenic[b]	<0.005	151	Strontium[a]	–	6201
Barium[a]	ND	26	Sulfate[a]	<0.1	48
Barium[b]	9.65	1740	Sulfate[b]	N-D	19
Boron[a]	N-D	56	Tin[a]	N-D	1.1
Bromide[b]	150	1149	Zinc[a]	N-D	0.022
Cadmium[a]	N-D	0.015	Zinc[b]	<0.02	5
Cadmium[b]	<0.02	1.21	TOC[a]	67	38,000
Calcium[a]	N-D	25,000	Surfactants[b]	0.08	1200
Calcium[b]	9400	51,300	Benzene[a]	1.8	6.9
Chloride[a]	1400	190,000	Benzene[c]	<0.010	10.3
Chloride[b]	81,500	167,448	Toluene[a]	0.857	3.37
Chromium[a]	ND	0.03	Toluene[c]	<0.010	18
Copper[a]	ND	0.02	Oil/grease[a]	6	60
Copper[b]	<0.02	5	Oil/grease[b]	2.3	38.8

Charter 2: (Chemical Composition of Produced Water)

Produced water, a byproduct of oil and gas operations, is a complex mixture of dissolved and particulate organic and inorganic chemicals. Its composition and characteristics vary significantly depending on geological location, the type of hydrocarbons produced, mineral depth, and the geochemistry of the hydrocarbon-bearing formation. The variability is further influenced by the chemical composition of the oil and gas phases within the reservoir, as well as any additives used during the production process. This complexity necessitates region-specific studies to accurately assess the environmental risks associated with produced water discharge.

Naturally occurring compounds in produced water, which have accumulated over millions of years within geological formations and migration pathways, include inorganic salts, metals, radioisotopes, and a wide array of organic chemicals, predominantly hydrocarbons. A thorough understanding of these components is essential for developing effective treatment strategies to minimize long-term environmental and ecological impacts.

The water-to-oil ration (WOR) or water-to-gas ratio (WGR) can vary significantly, ranging from zero up to over 50 (indicating 98% water and 2% oil). Typically, the WGR is higher than the WOR.The average worldwide WOR is about 2–3. Continuous discharge of produced water during production, especially in nearly depleted fields where it may constitute 98% of the output, raises significant environmental concerns. Increasing discharge volumes In mature offshore production regions, treated produced watre often has higher levels of potentially harmful organic compound and metals than the water into which it is discharged, heighten the risk of chronic ecological harm.[15].

Understanding the chemical composition of produced water is crucial for developing management practices that mitigate its adverse effects, ensuring both environmental protection and sustainable resource use.

Produced water is a complicated blend of dissolved and particulate organic and inorganic substances. Its physical and chemical properties vary widely depending on factors such as geological location, the type of hydrocarbons produced, mineral depth, and the geochemistry of the hydrocarbon reservoir. Similarly, the chemical composition of the oil and gas phases also varies.within the reservoir, along with any additives introduced during the production process, further contribute to this variability. Given the distinct nature of each produced water instance, it becomes imperative to conduct studies specific to each region to comprehensively assess the environmental risks associated with its discharge.

Produced water encompasses a numerous kinds of naturally occurring compounds that have been dissolved or dispersed over millions of years within the geological formations and migration pathways where the produced water resided. These compounds comprise inorganics salts, metals, radioisotopes, and a diverse array of organic chemicals, predominantly hydrocarbons.in order to deep understanding of PW is it essentially to analysis very filed PW for the best possible treatment without causing any environmental and ecological harms in long term.

2.1 Salinity and Inorganic Ions

The salt concentration(salinity) of produced water may range from a few parts per thousand (%) to that of a saturated brine (~300‰;(7), compared to a salinity of 32–36‰ for seawater (7). The salinity is often measured as total dissolved soils (TDS) Most produced waters have salinities greater than that of seawater due to the dissolution of salts from the surrounding rocks formation and so, are denser than seawater.[16]

Produced water contains the same salts as seawater, with sodium and chloride the most abundant ions. The most abundant inorganic ions in high-salinity produced water are, in order of relative abundance sodium, chloride, calcium.[6]

Table 2.1 Concentrations (mg/kg or parts per million) of several elements and inorganic ions in produced waters of different geologic ages compared with average concentrations in 35 % seawater (16)

Element-ion	Seawater	PW-highiest concentration (age)	Range of mean-concentrations
Salinity (S)	35,000.1	-	<5,000.1–>300,000,001
Na	10,762	120,001 (J)	23,001–57,320
Cl	19,354	270,001 (P)	46,101–141,002
Ca	417	205,001 (P)	2,531–25,8001
Mgn	1,295	26,001 (D)	531–4,301
K	386	11,601 (D)	131–3,101
SO42−	2,711	8,401 (T)	211–1,171
Br−	88	6,001 (J)	7.1-1,001
Sr	0.009	4,501 (P)	24-301
NH4+	-	3,301 (P)	79-562
HCO3−	143	3,602 (T)	3.5-211
I−	166	1,411 (P)	7.5-42
B	4.43	455 (T)	8.2-452
CO32−	-	455 (M)	32-454
Li	0.15	455 (j)	3.5–51

(D-Devonian) (J-Jurassic) (M-Missisipian) (P-Pennsylvanian) (T--Tertiary)

magnesium, potassium, sulfate, bromide, bicarbonate, and iodide. In many of these ions the ratio of concentration are quite different specially contributing to the aquatic toxicity of the of pw in the sea water [17]

2.2 Total organic Carbon:

The concentration of total organic carbon (TOC) in produced water is highly variable from well to well but the ranges from less than 0.1 to more then 11,000mg/Produced water from Hibernia has a TOC concentration of approximately 300mg/L. [98]

Managing TOC I produced water is critical for minimizing its impact on the environmental and human health. Effective treatment methods and stringent monitoring are essential for ensuring that TOC level in Pw is within acceptable limits before discharge or reuse. if not properly managed or treated before discharge or recuse. therefore, oil and gas companies often employ various treatment methods such as filtration, chemical treatment or biological processes to reduce TOC level in produced water before disposal or reuse. [15]

2.3 Organic Acids:

Produced water from oil and gas operations can contain a variety of organic acids, which are formed because of the degradation of hydrocarbons and other organic materials in the reservoir.

The organic acids present in produced water include mono- and di-carboxylic acids (COOH) of both saturated (aliphatic) and aromatic hydrocarbons. A significant portion of the total organic carbon (TOC) in produced water is made up of low molecular weight carboxylic acids, such as formic, acetic, propanoic, butanoic, pentanoic, and hexanoic acids [15].

Organic acids produced water can have various implications for environmental management, treatment processes, and overall operational efficiency. Here are some key points regarding organic acids in produced water.

2.3.1 Biodegradation:

Organic acids can be formed through the microbial degradation of organic compounds present in the reservoir fluids, including crude oil and associated hydrocarbons. Microorganisms naturally present in the reservoir or introduced during production can metabolize these organic compounds, producing organic acids as byproducts.

2.3.4 Chemical Additive:

Some organic acids may also be introduced into produced water as a result of the use of chemical additives in oilfield operations. For example, certain organic acids, such as formic acid or acetic acid, may be used as corrosion inhibitors or as part of hydraulic fracturing fluids.

Formic or acetic acid is generally the most prevalent organic acid, with their abundance typically decreasing as the molecular weight increases.[18].

Low molecular weight organic acids are easily biodegraded and synthesized by bacteria, fungi, and plants, serving as nutrients for zooplankton and promoting phytoplankton growth. These organic acids are formed through hydrous pyrolysis or microbial degradation of hydrocarbons within the hydrocarbon-bearing formation.[20]

Table 2.2 Concentrations (mg/L = ppm) of low molecular weight organic acids in produced water from four production facilities on the Norwegian continental shelf (20), in the Gulf of Mexico off the Texas and Louisiana coast, and in the Santa Maria Basin off the California coast (21)

Organic acid-Formula	Offshore-USA	Norwegian North Sea
Formic-CHOOH	N-D –69	26–584
Acetic-CH_3COOH	8.1–5,745	N-D
Propanoic-CH_3CH_2COOH	N-D –4,40.1	36–98
Butanoic-$CH_3(CH_2)_2COOH$	N-D –45	ND–46
Pentanoic-$CH_3(CH_2)$3COOH	N-D –25	ND–33
Hexanoic-$CH_3(CH_2)$4COOH	N-D	ND
Oxalic-COOCHCOOH	N-D –496	N-D
MalonicCH2$(COOH)_2$	N-D –1,541	N-D
Total measured organic acids	98–7,161	60–762

N-D: not detected

In oil and gas reservoirs, anaerobic bacteria might be common if the formation temperature is below roughly 100°C.[15]

Naphthenic acids, which can be found in crude oil and produced water, pose a concern for the oil and gas industry due to their acidity, which can cause corrosion of production pipelines, and their contribution to the toxicity of produced water.[22]

Produced water (PW) primarily contains petroleum hydrocarbons, which are organic compounds composed exclusively of carbon and hydrogen. These hydrocarbons are of significant environmental concern. They are divided into two major categories: saturated hydrocarbons and aromatic hydrocarbons. The solubility of petroleum hydrocarbons in water decreases with increasing molecular size, and aromatic hydrocarbons are more soluble in water than saturated hydrocarbons of the same molecular weight. In PW, hydrocarbons can exist both in a dissolved state and as dispersed oil droplets.

Current oil/water separation technologies, such as hydro-cyclones, are efficient in eliminating oil droplets from produced water but are less effective in removing dissolved hydrocarbons, organic acids, phenols, and metals. As a result, even well-treated produced water released into the ocean still contains dissolved low molecular weight aromatic hydrocarbons and traces of saturated hydrocarbonsAs no treatment process is completely effective, treated produced water still contains some dispersed oil, with droplet sizes ranging from 1 to 10 micrometers. These droplets typically contain higher molecular weight, less soluble saturated and aromatic hydrocarbons. In PW, petroleum hydrocarbons encompass a variety of compounds that differ in molecular weight and complexity, including aliphatic, aromatic, cyclic, heavy, and other hydrocarbons.[33]

2.4.1 Volatile Hydrocarbons: (B-T-E-X and Benzenes)

The main hydrocarbons present in produced water include single-ring aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (collectively referred to as B-T-E-X), along with low molecular weight saturated hydrocarbons. B-T-E-X can reach concentrations of up to 600 mg/L in untreated produced water from various origins. Additionally, traces of C3- and C4-benzenes are present. Benzene typically dominates in abundance, with its concentration decreasing as alkylation increases(25)

Compound	7-Gulf of Mexico produced waters	3-Indonesian produced waters
C_6H_6	0.45–2.81	0.085–2.31
C_7H_8	0.35–1.701	0.090–0.81
C_8H_{10}	0.027–0.12	0.027–0.057
$C_6H_4(CH_3)_2$ (3 isomers)	0.17–0.71	0.014–0.49
Total BTX	0.97–5.34	0.34–3.65
$C_6H_5(C_3H_7)$ (2 isomers)	N-A	(N-D)–0.02
$C_6H_5(CH_3)(C_2H_5)$ (3 isomers)	N-A	0.032–0.053
$C_6H_3(CH_3)_3$ (3 isomers)	N-A	0.055–0.11
Total C3-benzenes	0.013–0.31	0.065–0.15
C6H5(CH3)8C3H7) (5 isomers)	N-A	(N-D)–0.005
$C_6H_4(C_2H_5)_2$ (3 isomers)	N-A	(N-D)
$C_6H_4(CH_3)_2(C_2H_5)$ (6 isomers)	N-A	(N-D)–0.034
Total C4-ben-zenes	N-D–0.12	(N-D)–0.067

Table 2.3 Concentrations (mg/L) of BTEX and selected C_3- and C_4-benzenes in produced water from four platforms in the US Gulf of Mexico and from three offshore production facilities in Indonesia [7,33].

Saturated hydrocarbons typically exist at low concentrations in produced water due to their low solubilities, unless there are issues with the produced water treatment system. In produced water samples from the US Gulf of Mexico and offshore Thailand, total C10 to C34 n-alkanes were found in concentrations ranging from 0.6 to 7.8 mg/L. Shorter chain-length alkanes, specifically those from C10 to C22, were more prevalent compared to longer chain-length ones. It is likely that most of these alkanes were associated with droplets. [7,33].

BTEX and benzene in Pw are a concern due to their potential to contaminate soil and water sources, as well as their impact on human-health and aquatic life.

2.4.2 Polycyclic Aromatic Hydrocarbons.

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that consist of multiple aromatic (benzene) rings. PAHs are common contaminants in produced water from the oil and gas industry and can pose significant environmental and health risks due to their potential toxicity and persistence in the environment.(marine environment).[7,33].

The levels of total polycyclic aromatic hydrocarbons (PAH), which mostly consist of the most water-soluble congeners, in generated water normally range from 0.040 to 3 mg/L. Two- and three-ring PAH, such as naph-thalene, phenan-threne, and their alkyl counterparts. Heavier molecular weight PAHs, consisting of 4- to 6-ring structures, are seldom found in properly treated produced water due to their low solubility in water.[23,26].

noted that approximately 5-10% of the total produced water can contain PAH in a "dissolved" state, consisting mostly of alkylnaphthalenes with trace amounts of alkylphenanthrenes. The particulate fraction, linked to scattered oil droplets, also includes almost all of the dibenzothiophenes, fluoranthenes/pyrenes, and chrysenes found in the generated water, as well as increased concentrations of naphthalenes and phenanthrenes.

2.4.3 Phenols

The concentration of total phenol in generated water usually stays below 20 mg/L. Measured values, for example, range from 2.1 to 4.5 mg/L in generated waters from the Louisiana Gulf coast to 0.36 to 16.8 mg/L in the Norwegian Sector of the North Sea. [7,33,23].

These fluids are mostly composed of phenol, methyl phenols, and dimethyl phenols. When it comes to alkyl phenols, their frequency often drops logarithmically as the number of alkyl carbons rises. With seven to nine alkyl carbons, long-chain alkylphenols are especially hazardous and have strong impacts on endocrine disruption. On the other hand, generated water from the Norwegian continental shelf rarely contains them. Six Norwegian platforms' generated waters have 4-n-nonylphenol concentrations ranging from 0.001 to 0.012 mg/L, the most dangerous alkylphenol. Five other samples showing no detectable concentrations of nonylphenol.[27]

Furthermore, there is a strong correlation between the concentration of scattered oil droplets in generated water and the concentrations of C6–C9 alkylphenols. Sometimes, in production systems, alkylphenol ethoxylate surfactants—which contain octyl- and nonylphenols—are used to help pump viscous or waxy crude oils. Nevertheless, some alkylphenols might dissolve in the resulting water if these surfactants break down. Alkylphenol ethoxylate surfactants have been substituted in applications where the surfactant or its degradation products might have a major environmental impact due to the toxicity of highly alkylated phenols as endocrine disruptors. The toxicity of phenol and its derivatives can adversely affect aquatic life and other organisms, posing health risks to humans through direct exposure or ingestion. Additionally, phenolic compounds can persist in the environment and may prove challenging to naturally degrade

2.5 Metals

Produced water generated by the oil and gas sector may carry diverse metal contaminants originating from geological formations encountered during drilling and production activities. These metals may occur naturally in underground formations or be introduced via equipment and additives used in operations. Their presence in produced water can potentially pose environmental and health hazards, necessitating treatment prior to disposal or potential reuse

Different metals in dissolved or microgranule form may be present in produced water. The geological features and age of the oil and gas deposit, as well as the volume and make-up of any flood water pumped into the reservoir, all affect the presence, concentration, and chemical makeup of these metals. Certain metal concentrations in generated water can occasionally be discovered to be far greater than those in pure seawater—sometimes by a factor of 1,000 or more. Barium, iron, manganese, mercury, and zinc are a few of the metals that are frequently found in generated water at higher concentrations than in saltwater.(16–17)

2.6 Common Metals in Produced Water:

Heavy Metals:

Lead(pb): Can be toxic to humans and aquatic-life even at low concentrations.

Cadmium (cd): Known for its toxicity and potential to cause kidney and liver damage.

Mercury (Hg): A highly toxic metal that can bioaccumulate in the food chain.

Arsenic (As): Can be naturally present in the subsurface and is known for its toxicity.

Chromium (Cr): Particularly hexavalent chromium, which is toxic and carcinogenic.

Due to the anoxic nature of formation water, high concentrations of iron and manganese may be dissolved within it. Nevertheless, the iron and manganese precipitate out as iron and manganese oxyhydroxides when these formation waters are raised to the surface and exposed to ambient oxygen. Additionally, other metals in the generated water may co-precipitate with the iron and manganese, causing the very thin, solid hydrous iron and magnesium oxides in the receiving fluids to be distributed, adsorbed on, or complexed. Lead and zinc in generated water may have come from other waste streams that were treated in the oil/water separator system or from galvanized steel structures that came into contact with the produced water.

2.7 Environmental and Health Concern

Toxicity: Many metals are toxic to aquatic life and can cause health problems in humans if ingested in drinking water.

Bioaccumulation: Some metals, like mercury, can accumulate in the food chain, posing risks to both wildlife and humans.

2.6 Radioisotopes

Isotopes are variants of a particular chemical element that have the same number of protons but a different number of neutrons in their nuclei, leading to variations in atomic mass. some isotopes are naturally occurring and radioactive, meaning they spontaneously undergo radioactive decay, emitting particles and radiation in the process. [83].

Naturally occurring radioactive material, or NRM, is frequently discovered in generated water in many different parts of the world. The main naturally occurring radioactive decay products of uranium-238 and thorium-232 linked to certain rocks and clays in the hydrocarbon reservoir are radium-226 and radium-228 (226Ra and 228Ra), which are the main NORM radionuclides found in generated water.Radium-226 is an alpha-emitting daughter of uranium-238 and uranium-234, with a half-life of 1,601 years; on the other hand, radium-228 is a beta-emitting daughter of thorium-232, with a half-life of 5.7 years [7,100].

Radium-226, a uranium decay product, has a half-life of roughly 1600 years.Radium-228 is a thorium decay product with a half-life of roughly 5.75 years.Because radium isotopes are soluble in water, they can become mobilized when producing oil and gas.

Uranium: Naturally occurring uranium can be present in produced water, typically in trace amounts.

Thorium:

Trace levels of naturally occurring thorium are also present in generated water.

Lead: Lead-2010 is a 22-year-half-life decay product of uranium-238.Produced water may include lead-210 contamination.

Potassium-40:

A naturally occurring radioisotope with a half-life of about 1.25 billion years.

Potassium-40 can be present in produced water, though typically in low concentrations.

Others Radionuclide:

A number of additional radionuclides, in addition to radium-226 and radium-228, may be present in generated water at low radioactivity levels. Only 210Pb, a daughter of 226Ra, is a radioisotope that can sporadically be found at activity levels higher than those of 226Ra and 228Ra. In treated generated water from four platforms off the coast of Louisiana, the mean 210Pb activity varied from 5.60 ± 5.50 pCi/L to 12.50 ± 2.60 pCi/L. Owing to its relatively short half-life of 138.4 days, 210Po, another daughter of 226Ra, is also discovered in generated water from the North Sea at low activity levels. The parent isotopes of radium, 238U and 232Th, as well as the short-lived 224Ra, which has a half-life of 3.66 days, have relatively modest activities. [7]

Table 2.4 Mean or range of activities of ^{226}Ra and ^{228}Ra in produced water from different locations, activities are pCi/L (1 pCi = 0.037 Bq [7].

Location	Radium-(226)	Radium-(228)
Ocean-water (background)	0.028−0.05	0.006–0.013
Worldwide	0.06–32,401	8.2–4,861
Scotian Shelf	1.3	9.3
Grand Banks	34.0	229.8
Texas	0.1−5,151	N-A
Louisiana Gulf Coast	N-D−1,566	N-D−1,509
Offshore US Gulf of Mexico	91.3−1,495	162−600
Santa Barbara Channel, CA	166	137
Cook Inlet, AK	<0.5 – 9.8	N-A
North Sea	44.9	106
Dutch North Sea	<53–8,155	<28–541
Norwegian continental shelf	N-D–433	N-D–566
S. Java Sea, Indonesia	7.5−56.6	0.7−17.8
Offshore Brazil	0.4–295	<2–184

With the exception of the northern Gulf of Mexico, radium activity in produced water (PW) from offshore production locations is generally low, with mean 226Ra and 228Ra activity being less than 200 pCi/L. Nonetheless, PW from some North Sea production sites, particularly in the Dutch sector, may show elevated 226Ra activity. While radium isotope activity in produced water from platforms that discharge to Atlantic Canada is initially low, it is many orders of magnitude higher than in natural seawater. However, because of substantial natural dispersal, seawater samples taken close to production platforms on the Grand Banks and the Scotian Shelf only show background activity (94).On the Norwegian continental shelf, somewhat increased radium isotope activity has also been noted close to production facilities .[101]

Produced water may also have low activity levels of a number of additional radionuclides. 210Pb, a daughter of 226Ra, is the only radioisotope that is occasionally detected with higher activity in generated water than 226Ra and 228Ra. The treated generated water from four platforms off the coast of Louisiana had mean 210Pb activity ranging from 5.60 ± 5.50 pCi/L to 12.50 ± 2.60 pCi/L. Because of its brief half-life of 138.4 days, 210Po, another daughter of radium, is present in generated water from the North Sea at low activity. The radium parent isotopes, 238U and 232Th, are also taken into consideration for their activities. [7]

Table 2.6 Activity (pCi/L, except as indicated) of generated water and seawater containing radium isotopes and some of their parent and daughter isotopes [7]

Radio-nuclide	Sea-water	Produced-water
226 Ra	0.026-0.05	0.055–32,401
228 Ra	0.006-0.04	8.1–4,861
224 Ra	0.0003-0.009	13.6–1,081
238U	1.10	0.008–2.8
232 Th	0.004	0.008–0.027
210 Pb	0.027–0.13	1.34–5,131
210 Po	0.018–0.068	0.005–0.17

2.7 Production Chemicals

Large numbers of specialty additives (treatment chemicals) use in the production system of a well to aid in recovery and pumping of hydrocarbons, to protect the system from corrosion, to facilitate the separation of oil, gas, and water, and prevent methane hydrate (ice) formation in gas production systems. These include biocides, scale inhibitors, emulsion breakers, and gas-treating chemicals.Many of these chemicals are more soluble in oil than in produced water and remain in the oil phase. Others are water-soluble, remain in the produced water, and are disposed with it.Concentrations of most production chemicals are low in treated produced water.

Corrosion inhibitors, scale inhibitors, and gas treatment chemicals (glycol and methanol) may be high in production systems with these problems.

Activity (pCi/L, except as indicated) of generated water and seawater containing radium isotopes and some of their parent and daughter isotopes.[7]

Produced water may usually from oil field contain there following chemical which it used in different stages of drilling and production operation can be environmental concern it not treated properly.

2.7.1 Corrosion inhibitors:

Corrosion inhibitors are used to protect equipment such as pipelines and storage tanks from corrosion caused by water and other chemicals.Common types include amines, phosphates, and azoles.

2.7.2 Scale Inhibitors:

Scale inhibitors prevent the buildup of mineral deposits (scale) on equipment, which can reduce efficiency and cause blockages. Common types include phosphonates, polyphosphates, and organic acids.

2.7.3 Biocides: Biocides control or eliminate microbial growth in produced water, which can cause biofouling, corrosion, and other issues. Examples include glutaraldehyde, quaternary ammonium compounds, and oxidizing agents such as chlorine.

2.7.4 Emulsion Breakers: breakers separate water from oil or gas, making the produced water easier to treat and manage.

Common types include surfactants, alcohols, and organic acids.

2.7.5 Flocculants and coagulant: These chemicals help remove suspended solids and other particulates from produced water by causing them to clump together for easier removal. Common types include polymers and inorganic salts such as aluminum sulfate.

2.7.6 Demulsifies: Demulsifiers break down water-in-oil emulsions, facilitating the separation of water from oil during processing. Often composed of surfactants and solvents.

2.7.7 Oxygen Scaven-gers: Water's dissolved oxygen is eliminated by oxygen scavengers to stop corrosion and enhance the functionality of other chemicals. Hydrazine and sodium bisulfite are two common varieties.

2.7.8 Paraffin Inhibitors and solvents: Paraffin inhibitors and solvents prevent or remove paraffin wax deposits in pipelines, improving flow and efficiency.

Often include solvents such as xylene or surfactant-based inhibitors.

2.7.9 ph Adjuster and Buffering Agents:

These chemicals adjust the pH of produced water to optimize other chemical treatments and protect equipment.Common types include acids (e.g., hydrochloric acid) and bases (e.g., sodium hydroxide).

Chapter: 3

Environmental effects of Produced water:

Produced water contains many different constituents, each has a different impact on the environment. The environmental impact PW has a deep-rooted history intertwined with the development of the oil industry. Originating in the mid-18 and the century, the rapid expansion of the oil industry brought unprecedented economic technological advancements. but also raised concerns about environmental pollution. In the early days of oil production, little attention was paid to the disposal of produced water, and primitive methods such as surface discharge or open evaporation ponds were commonly used.

These practices resulted in widespread environmental degradation, with reports of contaminated water bodies, soil pollution, and adverse effects on human health and wildlife. As public awareness of environmental issues grew, concerns about the impacts of PW on ecosystems and communities living near oil/gas fields intensified.

In response to mounting pressure, regulatory frameworks began to emerge to address environmental concerns associated with produced water. However, challenges persisted, particularly in regions where industrial activities were prevalent and water resources were scarce.

Over time, technological advancements and regulatory measures have led to improvements in produced water management practices. Treatment technologies such as membrane filtration, evaporation, and crystallization have been developed to treat and recover valuable resources from produced water, reducing its environmental footprint.

Despite these advancements of technologies, the management of produced water remains a complex and expansive issue , requiring a delicate balance between economic considerations and environmental stewardship. Continued research, innovation, and collaboration among stakeholders are essential to minimize environmental impacts and ensure the sustainable use of natural resources in the oil industry to minimize environmental impacts and ensure sustainable resources use and the following effects should be always in consideration while taking about PW from oil and gas industry.

1-Produced water effects on Marin environment:

Produced water contains various chemical compounds, including hydrocarbons, heavy metals, and organic compounds such as benzene, toluene, ethylbenzene, and xylene (BTEX). PW undergoes change in its physical chemistry including precipitation of heavy melts after being discharge and mix with ambient seawater. These chemicals can have toxic effects on marine environment and their organisms, affecting their growth, reproduction, and overall health. Chronic exposure to these contaminants can lead to bioaccumulation and biomagnification in marine food webs.

Studies have shown that produced water can exhibit acute and chronic toxicity to marine organisms, including fish, crustaceans, and plankton. Toxicity tests have revealed adverse effects such as developmental abnormalities, reduced reproductive success, and impaired behavior in exposed organisms. The degree of toxicity depends on factors such as the composition of produced water, its concentration, and the sensitivity of the organisms.(30)

PW which is also contain the flow-back water while injecting back and mix with formation water and produced again. A treated PW discharge typically contains dispersed oil (normally 10–100 mg/L range), dissolved hydrocarbon (HC) gases, suspended particles (eg.clay), inorganic salts, organic acids, aromatic hydrocarbons, ketones, phenol/alkylphenols, heavy metals, and naturally occurring radioactive materials (NORM) and often also chemicals added to the production system to aid the extraction processes or to protect against biofouling and corrosion (31, 32, 33, 34, 45)

1.2 Produced water (PW) discharge into the sea water can lead the following effect:

1.2.1 Sediment accumulation:

Produced water discharged into the sea can goes down (due to Higher density) and accumulate in sediments, leading to contamination of benthic habitats. This can alter sediment composition, disrupt benthic communities, and impact sediment-dwelling organisms such as burrowing invertebrates, which play essential roles in sediment stability and nutrient cycling.

1.2.2 Bioaccumulation and Biomagnification:

Some contaminants present in produced water have the potential to bioaccumulate in the tissues of marine organisms. Through biomagnification, these contaminants can become more concentrated as they move up the food chain, posing risks to higher trophic level predators such as fish, marine mammals, and seabirds. This phenomenon can lead to chronic exposure and adverse effects on top predators in marine ecosystems.

1.2.3 Disruption of ecosystem functioning:

The discharge of produced water can disrupt natural ecosystem processes and functions in marine environments. For example, toxic chemicals may inhibit photosynthesis in phytoplankton, leading to changes in primary productivity and nutrient cycling. These disruptions can have cascading effects throughout the marine food web, affecting the abundance, distribution, and diversity of marine species.

1.2.4 long-term ecological impacts:

While acute effects of produced water discharge may be readily observable, the long-term ecological impacts can be more subtle and pervasive. Chronic exposure to low levels of contaminants over time can result in population-level effects, such as reduced reproductive success, changes in species composition, and altered community structure. These long-term impacts can have significant implications for the resilience and sustainability of marine ecosystems.

1.2.5. Habitat Degradation:

Produced water discharge can cause physical and chemical changes to marine habitats, including coral reefs, seagrass beds, and mangrove forests. Contaminants can smother benthic organisms, degrade habitat quality, and reduce habitat complexity, making ecosystems more vulnerable to further degradation from other stressors such as climate change and ocean acidification.

Discharge can alter water quality, including temperature, salinity and PH disrupting marine habitats and effecting the distribution and abundance of species.

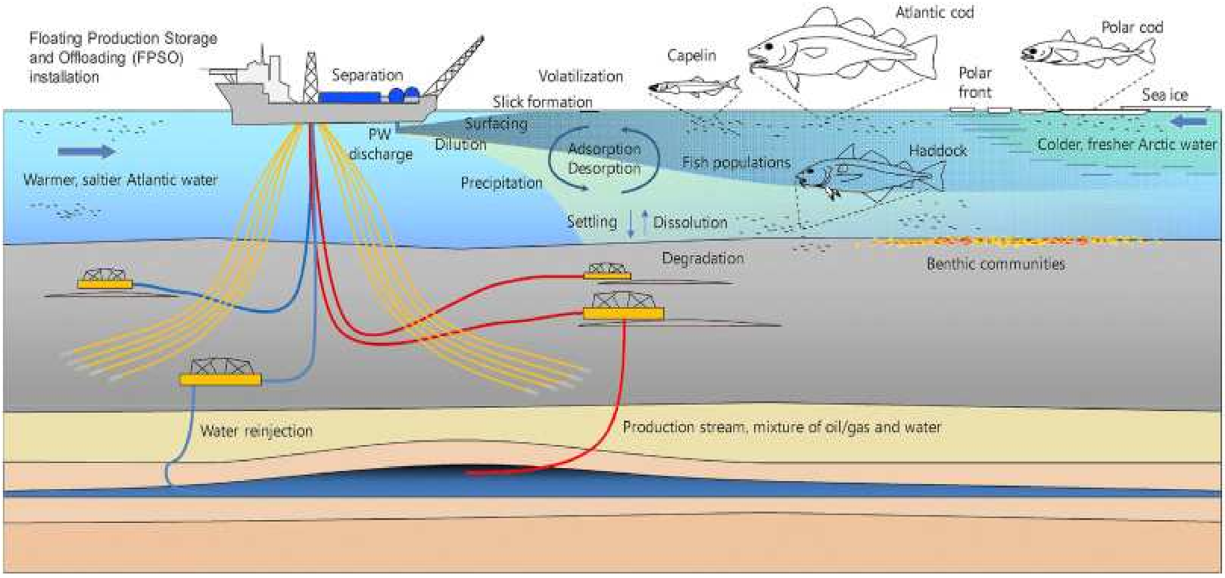


Fig. 3.1-Research and monitoring of offshore oil and gas production's discharged produced water indicate mild acute effects on water column biota near outfalls, but the extent of chronic ecological impacts downstream, particularly in the sub-arctic Barents Sea, and the potential sensitivity of local ecosystems remain uncertain, warranting ongoing investigation [36].

2- Produced water effects on ground water:

One of the most important problems related to the Produced water and Flow back water potentially lead to migration of pw into the groundwater (water well) thought pathway of fracture and permeable zone while oil and gas drilling and production and injection operation. Which can have a direct effect on human and animal while drinking or dermal contact.
Wastewater (PW) extracted from oil is usually chemically treated and returned to the environment, thus it is one of the most significant sources of ground water contamination, especially if it has elevated levels of natural radioactivity. [37,38]

If produced water is disposed of in the environment finds its way into aquifers it could pollute the water table. Groundwater movement is generally very slow compared to movement of surface water and usually travels less than 100 feet a year. [2]
So therefore, the radioactivity could concentrate in slow moving water bodies and persist for many years eventually posing a lethal to the ecosystem.

A Study which conducted tests on water well near the oil and gas filed in US to understand the changing effects on water well due to the PW and flow back water. the results shows that there has been an increase in water well. Water chemistry results show elevated cations and anions including manganese, iron, bromide and chloride. Different wells had different contaminants although the majority had manganese above the MCL. Light hydrocarbon analyses suggested a thermogenic source for the methane in some wells.[40]

Incorrect disposal of produced water can lead to groundwater contamination. A case study in India demonstrated that seepage from brine (PW) led to the contamination of the source well, which subsequently increased the groundwater hardness. [102]

2.1 PW from Hydraulic Fracture:

PW from hydraulic fracturing raise serious worries regarding the possibility of contaminating surface and groundwater because to the chemical utilized. Because radium is somewhat water soluble in underlying rock, a large portion of the pw—up to 40% of the injected water—comes back out of the gas well radioactively. Although fracking for natural gas offers substantial financial advantages and natural gas is a superior fossil fuel in theory than coal and oil, the current methods of fracking have a negative impact on the health of nearby inhabitants and workers.

Because conventional waste-water treatment plants are typically unable to remove the chemicals or radioactive compounds, the disposal of the produced water presents a significant challenge. Contamination of surface and ground waters has been documented.

Because conventional waste-water treatment plants are typically unable to remove the chemicals or radioactive compounds, the disposal of the produced water presents a significant challenge. Contamination of both surface and ground water has been documented in the literature [4,5], because of waste-water disposal, well casing leaks, transportation spills, and leaks through cracked rock. Drinking water contamination by methane is an issue. [6,7]

Injecting produced water deep into the ground has been one approach to handling it. But as a result, there has been a noticeable rise in earth-quakes.Understanding the passible contaminations that may result from pw generated during hydraulic fracturing is therefore essential.[9]

2.2 Groundwater Contamination:

Groundwater contamination is a primary risk associated with hydraulic fracturing (HF) [95] Various factors contribute to this risk including:

• A blowout, which is the unintentional discharge of hydrocarbons, PW, and flow-back; frac fluid released by container leaks; and production water pipeline leaks.

• Leaking drainage wells used to dispose of produced water; this also includes leaking boreholes caused by inadequate casing and cementing.

• The movement of constituents of frac fluid from deeper formations into shallower ones.

• Gas rising (also known as "thermogenic methane").

• Production water from deep wells rising to the surface. [95]

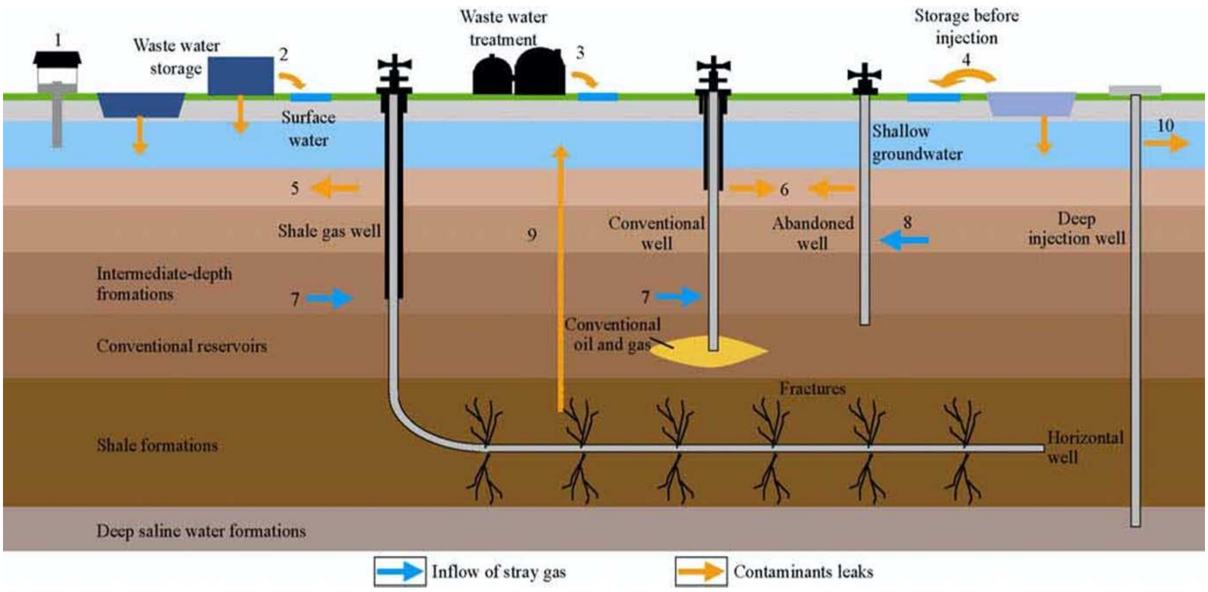


Figure 3.2. Transport of fluids in shallow formations: Faulty cementing and casing can let fluids to seep out, contaminating shallow aquifers. This problem may affect one percent to three percent of conventional oil and gas wells, but it may affect a larger percentage of unconventional oil and gas wells than conventional ones. Poor cementing, which creates flowing space between the casing and the formatio, and casing damage, which results in leaky channels, are among the reasons of shallow fluid leakage and transport. [106]

2.3. Potential human health and environmental concerns due to flow-back water from fracturing:

One primary concern is the contamination of drinking water sources. By consuming water contaminated with high levels of salts or toxic chemicals can result in adverse health effects, including gastrointestinal issues, kidney damage, and neurological disorders.

In addition to direct ingestion, exposure to produced water contaminants can occur through other pathways, such as dermal contact and inhalation. Contact with contaminated water during recreational activities or occupational tasks can lead to skin irritation, rashes, and allergic reactions. Inhalation of volatile organic compounds (VOCs) and airborne particulates generated during produced water handling and disposal activities can also pose respiratory health risks, including irritation of the respiratory tract, exacerbation of asthma, and long-term respiratory ailments.

Furthermore, the presence of carcinogenic substances, such as benzene, arsenic, and polycyclic aromatic hydrocarbons (PAHs), in produced water can raise concerns about the potential for cancer development among individuals exposed to contaminated environments over the long term. Vulnerable populations, such as children, the elderly, and individuals with pre-existing health conditions, may be at higher risk of experiencing adverse health effects from exposure to produced water contaminants.
Addressing the potential health impacts of produced water requires comprehensive risk assessment and management strategies. This includes implementing robust regulatory frameworks to monitor water quality, establishing safe disposal practices to prevent contamination of drinking water sources, and conducting health impact assessments to identify and mitigate risks to human health. Additionally, public awareness and education initiatives are essential for informing communities about the potential health hazards associated with produced water exposure and promoting preventive measures to safeguard human health.

3.Produced water effects on soil and vegetations:

the chemical and physical properties of soils can alter by the salt amount in PW because of the high number of soluble salts (NaCL) negatively impact on soils properties.

In the vicinity of the spill area, elevated chloride levels pose toxicity risks to numerous biological species. Sodium, acting as a natural dispersant, has the potential to induce soil swelling and dispersion, albeit contingent upon the soil's total salt content falling below a critical flocculation threshold. To foster soil cohesion and structure, a flocculant like calcium is essential, as it binds soil particles together, promoting stability and integrity.

Swollen soils maintain their inherent structure, but once dispersion sets in, soil integrity diminishes. This structural deterioration hinders water infiltration and movement within the soil, heightening the risk of erosion. [41]

Effects on the Soil Resource. Potential soil quality and plant impacts from OGPW include the following [100]

1. (i) Clays that are too sodicated may deflocculate, which reduces the permeability of soil to water and air.

2. (ii) Plants that are overly soluble in salts will dry out and die. In areas with little natural precipitation, salts can build up in the soil to dangerously high amounts.

3. (iii) Chemical alterations in soil brought on by interaction with OGPW may cause new plant species to replace existing ones.

4. (iv) The distribution of plants that can withstand salt may expand. [42]

Elevated amounts of sodium, chloride, and boron in reject effluent with high salt contents might decrease soil and plant productivity and raise the possibility of soil salinization. Additionally, it can cause specific ion toxicity and modify the electrical-conductivity of soil, hence altering the sodium ad-sorption ratio (S-A-R). By determining the relative concentrations of sodium, calcium, and magnesium, (S-A-R) determines the impact of sodium on soil properties . Reduced perme- ability may result from higher SAR values. Sodium alters soil structure and hinders water infiltration, which impacts plant growth even if it does not lower the amount of water that plants use [43,44,45].

Additional effects include low aeration, increased irrigation and precipitation runoff, and decreased salt leaching from the root zone due to weak permeability. Inorganic chemicals and heavy metals accumulate in groundwater sources and the soil, which can lead to long-term health issues. (Ratio of sodium adsorption to SAR)

It is crucial to evaluate the amount and speed at which pollutants from the discharged brine on inland desalination facilities migrate through the soil profile. It offers ways to deal with the problems with water quality caused by reject brine's profound percolation when it is improperly discharged as a byproduct of desalination. Furthermore, assessing the detrimental effects of concentrated brine and heavy metals on the environment, as well as resolving the legal and regulatory concerns of brine reject discharge, require an understanding of the flow of these substances. Numerous researchers have created and studied models that explain the physical', chemical', and biological processes connected to the solutes mobility in the soil-profile [47,44, 48]

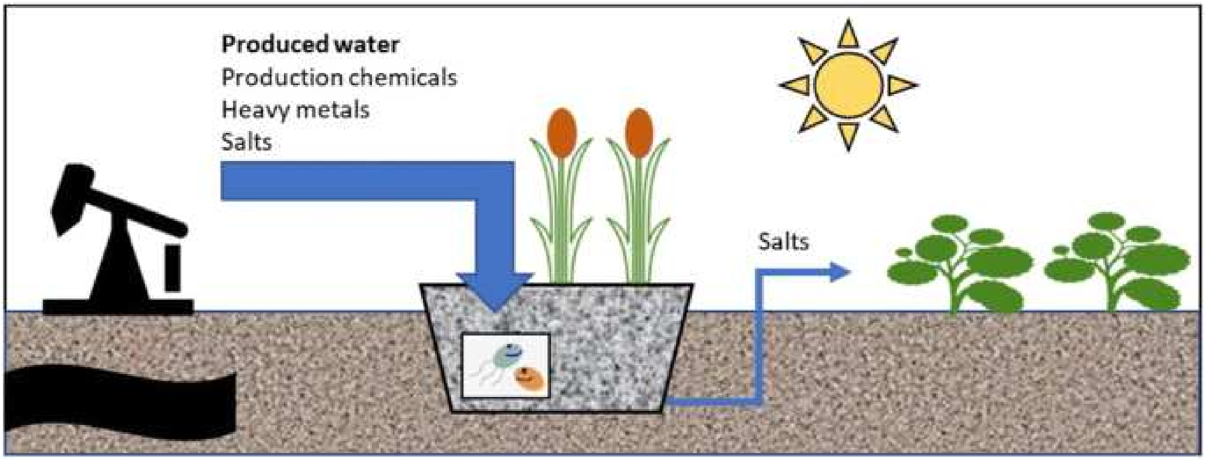


Figure 3.3. The following picture shows that how produced water are produced brought into the surface with oil and gas production with chemical and all toxic substances which can goes into the soil to effects vegetation specially from high silane behavior. [49]

4.Produced water impact on human health:

The rise in global Produced-water (PW) volume each year and its ongoing impacts have far-reaching effects on both current and future gener-ations. The use of polluted water carries numerous adverse effects on human health, including diseases like typhoid, cholera, hepatitis, and various other ailments. Despite the harmful nature of produced water and its consequences for human well-being, there has been insufficient attention given to this issue, with very limited research conducted.

4.1 Risk associated by heavy metals in PW:

Contamination by heavy metals poses a significant concern, presenting various health risks. According to the Agency for Toxic Substances and Disease Registry, metals and metalloids such as arsenic, chromium, cadmium, nickel, copper, zinc, and lead are classified among the 275 most toxic pollutants. To put all together, the harmful effects of toxic heavy metals are expressed in figure 1.

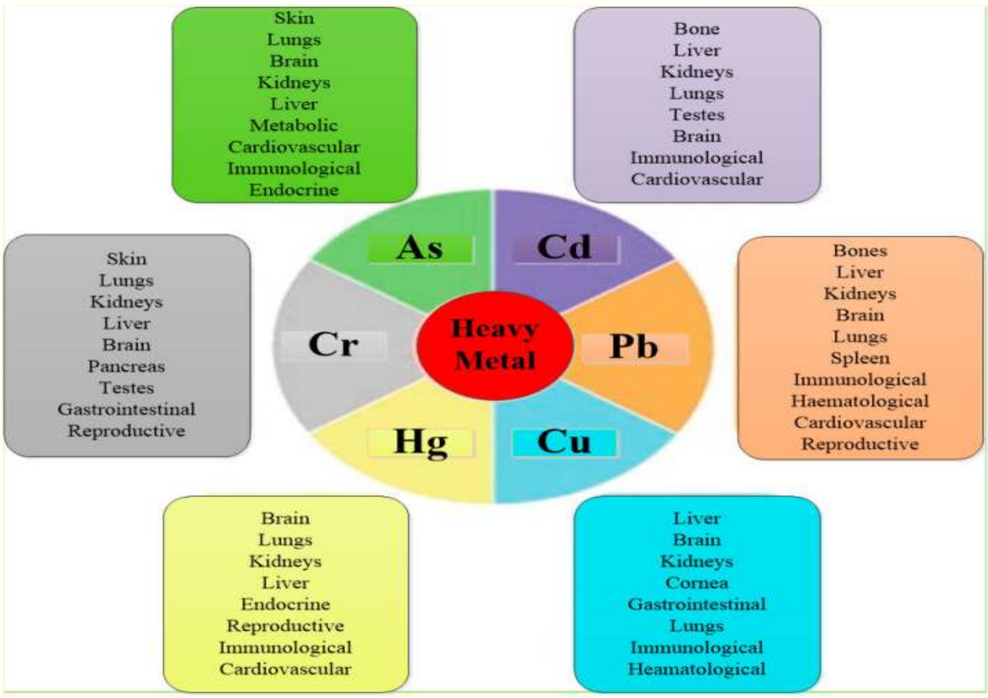


Figure 3.4. Harmful effects of heavy metals in produced water on human health [61]

Fish organs and fertility are negatively impacted by exposure to alkylphenols, since studies have shown that metals and hydrocarbons from oil fields are harmful. Acute or chronic toxicity can be found in generated water. While the long-term consequences are more challenging to detect, acute toxicity is measured using the LC 50 test. According to Holdway et al. [56], prolonged chronic exposure may result in fecundity, reduced reproductive success, growth and developmental issues, and genetic diversity. In addition, it might result in endocrine disturbance, physiological problems, and pulmonary problems. [51,52,53, 54, 55,56, 61]

4.2 Presences of Norms in Pw direct impact on Human health:

NORMS scaling is a naturally occurring radioactive material concentrate with greater radiation levels than background that precipitates and accumulates throughout manufacture. Radionuclides from the decay chains of Thorium 232 and Uranium 238 are present in oil and gas streams. The reservoir rock that holds the gas, oil, and formation water does not mobilize these constituents. Radium is present in the produced water together with many other cations, mostly alkaline earth compounds, when it is brought to the surface. Radium is extremely toxic, hence it is highly desirable to effectively separate these radiotoxic chemicals from non-toxic compounds. [57,61] Exposure to elevated Alpa and Gamma radiation creates serious biological problem especially genetic damage, which usually arise from exposure to low doses over an extended time period. [15,61]

The primary priority is safeguarding the ecosystem from potential hazards such as the bioaccumulation of Ra-226 in the food chain. Radium is metabolized by the human body in a manner akin to that of calcium. When small amounts of radium are consumed orally, it builds up in the bones and causes significant harm. In the end, the harm from ongoing internal radiation exposure may result in sinus and bone cancer. Tumors in the nasal mucosa are the most prevalent type, followed by bone tumors. [15,61]

Radioactivity is inherently present in the earth’s-crust' and can be found thought the environment. so, there are many naturally occurring materials contain radioactive elements such as radionuclides.

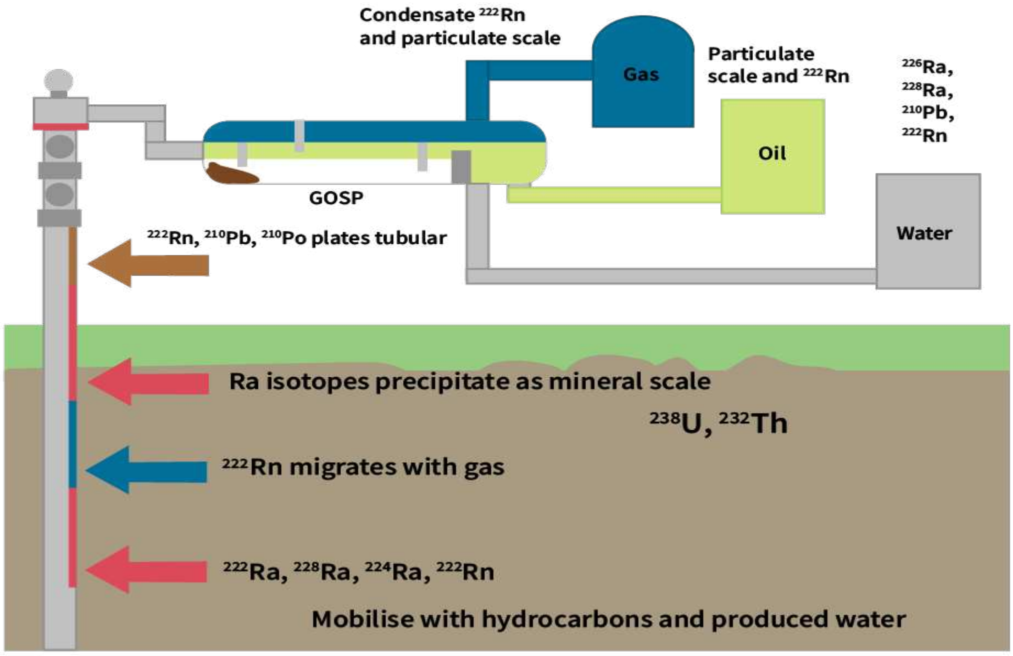


Figure 3.5. The following diagram show that how Norms from formation water, from can be present in Produced water while producing with oil and gas and going further into the environment. [50]

Exposure to NORMS is often increased by human activities specially the hydrocarbon production' operation. The petroleum industry is one of the main sectors dealing with aqueous TENORMS (Technologically enhanced naturally occurring radioactive material). As we can see formation water in the following scheme the norms can be present in formation water in the reservoir due to the extraction activity its produced with oil and gas. The distinct range of radioactivity found in produced water underscores the importance of assessing its impact on public health. Emissions of radionuclides and their prolonged presence in the environment can potentially lead to extended periods of external irradiation or internal contamination through the consumption of food or water by populations residing in affected areas.

4.3 Health risks associated with NORMs:

Compounds containing radionuclides have two distinct dangers. Radiotoxicity is the negative consequences of radioactive elements and nuclides, whereas chemical toxicity is caused by the chemical characteristics of the components and molecules that make up the material. Even minute amounts of radium isotopes (226 Ra, 228 Ra, and 224 Ra) can accumulate by consumption or inhalation and have serious long-term health effects. Cancers of the sinuses and bones are linked to prolonged exposure to radium.Moreover, norms have the potential to stigmatize common illnesses like bone tumors and nasal mucosa [58, 61]

A study reported that the activity concentrations of uranium and thorium isotope in produced water are less than 20 Bq. L−1.That water polluted with depleted uranium or thorium will undoubtedly cause many diseases to the consumer due to its penetration into the soil and water [59,61,73]

Concerns about the potential radioactive impacts of produced water on environment elements, including living things, are raised by TENORM discharges that are shepherding it. The problem of TENORM leaks from those water sources has drawn significant attention and substantial effort in recent years from scientists and technical personnel in various parts of the world [9-11-12-15].

This is because the leaks could have significant effects on environmental components. Numerous researches have reported on the radioisotopes that are most commonly found in generated water and its levels in various parts of the world.

These are the causes that can affect people, animals, and birds. Additionally, keep in mind that living things and long-term environmental influences can allow modest doses of norms over time to become high enough to cause serious issues, which are already covered in this chapter's discussion of potential causes.

5.5. Hazards of NORM in Produced water:

Hazardous to humans, animals, and the environment, radioactive wastes from the exploration and extraction of oil and gas are thought to be carcinogenic, mutagenic, and teratogenic [80]. These Naturally Occurring Radioactive Materials (NORM) must be managed to prevent adverse health and environmental impacts.TENORM, a word used to describe technologically improved NORM, is usually produced not in offshore operations but in certain downstream processes like ethylene cracking. [80]

Improper handling, storage, and transfer of contaminated TENORMs or radioactive waste can contaminate surrounding land areas, potentially exposing the public. Soil, rock, and water bodies can get contaminated by TENORMs released into the environment by the petroleum industry's generated water discharge. While generated water typically has modest levels of radioactivity, over time, the buildup of these materials can present serious environmental radiological risks.

Serious biological issues are brought on by elevated alpha and gamma radiation exposure, particularly genetic damage, which frequently results from low-dose exposure over long periods of time.Ra-226 bioaccumulation in the food chain poses a risk, so safeguarding the ecosystem from these dangers should be the first priority. Radium is metabolized by the human body in a manner similar to that of calcium, which causes it to accumulate in bones when consumed in small amounts. Constant internal exposure to radium can result in significant harm, possibly even sinus and bone cancer, with malignancies of the nasal mucosa coming in second most often. [15].

5.5.1 Risks of TENORMs exposure and inhalation by human health:

Water created by TENORMs has the potential to emit several forms of radiation, including beta and gamma particles. As a result, TENORMs may be regarded as a possible source of radiation intake and exposure, to which an individual may be exposed by the well-known internal and external exposure routes. The following scheme indicate that how norms can reach to human from produced water.

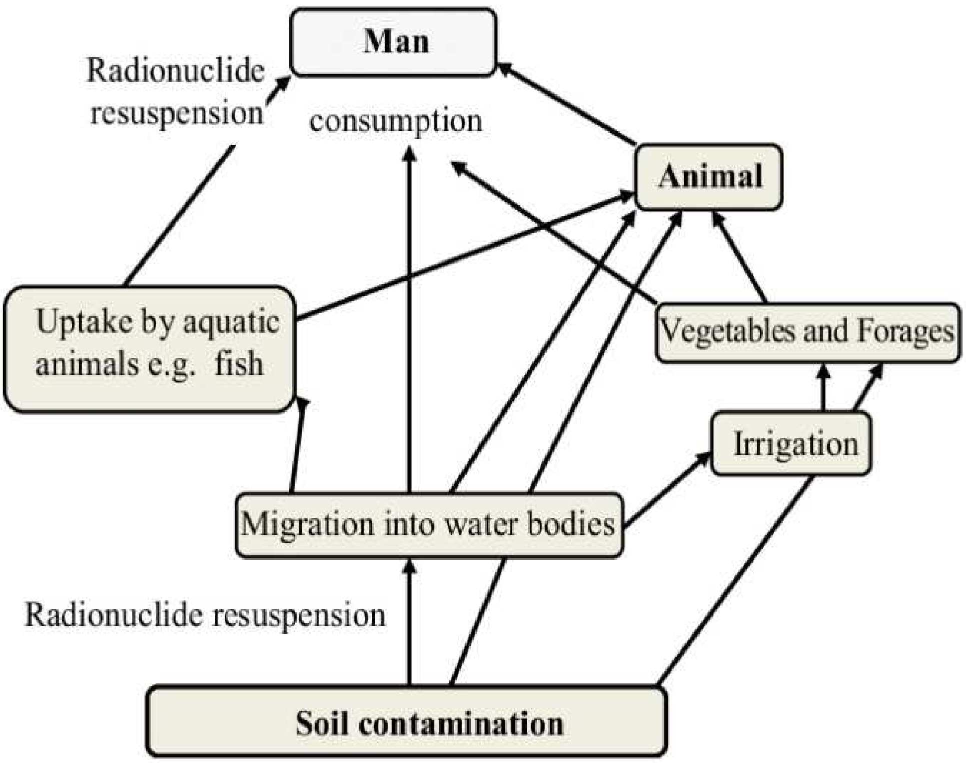


Figure 3.6. show how norms can reach to the human body thought different stages [60]

5.5.1. External exposure irradiation (risk to workers/local population):

The source of the external exposure or radiation stays outside the body. Workers may be exposed to beta and alpha radiation or gamma radiation from nearby sources while performing ordinary tasks. The gamma ray radiation can penetrates steel walls of the pipes or concrete wall that containing the produced water. The dosage rate can range from several micro-Sievert on the surface of highly polluted pipelines and utensils to fractions of micro-Sievert per hour for weak sources. The personnel might have been exposed to gamma radiation, TENORM dust, and radon during the petroleum plan's maintenance and shutdown times. Numerous investigations, including. [69,77,78]

5.5.2. Internal exposure (contamination).

Since radioactive material can enter the human body by ingestion or absorption, internal exposure is thought to be the most harmful. It is possible for the sulfate scale or sludge to have a radium equivalent activity concentration higher than 500 Bq.g−1. This means that radiation doses from even minute amounts of breathed dust can surpass the annual exposure limit of 1 m Sv.y-1 for the general public. Concentrations of radon in non-aerated vats of generated water can lead to increased radiation exposure even when the amount of radon released is minimal. [67,70,75,79]

The contamination of produced water with TENORMs result harmful radiation does that can impact human health and the environment at various levels. Higher radioactivity in produced water increases the radiation effects, particularly though internal pollution when dust is absorbed during water treatment or when in proximity radiation sources. Accumulated radiation does can exceed public safety limit, posing significant health risks. Workers in oil operation and nearby residents face potential exposure risks, highlighting the need for further research to quantity and mitigate these risks effectively. [73,76,79]

5.5.2 Human health effects related to Produced water discharge in marine environments:

Produced water discharge into marine environments can lead to indirect ingestion by humans through bioaccumulation in finfish and shellfish species. Radium, present in NORM, accumulates in bones, shells, and exoskeletons, posing various health risks.

PW discharge in marine environment can led indirect ingestion into human body. The bioavailability and bioaccumulation features of naturally occurring radioactive materials (NORM) in human-consumed finfish and shellfish species raise concerns about the potential health implications of these materials on humans. Radium, which shares chemical similarities with calcium, is typically found in bones, shells, and and ex- oskeletons. which can pose risks to human health through various exposure routes.

Chapter 4:
Produced water regulation:

1. Legal framework, policy, and regulations in US:

Once producing pw with oil and gas into the surface, produced water is separation from oil can be done by by gravity separators. However, the produced water may still contain addi- tional emulsions and dissolved oil that are harmful to the receiving environments. Therefore, different guidelines, permits, regulations, and laws are cautiously developed and strictly enforced by local legislations and administrations, in order to minimize the potential impacts of produced water disposal and reinjection.

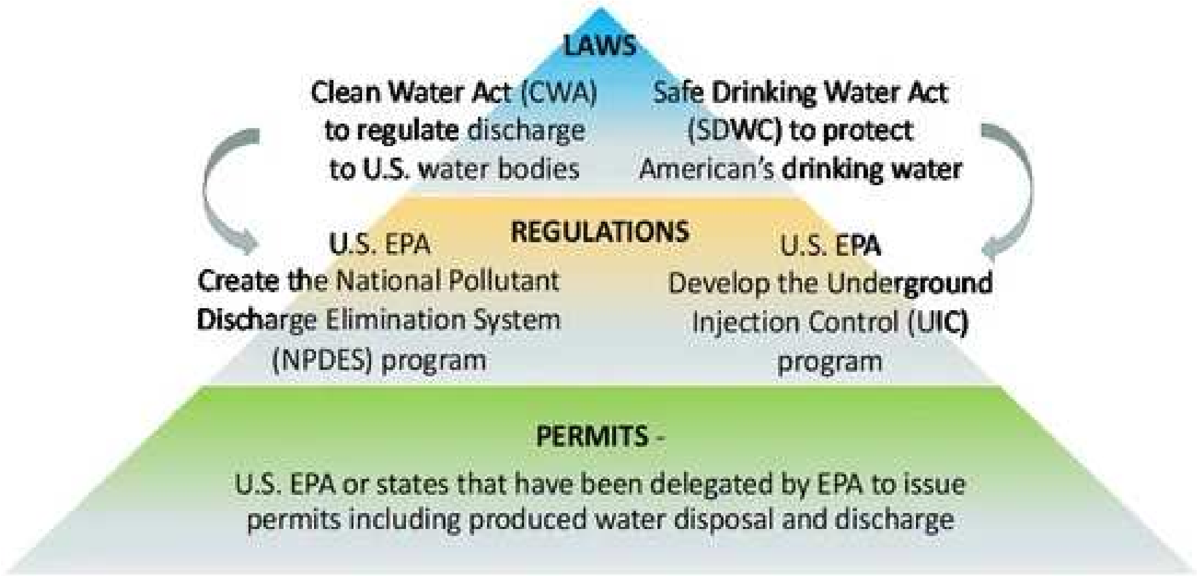


Figure 4.1 The U.S. legal and regulatory framework for produced water management [68]

In the United States, produced water management is generally catego- rized into disposal and injection operations. Most of the onshore produced water is injected while most of the offshore produced water is discharged, regulated by different federal and state laws. At federal level, the Clean Water Act (CWA), Underground Injection Control (UIC), Safe Drinking Water Act (SDWA), and Effluent Limit Guidelines (ELGs) are highly relevant to oil and gas produced water management. SDWA and UIC are used to regulate activities related to reinjection of produced water into formations. CWA regulates the dis- posal of produced water to the surface environment, stating that all dis- charges of pollutants at the surface must by authorized by the National Pollutant Discharge Elimination System, in order to prevent high- concentration toxic substances flowing into surface water bodies. ELGs are national technology-based minimum discharge requirements set by the Code of Federal Regulations (CFR). There are also different regional limits with respect to discharge rate, toxicity testing, and monitoring for certain harmful constituents, varying from state to state. In general, state programs are more stringent than federal requirements. The highlights of those guidelines, permits, regulations, and laws in the United States include: [97]

- Onshore oil and gas operations may not discharge produced water into navigable waters with two specified exceptions according to Subpart C of 40 CRF Part 435: (1) facilities located west of the 98th meridian and (2) facilities that produced 10 barrels per day or less of crude oil.
- Oil and gas operations in coastal waters may not discharge produced water to the marine environment. Cook Inlet in Alaska is the only coastal location in the United States that allows disposal of produced water with the oil and grease limits of 42 mg/L daily maximum and 29 mg/L monthly average.
- Offshore oil and gas operations are allowed to discharge produced waters into sea, under the ELGs that set the limits for oil and grease at 42 mg/L daily maximum and 29 mg/L monthly average.
- Underground injection is grouped into five classes. Class I wells are used for the emplacement of hazardous, industrial, and municipal waters, and these wells are most strictly regulated by SDWA and Resource Conservation and Recovery Act. Class II includes wells with injection of brines and fluids associated with oil and gas. Class III includes wells with injection of fluids associated with minerals. Class IV includes wells with injection of hazardous or radioactive materials
- into or above sources of drinking water, and this class is highly restricted. Class V includes the rest of injection wells. In general, the wells used to reinject produced water belong to Class II, with Class IIR for oil enhancement and Class IID for disposal purposes. According to 40 CRF, all Class IID wells are required to apply for a permit for the first year while Class IIR wells require authorization for the life of a well. Every new Class IID and Class IIR well must be authorized before construction and injection can commence. Operators must demonstrate the internal and external integrity of the proposed injection wells. Operators must plug and abandon injection wells that have

not been involved in any activity for 2 years. During any operation, the injection pressure cannot exceed the maximum injection pressure that may initiate new fractures. The owner must monitor and report conditions of injecting wells following the requirements by the guidance.

- The Bureau of Land Management in the US Department of the Interior has jurisdictions over onshore leasing, exploration, and pro- duction over federal lands while the Bureau of Safety and Environmental Enforcement (the BSEE) manages the operations on the Outer Continental Shelf. [97]

Varying from country to country, there are different national limits with respect to discharge rate, toxicity testing, and monitoring for certain harmful constituents.

2. Regulatory Framework of United states comparison with Pakistan.

The US has a comprehensive regulatory framework governing produced water management, primarily overseen by the Environmental Protection Agency (EPA) at the federal level and various state regulatory agencies.

Regulations such as the Clean Water Act (CWA) and Safe Drinking Water Act (SDWA) establish guidelines for the discharge and disposal of produced water, emphasizing pollution prevention and control.

Pakistan:

In Pakistan, the regulatory landscape for produced water management is still evolving, with oversight fragmented among different government agencies at the federal and provincial levels. While environmental laws exist, such as the Pakistan Environmental Protection Act (PEPA), enforcement and implementation may vary across regions, leadingto inconsistencies in produced water management practices.

Technological Solutions:

United State:

The US oil and gas industry has developed advanced technologies for produced water treatment and recycling, including membrane filtration, chemical treatments, and thermal processes.

Water reuse and recycling initiatives are increasingly adopted to minimize freshwater consumption and reduce disposal volumes, driven by both regulatory requirements and economic incentives.

Pakistan:

In Pakistan, technological solutions for produced water management are less widespread, with a greater reliance on conventional treatment methods and disposal practices.

Limited access to advanced treatment technologies and infrastructure constraints may hinder the adoption of more sustainable produced water management practices.

Environmental Impacts:

United stat:

Despite advancements in produced water management, concerns remain regarding potential environmental impacts, including groundwater contamination and surface water pollution.

Efforts are ongoing to mitigate these impacts through improved regulatory oversight, enhanced monitoring programs, and the development of best management practices.

Pakistan:

In Pakistan, the environmental impacts of produced water discharge and disposal are less studied and understood compared to more developed regions.

Rapid industrial growth and inadequate regulatory enforcement raise concerns about the potential for water pollution and ecosystem degradation in areas with significant hydrocarbon production activities.

Challenges and Opportunities:

United state:

Challenges in the US include balancing economic interests with environmental protection, addressing legacy contamination from historical practices, and ensuring adequate infrastructure for produced water management.

Opportunities lie in continue innovation in treatment technologies, increased collaboration between industry and regulators, and promoting sustainable water management practices.

Pakistan:

Challenges in Pakistan include improving regulatory enforcement, enhancing public awareness of environmental issues, and investing in infrastructure for water treatment and disposal.

Opportunities exist for knowledge sharing and capacity building through international partnerships, leveraging lessons learned from other countries' experiences in produced water management.

Future Directions:

Both the US and Pakistan face evolving challenges in produced water management amidst changing regulatory landscapes and growing water scarcity concerns.

Collaboration between stakeholders, including government agencies, industry players, academia, and non-governmental organizations, will be crucial for advancing sustainable solutions and mitigating environmental risks associated with produced water handling and management.

Chapter 05 : Produced water Management:

The petroleum industry generates produced water (PW), which is an unwanted waste that must be managed due to its large volume and complexity. Typically, PW is used internally for oil and gas operations, with the remaining volumes being disposed of through various means. However, there has been a recent need to repurpose the volume of water that is typically disposed of for applications in other industries. This presents a potential opportunity to reduce excessive freshwater usage in oil and gas operations and reduce water depletion in other industries, thereby aiding water conservation—one of the goals for sustainable development. Although external uses are a viable and logical solution, there are obstacles related to PW characterization, treatment technology, and project economics.

Consequently, taking into account the environment, technical factors, and economics, the petroleum sector continues to face significant challenges regarding the efficient treatment technology, utilization, and disposal of PW. All parties involved must work together to fully utilize the benefits and possibilities of external PW reuse for economical and ecologically responsible treatment technology solutions, as well as for any other component of PW management. This analysis provides a thorough introduction of PW management, as well as prospects for application in other sectors and existing petroleum industry practices. Every disposal technique is explained in full, along with any potential external uses and a list of related difficulties and solutions. [104]

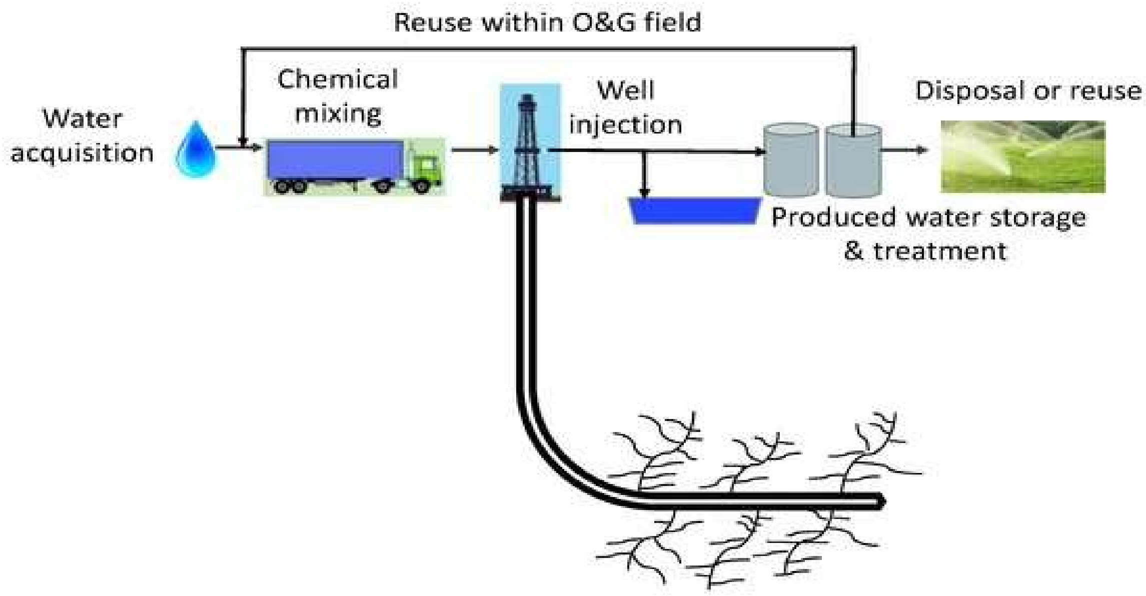


Figure 5.1 Schematic diagram of produced water how it produced with oil and gas into the surfaces then management and reuse. [103]

5.1- History of Produced water Management:

In the early stages of oil and gas extraction, produced water was often mishandled, sometimes being discharged directly into surface water bodies, spilled onto land, or left to evaporate in pits. The practice of re-injecting water into oil reservoirs to enhance production, known as waterflooding, started in Pennsylvania as early as 1865 and gradually spread to other states, becoming widespread by the 1950s. It is unclear if early waterflooding utilized produced water or local surface water, but in arid regions with scarce surface water, companies eventually began using produced water for this purpose. Initially, the process of managing produced fluids involved simple gravity separation to divide oil, gas, and water. This method was used to prepare produced water for re-injection, though additional steps like filtration and chemical treatments became necessary to prevent issues such as formation pore blockages.

As oil and gas production continued, the proportion of water in the produced fluids increased. This necessitated further management techniques, including separating oil and gas from water in free-water knockout tanks and treating the water to remove any remaining oil and solids. Over time, produced water not required for waterflooding was disposed of by injecting it into non-hydrocarbon-producing formations. This method of injection, for either reuse or disposal, has been the primary approach for managing produced water in the oil and gas industry for many years. According to surveys by the American Petroleum Institute, injection accounted for 92% of produced water management in 1985 and 1995, and a 2007 study reported that 98% of produced water was handled this way. [107]

5.2- Role of the produced water in Oil & Gas Industry:

Drilling, Hydraulic Fracturing (HF), and Enhanced Oil recovery procedures all require water. Municipal water supplies, groundwater or surface water resources, as well as recycled or repurposed water from other sources, can all provide water for such uses. A large portion of the water used for drilling and well completion is also returned to the surface and needs to be managed as waste. Water discharged from subterranean geologic formations as a consequence of completion, fracturing, or drilling activities may also be included in the waste stream.

5.3- Re-uses of Produced water in different sectors:

Produced water (PW) can be utilized in several beneficial ways both within and outside the energy sector. Here are six main areas where PW can be repurposed.

5.3.1- Irrigation:

Treated produced water can be reused for agricultural purposes, especially in countries facing water scarcity, such as Pakistan. This provides a viable solution for areas already experiencing water shortages.

5.3.2- Hydraulic Fracturing (HF)

The use of PW in hydraulic fracturing is increasingly popular worldwide. This method not only helps extract more oil but also conserves a substantial amount of freshwater, making PW an optimal choice for fracturing operations.

5.3.3- Surface Water Discharge:

Surface water discharge is a less favorable option due to insufficient research on the long-term environmental impacts of PW, even when treated. However, in regions where other uses of PW are not feasible, surface discharge might be considered.

5.3.4- Groundwater Recharge:

Groundwater recharge with treated PW can be considered, provided the water is thoroughly treated to eliminate any toxicity. This option requires meticulous care to ensure the groundwater remains uncontaminated.

5.3.5- Municipal Use:

Municipal use of PW can be a viable solution if the water is treated to ensure it is non-toxic. This application helps alleviate water scarcity issues without posing significant risks to public health.

5.3.6- Industrial Use:

Industrial processes often require substantial amounts of water. Using PW in industrial applications can be beneficial, provided it does not harm the environment or human health. However, this option depends on the proximity of oil and gas fields to industrial areas, as transportation of PW can be challenging, especially if the fields are in remote or offshore locations.

Overall addressing water-scarcity issues is more feasible by reusing PW within the energy sector' rather than in other sectors. Substantial research is needed to safely reuse PW for agricultural purposes, surface water discharge, or groundwater recharge. This involves analyzing all potential effects and treating PW to prevent long-term problems.

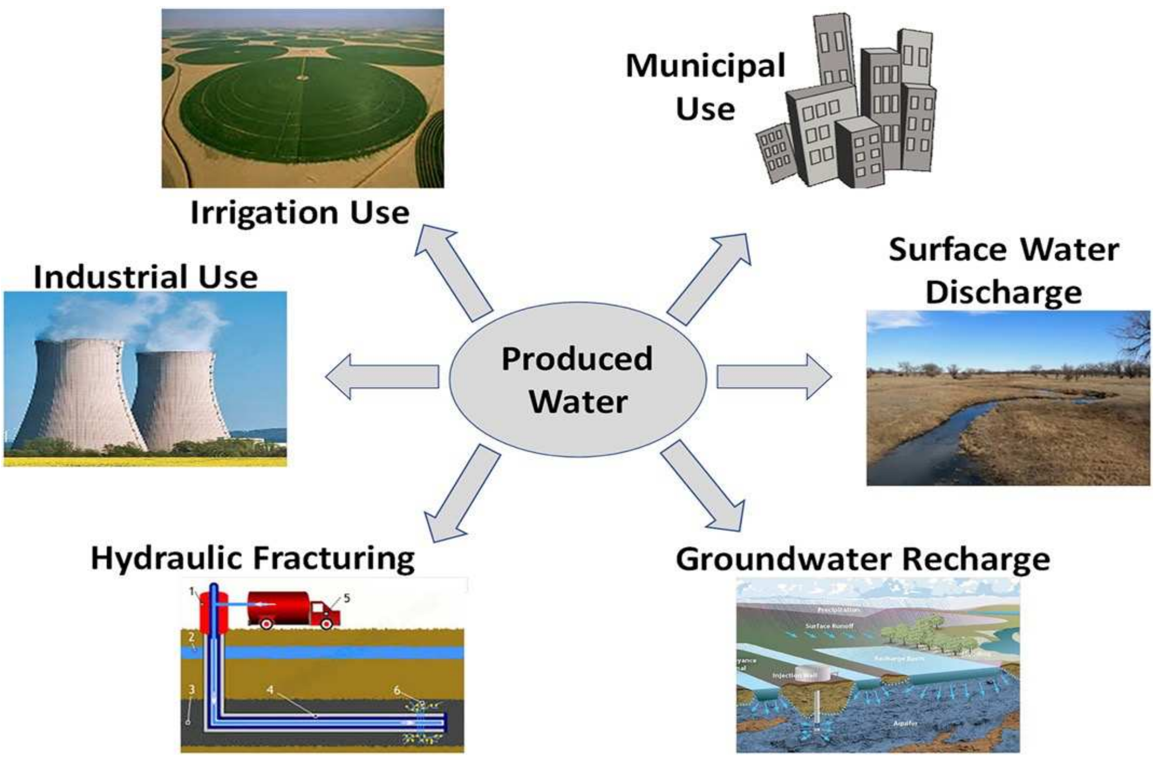


Figure 5.2 the scheme show that Produced water can benifically used for the following six uses after treatment. [97]

5.4- Produced Water Management in US:

Produced water management in the United States is a critical aspect of the oil and gas industry, given the vast quantities generated during hydrocarbon extraction. The United States, as one of the world's largest producers of oil and gas, faces substantial challenges in handling and treating this byproduct. Annually, the industry generates billions of barrels of produced water, necessitating robust management strategies to mitigate environmental impacts and comply with stringent regulatory frameworks.

One of the primary methods for managing produced water in the U.S. is through reinjection into underground formations. This practice serves multiple purposes: it helps maintain reservoir pressure, which is essential for enhancing oil recovery, and it provides a means of safe disposal for the produced water. The Environmental Protection Agency (EPA) oversees this process through the Underground Injection Control (UIC) program, which ensures that injected fluids do not contaminate underground sources of drinking water. Reinjection is particularly prevalent in regions like Texas and Oklahoma, where it is an integral part of enhanced oil recovery operations.

In addition to reinjection, the U.S. has seen significant advancements in produced water treatment technologies. Various treatment methods are employed to remove contaminants such as salts, heavy metals, and hydrocarbons, making the water suitable for reuse. Techniques such as membrane filtration, reverse osmosis, and thermal distillation are increasingly being used to treat produced water. Treated water can then be repurposed for agricultural irrigation, industrial applications, or even as a source of fresh water in arid regions. This not only reduces the environmental' foot-print of the oil and gas' industry but also addresses water scarcity issues in regions facing drought.

Regulatory oversight in the U.S. plays a crucial role in produced water management. Agencies like the EPA and state-level regulatory bodies have established comprehensive guidelines and standards for the treatment and disposal of produced water. These regulations ensure that the environmental impacts are minimized, and public health is protected. Compliance with these regulations is mandatory for operators, and failure to adhere can result in significant penalties and operational shutdowns.

Economic considerations also influence produced water management practices in the U.S. The costs associated with treatment and disposal are significant, driving the industry to seek cost-effective and sustainable solutions. Innovations in produced water treatment technologies are not only improving efficiency but also reducing costs, making it more feasible for operators to treat and reuse produced water. This shift towards more sustainable practices is also driven by increasing societal and regulatory pressures to minimize the environmental impact of oil and gas operations.

To sum up, produced water management in the United States involves a combination of regulatory oversight, advanced treatment technologies, and economic considerations. The industry is increasingly adopting sustainable practices to mitigate the environmental impacts associated with produced water. By reinjecting, treating, and reusing produced water, the U.S. oil and gas sector is working towards a more sustainable future, balancing the demands of energy production with the need to protect water resources and the environment. Continued advancements in technology and regulatory frameworks will be essential in meeting the challenges of produced water management in the coming years.

Produced water characteristics changes over time and differ from geographical and geological location. These variations coupled with different regulatory requirements, economic constraints, climates, and infrastructure affect which management practices are used.

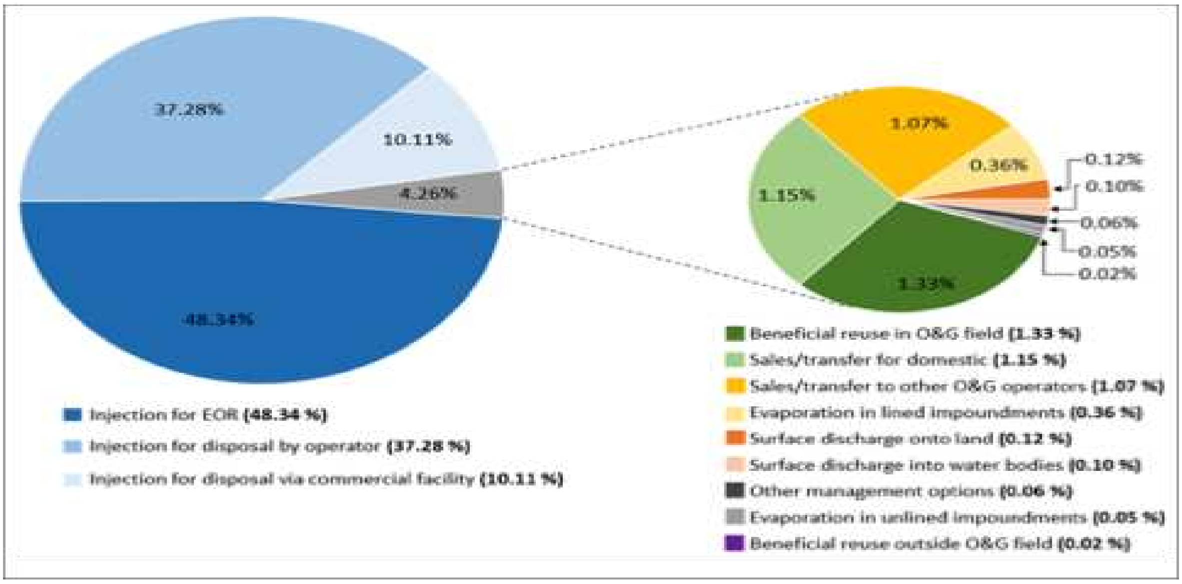


Figure 5.3 PW management in the United States in 2021. [97]

So overall in united sate there are three main method to manage the PW the first one major Pw water is re-injected for enhance oil recovery and secondly the injection for disposal by the operation the third one major part of PE used for commercial facility and finally some small amount used for other purposes.

- Beneficiale ruese in O&G 1.33%
- Sales/transfer for domestic 1.15%
- Sales/transfer for other O&G operation %
- Evaporation 0.36%
- Surface discharge into land 0.12%
- Other management operation 0.06%
- Evaporation in unlined impoundments 0.05%
- Beneficial reuse outside O&G field 0.02%

5.5- Produced water Management in Pakistan:

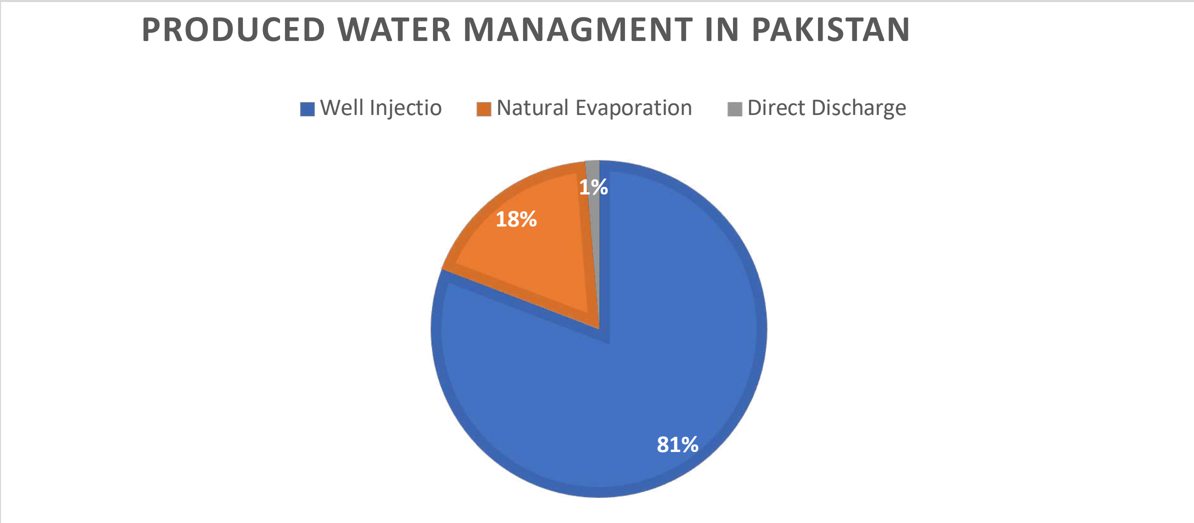
Produced water management in Pakistan is a critical issue given the country's significant oil and gas production and the overarching challenge of freshwater scarcity. With an increasing population, pollution, climate change, and inefficient water management practices exacerbating water stress, the need for effective produced water management has become paramount. The oil and gas industry, a major contributor to the country's economy, generates large volumes of produced water daily. This necessitates the development and implementation of effective strategies to handle and treat produced water to mitigate environmental impacts and conserve freshwater resources.

S.no	Company	PW Production (bbls/day)	Mode of disposal
1	MPCL	850	Well injection
2	MPCL	55	Natural Evaporation
3	PPL	2034	Well Injection
4	PPL	22	Natural Evaporation
5	OGDCL	3090	Well Injection
6	OGDCL	279	Direct-Discharge
7	ENI	600	Well injection
8	PEL	2600	Well injection
9	PEL	25	Natural evaporation
10	POL	8500	Well injection
11	MOL	3850	Natural evaporation
Totally	togather	16824	Well injection
total	togather	3952	Natural evaporation
Total	togather	279	Direct -Discharge

Table: the following table shows all Oil and gas company management /handling the Produced water in Pakistan [84-85-86-87-88-89-90-91-92-93-94]

In Pakistan, produced water is primarily managed through well injection and natural evaporation, with a small portion being discharged directly into the environment. The major oil and gas companies operating in the country, such as Mari Petroleum Company Limited (MPCL), Pakistan Petroleum Limited (PPL), Oil and Gas Development Company Limited (OGDCL), Eni, Petroleum Exploration Limited (PEL), Pakistan Oilfields Limited (POL), and MOL Pakistan, adopt various methods for produced water disposal. According to data, these companies collectively produce approximately 20,000 barrels of produced water per day, with the majority (16,824 barrels per day) being disposed of through well injection, which is a method of reinjecting the water into underground formations to maintain reservoir pressure and enhance oil recovery. Natural evaporation accounts for around 3,952 barrels per day, while a smaller amount (279 barrels per day) is directly discharged into the environment.

Figure 5.4 Pw management in Pakistan



The reinjection of produced water is a beneficial practice for the oil industry as it helps in maintaining reservoir pressure and enhancing the recovery of hydrocarbons. This method is particularly effective in oil reservoirs where the injected water can mobilize heavy hydrocarbons, thus improving the overall recovery rate. However, this practice is less beneficial for gas reservoirs as water does not contribute to the mobilization of natural gas. Well injection not only aids in resource extraction but also serves as a method of produced water disposal, minimizing the risk of surface and groundwater contamination.

In terms of environmental impact, natural evaporation and direct discharge are less favorable methods. Natural evaporation involves leaving produced water in open pits or ponds to evaporate, which can lead to soil and air contamination if not properly managed. Direct discharge, although practiced on a smaller scale, poses significant risks to surface water bodies, potentially leading to water pollution and affecting aquatic ecosystems. Thus, it is crucial for Pakistan to move towards more sustainable and environmentally friendly produced water management practices.

Opportunities for the reuse of produced water in Pakistan include its potential application in agriculture, industrial processes, and municipal water supplies. Given the country's water scarcity issues, treated produced water could be a valuable resource for irrigation, which is the largest water-consuming sector. Additionally, utilizing produced water for hydraulic fracturing in the oil sector could reduce the environmental footprint and alleviate the pressure on freshwater resources. However, the quality of produced water needs to be adequately treated to meet the requirements for these applications.

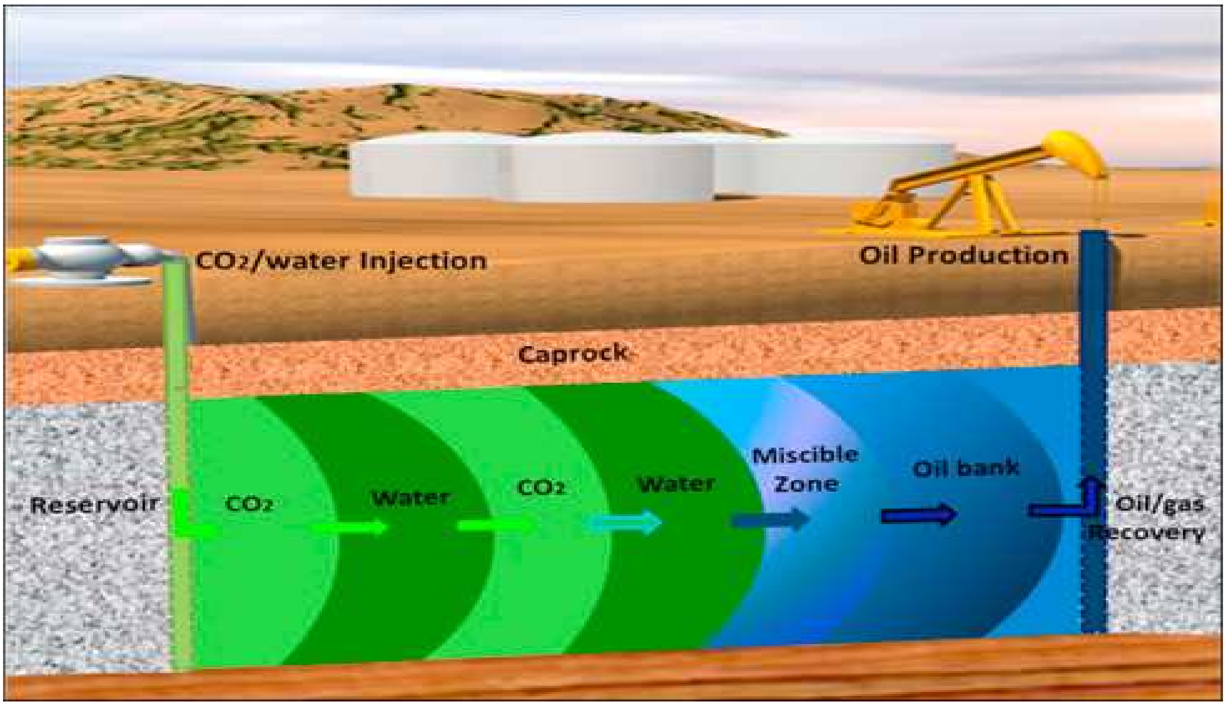


Figure 5.5 Water/CO_2 flooding process: water and CO_2 is injected into a formation to enhance oil recovery, pushing oil from injectors well to producers well.

Overall, effective produced water management is essential for Pakistan to address its water scarcity challenges and ensure sustainable oil and gas operations. The current practices of well injection, natural evaporation, and direct discharge need to be optimized to minimize environmental impacts and enhance the reuse of produced water. By adopting advanced treatment technologies and exploring alternative uses for produced water, Pakistan can mitigate the adverse effects of oil and gas production on its water resources and contribute to a more sustainable future.

5.6- Produced water management comparison between United State and Pakistan

5.6.1- Provincial Regulations:

Each province in Pakistan has its own environmental protection agency, such as the Punjab Environmental Protection Agency (EPA), Sindh EPA, Khyber Pakhtunkhwa EPA, and Baluchistan EPA. These agencies have their Owen specific regulations or guidelines pertaining to produced water management within their respective jurisdictions. But there is not particular regulation which is open to the public mostly the government make contact to company and deal with them about their specific regulation about PW.

5.6.2- Volume and Management Practices:

United States:

Managed volume of produced water closely matches the reported volume generated. Injection, primarily for enhanced oil recovery or disposal, is the dominant management method, consistently above 90% over a 15-year period. Variations in management methods influenced by factors like geographical/geological differences, regulatory requirements, economic constraints, climate, and infrastructure.

Other methods include:

- **Injection:**

Three types - enhanced recovery, operator disposal, and commercial disposal. Each method involves injecting water into specific formations for recovery or disposal.

- **Surface Discharge:**

Regulated by the EPA, permitted offshore with water quality standards met; limited onshore discharges, mainly in western states, with treatment and meeting NPDES standards.

- **Evaporation:**

Growing use, especially in warm, dry climates of western states; utilized to offset injection volumes in seismic sensitive areas.

- **Sale/Transfer**:

Introduced recently, involving voluntary actions between buyers and sellers, often not initiated by state agencies.

- **Beneficial Reuse:**

Increasing trend due to water treatment technology advancements and restrictions on disposal; includes reuse for fracking, limited agricultural irrigation during droughts, and dust/ice control on roads.

When comparing produced water (PW) management in Pakistan with the United States, significant differences arise. In the United States, stringent regulations and advanced treatment technologies are employed to manage PW. In contrast, Pakistan primarily relies on reinjection, natural evaporation, and, in some cases, direct discharge into the environment. A particularly concerning case is the Dakhni Oil Field, where direct discharge of PW into the surface poses serious threats to the environment, human health, and agriculture due to the presence of heavy metals, naturally occurring radioactive materials (NORMs), and other toxic chemicals.

6. Case study Dakhni Oil Field Punjab Province Pakistan:

The Dakhni Oil Field is a significant hydrocarbon reservoir located in the Punjab province of Pakistan. has a current population of approximately 2.17 million as of 2023. s situated in a rural area with various localities and villages nearby, including Lanewali, Dhok Loharan, and Jand.The field is not only an important industrial site but also affects the surrounding environment, which includes local wildlife and human populations

6.1 Location and Discovery

- Geographical Position: The Dakhni Oil Field is situated in the district of Attock, in the Punjab province of Pakistan. It's part of the Potwar Plateau, a region known for its geological significance and hydrocarbon potential.
- Discovery: The field was discovered in 1981 by the Oil and Gas Development Company Limited (OGDCL), Pakistan's largest petroleum exploration and production company.

6.2 Geological Features

- Reservoir Characteristics: The Dakhni Oil Field is primarily known for its carbonate reservoirs, with significant deposits found in the Eocene and Paleocene formations. The field's geological structure is a typical anticline, which is conducive to trapping hydrocarbons.
- Hydrocarbon Composition: The field produces both oil and gas. The natural gas from the Dakhni field is sour, containing a high concentration of hydrogen sulfide (H_2S) and carbon dioxide (CO_2), which requires specific processing techniques.

6.3 Production and Development

- Production Facilities: The Dakhni Oil Field is equipped with state-of-the-art facilities for the extraction and processing of oil and gas. OGDCL has implemented various technologies to optimize production and ensure safe handling of sour gas.
- Daily Output: The field's production includes thousands of barrels of oil per day and millions of cubic feet of natural gas. The exact figures can vary, but it has been a steady contributor to Pakistan's overall hydrocarbon output.

- Development History: Since its discovery, the Dakhni field has undergone several phases of development, including the drilling of multiple wells and the installation of infrastructure to support ongoing production.

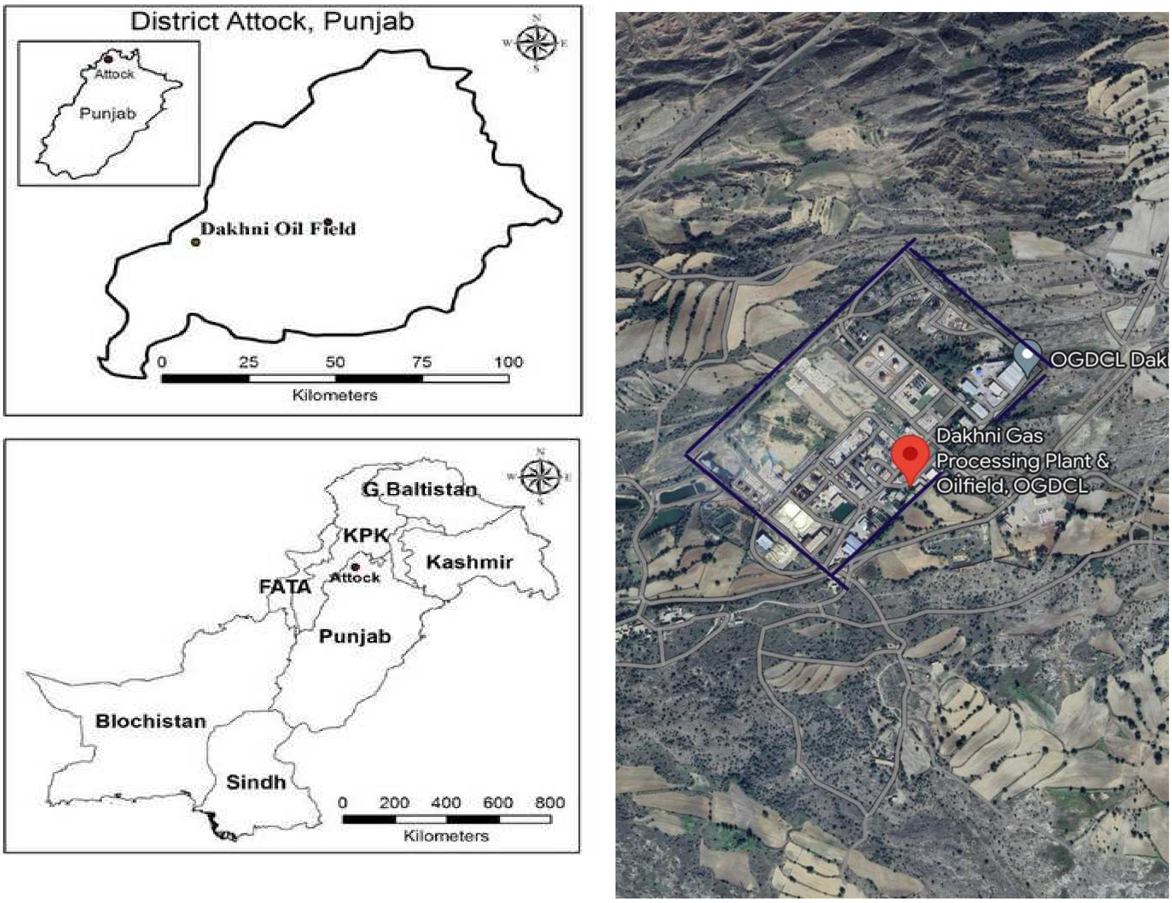


Fig.01 Map of the study area Dakhani Oil Field-Punjab, Paksiatn.

Sample location	PH	TDS	Na(mg/l)	k(mg/l)	Ca(mg/l)	Mg(mg/l)	Cr(mg/l)	F(mg/l)	Cl(mg/l)	Mn(mg/l)
Inlet	7.2	82600	1131	710	3345	260	1.3	2.9	31841.19	1.91
Inlet-A	6	47750	1452	645	6210	543	1.7	3.3	17689.55	2.66
Outlet-A	7.5	21900	1114	127.3	6544	654	1.8	1.2	12028.89	3.66
Inlet-B	6.2	26200	825	178.2	399	431	1.5	1.2	7075.82	1.19
Center-B	5.5	26300	802	165.1	396	234	1.4	1	6368.23	1.12
Outlet-B	6.3	28500	882	9.6	798	123	1.5	1.3	6368.23	1.4

Table,1. Physicochemical characterises of produced water of the study area.[65]

Data for the Chart

Parameter	Measured Range	Pak-EPA Limit	US EPA Limit
pH	5.5-7.5	6.0-9.0	6.5-8.5
TDS (mg/l)	2620-82600	3500	500
Sodium (Na) (mg/l)	802-1452	Not specified	20 (advisory)
Potassium (K) (mg/l)	9.6-710	Not specified	Not specified
Calcium (Ca) (mg/l)	396-6544	Not specified	Not specified
Magnesium (Mg) (mg/l)	123-654	Not specified	Not specified
Fluoride (F) (mg/l)	1-3.3	1.5	4
Chloride (Cl) (mg/l)	6368.23-31831.19	1000	250
Manganese (Mn) (mg/l)	1.12-3.66	0.5	0.05
Chromium (Cr) (mg/l)	1.3-1.8	0.05	0.1

Now, let's create the chart.

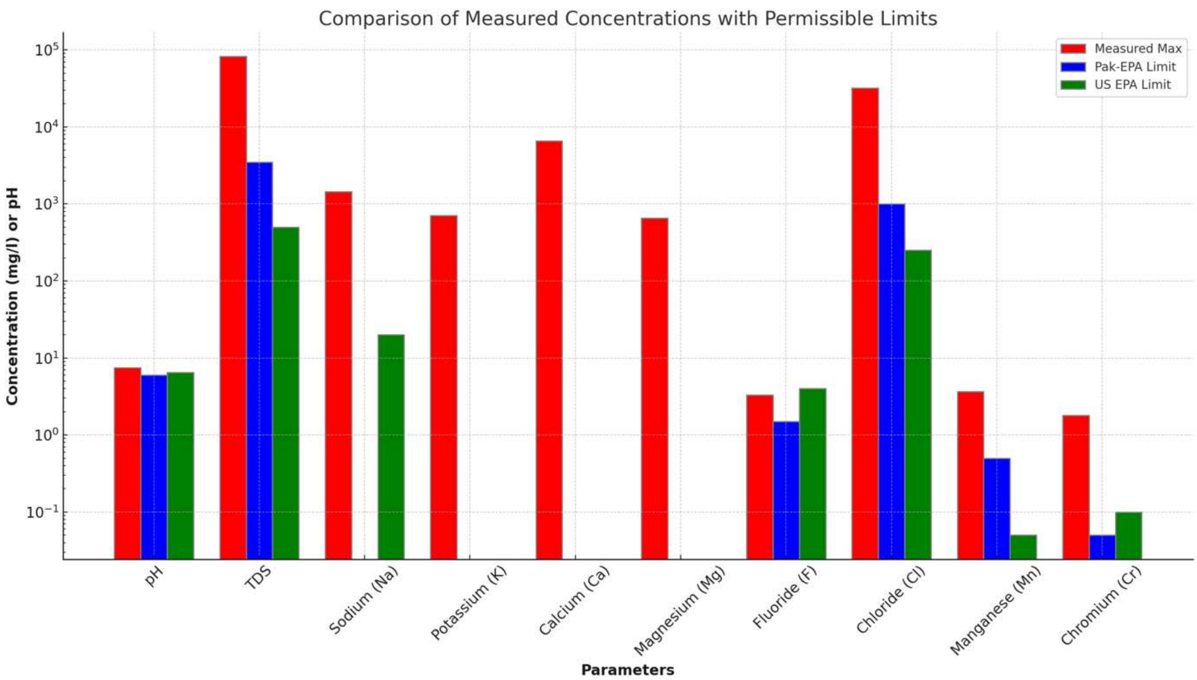


Chart-01 Here is a bar chart that visually compares the measured concentrations of various contaminants in the produced water with the permissible limits set by Pak-EPA and US EPA.

Pw samples were collected and analyze for physicochemical parameter and heavy metals concentration, so i compared the results with maximum permissible limits of Pakistan environmental protection agency, (Pak EPA), so the pH and F were with in permissible limit and results of ion analysis in produced water samples indicate that Cl values are much higher than the limits defined by Pak-EPA. Heavy metal results showed that Mn and Cr were above the permissible limit. The study concluded that untreated produced water that is discharged into surrounding area have detrimental effect on soil quality, agriculture and human health of the area and also pollute the ground water when percolates into the ground. Produced water is discharged into the surrounding area without any treatment. Environmental Protection Agency of Punjab should have regular monitoring system to check the illegal discharge of produced water into the natural streams and soil and it should be treated physically, chemically, biologically and mechanically properly before disposing off into the surrounding environment.

6.2.1 Health Risks Associated with Heavy Metals in Produced Water

Heavy metals in produced water (PW) from oil fields, such as the Dakhni Oil Field in Punjab, Pakistan, pose significant health risks due to their toxic nature. The contamination of soil and water by these metals can lead to various acute and chronic health issues for both humans and wildlife and Environment.

6.2.1 Health Risks to Local Population:

- Manganese (Mn) and Chromium (Cr) Exposure: The produced water from the Dakhni Oil Field contains concentrations of manganese and chromium that exceed permissible limits set by the Pakistan Environmental Protection Agency (Pak-EPA).
- Impact on Human Health: Chronic exposure to manganese can lead to neurological effects, including cognitive deficits and motor dysfunction. Chromium, particularly hexavalent chromium (Cr(VI)), is known to cause respiratory issues and is classified as a human carcinogen.
- Pathways of Exposure: Local communities near the oil field, such as Lanewali, Dhok Loharan, and Jand, are at risk of exposure through contaminated water sources and potentially through soil and agricultural produce irrigated with untreated produced water.

5.2.2 Environmental Impact:

- Soil and Water Quality: Untreated produced water, when discharged into the surrounding environment, adversely affects soil quality and contaminates groundwater. This pollution can persist over time, posing long-term risks to agricultural productivity and the ecosystem.
- Ecological Effects: Local wildlife and biodiversity may also suffer from the effects of heavy metal contamination, impacting ecological balance and biodiversity in the region.

6.2.3 Regulatory and Remedial Measures:

6.2.4 Monitoring and Regulation: There is a critical need for regular monitoring by the Environmental Protection Agency of Punjab to prevent illegal discharge of produced water and ensure compliance with environmental standards.

6.2.5 Treatment Requirements: Produced water must be treated effectively (physically, chemically, biologically, and mechanically) before disposal to mitigate its harmful effects on the environment and human health.

In conclusion, the case study of the Dakhni Oil Field illustrates how heavy metal contamination in produced water can lead to significant health risks for local populations and environmental degradation. It underscores the importance of stringent regulatory measures, proper wastewater management practices, and community awareness to mitigate these risks effectively.

The case study of the Dakhni Oil Field in Punjab, Pakistan highlights significant concerns regarding the contamination of produced water (PW) with heavy metals such as manganese (Mn) and chromium (Cr). While this study provides valuable insights into the adverse health and environmental impacts associated with heavy metal contamination, it also reveals a critical research gap concerning Naturally Occurring Radioactive Materials (NORMs).

7- Results:

Dakhni Oil Field, manganese (Mn) stands out as particularly beneficial to extract due to its versatile applications and economic value. Additionally, electrocoagulation offers a cost-effective and efficient solution for treating produced water, which can be tailored to address multiple contaminants simultaneously, including heavy metals like manganese.

7.1 Manganese (Mn): The Most Useful Heavy Metal to Extract (Benefits and Uses of Extracting Manganese)

7.1.1 Industrial Applications:

- Steel Manufacturing: Manganese is crucial in steel production for improving hardness, strength, and wear resistance. This makes it indispensable in the manufacturing of various steel alloys.
- Battery Production: Manganese dioxide is used in batteries, particularly in alkaline and lithium-ion batteries, which are essential for energy storage technologies. [12]

7.1.2 Economic Value:

- Market Demand: There is a consistent demand for manganese in various industries, making it a valuable commodity.
- Revenue Generation: Extracted manganese can be sold to industries or used to support local manufacturing, generating economic benefits.

7.1.3 Environmental Benefits:

- Reduction in Soil Contamination: Removing manganese from produced water helps reduce the environmental burden on soil and groundwater, preventing contamination and promoting ecological health.

7.1.4 Health and Safety:

- Mitigation of Health Risks: Reducing manganese in water minimizes potential health risks such as neurological effects and cognitive deficits associated with chronic exposure.

7.2 Extraction Method:

- Mechanism: Electrocoagulation uses an electric current to induce coagulation of suspended solids and dissolved metals. Manganese precipitates out of the solution, allowing for easy collection and further processing.

Cost: Approximately $0.10 - $0.30 per cubic meter of treated water, making it an affordable option for large-scale operations. .

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7.3 Effective Treatment Solution (Electrocoagulation)Why Electrocoagulation in Dakhani oil field case ?

7.3.1 Cost-Effectiveness:

- Low Operational Costs: With operational costs as low as $0.10 - $0.30 per cubic meter, electrocoagulation is an economical option for treating large volumes of water.
- Minimal Chemical Use: Reduces the need for chemical reagents, lowering ongoing expenses and simplifying handling and storage.

7.3.2 Efficiency in Removing Contaminants:

- Multi-Contaminant Removal: Effective in removing a range of contaminants, including heavy metals (Mn, Cr), TDS, and organics.
- High Removal Rates: Achieves high removal efficiencies for heavy metals, often exceeding 90%, which is crucial for meeting environmental discharge standards.

7.3.3 Environmental and Operational Advantages:

- Reduced Sludge Production: Produces less sludge compared to conventional chemical treatment methods, reducing disposal costs and environmental impact.
- Simple Operation: Easy to operate and maintain, requiring minimal training and infrastructure.

7.3.4 Scalability:

- Adaptable to Various Sizes: Can be scaled up or down based on the volume of produced water, making it suitable for different operational scales at the Dakhni Oil Field.

7.3.5 Local Applicability:

- Suitable for Pakistan: Electrocoagulation systems can be locally manufactured and maintained, supporting the local economy and ensuring easy access to replacement parts and expertise.

By focusing on the extraction of manganese from produced water and implementing electrocoagulation as a cost-effective treatment solution, the Dakhni Oil Field can achieve significant economic and environmental benefits. Manganese extraction not only provides valuable materials for industrial applications but also mitigates environmental and health risks. Electrocoagulation offers a practical, low-cost method to treat water, making it a suitable choice for large-scale deployment in Pakistan.

This approach not only aligns with sustainable water management practices but also contributes to local economic development and environmental protection.

8- Environmental and Health Impacts overall:

The PW discharged from Dakhni oil field contains heavy metals above the permissible limit. We don't have any study for NORMs concentration finding in the PW from this also in general form oil industry but there is high possibility to that the Pw also contain Norms, which can accumulate in the environment over time. This accumulation poses significant risks, including:

8.1- Human Health:

Chronic exposure can lead to respiratory issues, physiological disorders, endocrine disruption, and increased cancer risks (e.g., bone and sinus cancer due to radium exposure)

8.2- Wildlife and Agriculture:

Toxic substances can disrupt local ecosystems, affecting plant growth, animal health, and agricultural productivity.

8.3- Ecological Damage:

Long-term harm to the environment can arise from persistent exposure to pollutants. In animals, toxic heavy metals can lead to decreased reproductive success, issues with growth and development, and a loss of genetic diversity.

8.4- **Case Study Methodology**

To understand the full scope of the impacts, we conducted a comprehensive review of technical articles and studies from around the world. Our analysis focused on the

Overall, in this particular case we have like the heavy metal concentration abow the permissible limit so all effects related to heavy metal are applicable and for the Norms their a big research gap in Pakistan to finding norms concentration in PW but their it always high possibility that PW contain heavy metal, so I erectly suggest for

Collecting more sample and make details study to find out all possibility toxicity of pw from oil and industry in way we can remediate and safely handing pw and make clear future plan with harming human and the environment which of main concern whiling extracting oil and gas to main eco-system in way.

Chapter 6: Environmental Effects Monitoring and Research Needs

6.1 Introduction

Produced water (PW) discharged from oil and gas operations into the environment represents a complex environmental challenge. Over the past decade, significant progress has been made in understanding the composition, environmental fate, and biological effects of PW discharges. However, several unresolved questions remain, necessitating continued research and monitoring efforts. This chapter outline the key components of environmental effects monitoring, highlights current research gaps and proposes future research needs to enhance our understanding and management of PW-related risks.

6.2 Advances in Scientific Knowledge

Scientific discoveries have shed important light on the nature, fate, and consequences of PW releases. Due to the efficiency of natural dispersion processes fueled by tides and currents, the 2007 International Produced Water Conference drew attention to the modest effects of PW on specific development locations in the open ocean. Regarding the long-term ecological repercussions and possible implications on human health, the marine environment, and animals, however, doubts still exist.

6.3 Research Gap:

Currently, there is a notable absence of specific research on NORMs concentration in produced water from the oil and gas industry in Pakistan. NORMs are typically found in geological formations associated with hydrocarbon reservoirs, and their presence in produced water is well-documented globally. However, their specific concentrations and potential impacts in the context of Pakistan's oil and gas operations remain largely unexplored.

6.4 Recommendations:

Given the potential risks associated with NORMs in produced water, it is imperative to address this research gap through comprehensive studies and regulatory measures:

6.4.1 Comprehensive Studies: Conduct detailed studies to assess the concentrations of NORMs in produced water from the Dakhni Oil Field and other oil and gas operations across Pakistan. This should include sampling and analysis to determine the types and levels of NORMs present.

6.4.2 Regulatory Measures: Establish stringent regulatory frameworks and monitoring programs under the Environmental Protection Agency of Punjab to control the discharge of produced water containing NORMs. Implementing maximum permissible limits and regular inspections can help mitigate risks to human health and the environment.

6.4.3 Public Awareness and Stakeholder Engagement: Raise awareness among local communities, stakeholders, and industry personnel about the potential hazards of NORMs in produced water. Encourage collaboration between industry, government, and academia to develop sustainable practices for managing and treating produced water.

In order to resolve the remaining uncertainties and improve our comprehension and management of PW-related risks, ongoing research and monitoring activities are crucial. To give thorough knowledge on the environmental fates and impacts of low-level, chronic exposures to PW components, multidisciplinary research investigations under an ecosystem-based management strategy are required. Prioritizing research needs and encouraging stakeholder participation will help us create strategies that effectively reduce the negative environmental effects of produced water outflow and guarantee sustainable management.

In conclusion, while the current case study provides critical insights into the impacts of heavy metal contamination in produced water from the Dakhni Oil Field, the lack of research on NORMs represents a significant gap in understanding and addressing potential risks. Closing this gap through targeted research and proactive regulatory measures is essential to safeguarding human health, protecting the environment, and ensuring sustainable development in Pakistan's oil and gas industry.

Chapter 7: Results and Discussion:

Produced water (PW) discharged from oil and gas operations contains a wide range of contaminants, including hydro-carbons, heavy-metals, production chemicals, and Naturally-Occurring-Radioactive-Materials (NORMs). These constituents pose serious risks to both human health and ecosystems due to their toxicity and potential for bioaccumulation..

Produced Water Impact on Human Health

The increase in global PW volumes presents substantial risks to human health. Heavy metals and radioactive materials in PW can cause acute and chronic toxicity, affecting growth, reproductive success, and respiratory health. Naturally occurring radioactive materials (NORMs), such as radium isotopes, pose serious health risks, including genetic damage and cancer. The presence of technologically enhanced NORMs (TENORM) further exacerbates these hazards, necessitating stringent management to prevent adverse health impacts. Chronic exposure to heavy metals and NORMs has led to respiratory disorders, physiological problems, and increased cancer risks among the local population.

Heavy Metal Contamination in PW

Heavy metals in PW present significant health risks, with metals like arsenic, chromium, cadmium, nickel, copper, zinc, and lead among the most toxic pollutants. These metals can cause both acute and chronic toxicity, leading to a range of health issues such as respiratory disorders, physiological problems, and endocrine disruption. Chronic exposure to heavy metals can result in long-term health problems, including decreased fecundity, genetic diversity loss, and lower reproductive success.

Naturally Occurring Radioactive Materials (NORM) in PW

NORMs in PW, particularly radium isotopes (Ra-226, Ra-228, and Ra-224), pose serious health risks due to their radiotoxicity. These radioactive elements can cause genetic damage and various cancers, particularly bone and sinus cancers. The bioaccumulation of radium in the food chain further exacerbates these risks, highlighting the need for ecosystem and public health protection.

Health Risks Associated with NORMs

Exposure to NORMs results in both chemical and radiological toxicity, with inhalation or ingestion of radium isotopes leading to significant long-term health consequences, including cancer. Studies have shown that water contaminated with uranium or thorium can cause various diseases due to soil and water penetration. Stringent management of NORMs is essential to prevent adverse health impacts and ensure environmental sustainability.

Hazards of TENORM in PW

Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM) in PW pose carcinogenic, mutagenic, and teratogenic risks. Improper handling, storage, and transfer of contaminated TENORMs can lead to soil, rock, and water body contamination. Although the radioactivity levels in PW are generally low, the accumulation over time poses significant radiological hazards, particularly through internal exposure via ingestion or inhalation.

Case Study: Produced Water Management in the Dakhni Oil Field, Pakistan

Environmental Impact:

- Contaminants in Produced Water: Analysis of produced water samples from the Dakhni Oil Field revealed elevated levels of heavy metals (e.g., manganese and chromium) exceeding permissible limits set by Pak-EPA.
- Effects: Untreated produced water discharge adversely affects soil quality, pollutes groundwater, and poses health risks to local populations through agricultural and water sources.

Health and Environmental Impacts:

- Health Risks: Chronic exposure to manganese and chromium can lead to neurological effects and respiratory issues respectively, posing carcinogenic risks.
- Environmental Effects: Heavy metal contamination disrupts soil and water quality, impacting agricultural productivity and local biodiversity.

Research Gap and Recommendations:

- NORMs Research Gap: There is a significant research gap regarding Naturally Occurring Radioactive Materials (NORMs) in produced water in Pakistan's oil and gas operations.
- Recommendations: Urgently conduct comprehensive studies to assess NORMs concentrations and implement stringent regulatory measures to control and treat produced water before discharge.

Conclusion:

Produced water (PW) from oil and gas operations poses significant environmental and public health risks, especially in regions with inadequate regulatory frameworks and management practices. The presence of heavy metals and naturally occurring radioactive materials (NORMs) in PW threatens marine ecosystems, groundwater, soil health, and human well-being, necessitating immediate and comprehensive action, particularly where PW is discharged directly into the environment.

Our case study of the Dakhni oil field in Pakistan underscores the urgent need for improved PW management practices. Contaminants in PW from the Dakhni oil field exhibit elevated levels of heavy metals, such as manganese and chromium, exceeding the permissible limits set by the Pak-EPA. Treated PW can potentially be used for reservoir reinjection, hydraulic fracturing, and irrigation of non-edible crops, presenting both opportunities and economic challenges.

Given Pakistan's status as a water-stressed country, an effective solution for the Dakhni oil field is the treatment of PW through electrocoagulation, allowing for the extraction of manganese (Mn). Extracted Mn has significant industrial applications, including its use in steel manufacturing, where it improves hardness, strength, and wear resistance, and in battery production, particularly for alkaline and lithium-ion batteries essential for energy storage technologies.

Addressing these challenges through integrated management strategies will facilitate sustainable and responsible PW handling. This includes promoting public awareness and education to foster preventive measures and safeguard both ecological and human health in affected regions. Additionally, repurposing treated PW across various sectors in Pakistan can contribute to resource conservation and environmental sustainability.

A notable research gap exists concerning the long-term environmental effects of PW in Pakistan. Given the variability in PW composition due to geological and production method differences, further research is crucial to fully understand and address these impacts, especially the NORMs concentration, which can affect workers, residents, and the environment over the long term.

In summary, advancing PW management through stringent guidelines, innovative treatment methods, and comprehensive research is essential for ensuring a safer and more sustainable future for oil and gas-producing regions, thereby protecting the environment and public health from the harmful effects of produced water.

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