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TECHNIQUES FOR MANAGEMENT OF OILFIELD-PRODUCED  
SALINE GROUND-WATERS

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PREVIEW

**TECHNIQUES FOR MANAGEMENT OF OILFIELD-PRODUCED  
SALINE GROUND-WATERS**

**by**

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**THESIS**

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## ABSTRACT

Fresh, brackish and saline waste waters are almost always produced during the process of petroleum extraction. For many years, production and management of waste waters were of little concern and interest and disposal of produced waters was achieved simply through dumping into creeks and rivers. As U.S. oil and gas demand increased steadily in the twentieth century, the detrimental effects of surface impoundment of produced waters have accumulated. As a consequence brine disposal into underground formations became necessary. Today, the federal government and states have laws regulating the disposal of waste brines into bodies of fresh water. Now the field engineer must carefully consider various options of brine disposal in order to conform with pollution control laws.

In this study, the sources, types, constituents, and chemistry of oilfield-produced waters are introduced. Water production from oilfields in Texas is analyzed. Previous and current technologies for brine disposal throughout the U.S. is reviewed. The regulatory environment affecting brine handling is surveyed. Finally, innovative schemes for oilfield brine management are suggested.

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## Chapter 1

### INTRODUCTION

When oil is produced, from ground, large quantities of contaminated brines and waters, mixed with oil, is also produced. This brine and water, also known as produced water, is mixed in the production stream (Ostroff, 1965). In early days (prior to 1930) produced waters were dumped arbitrarily anywhere, causing an environmental problem. Today rules and regulations exist, mandated by the Environmental Protection Agency throughout the nation and by the Railroad Commission of Texas (RCT) in the state of Texas, and of major concern to engineers and scientists all over the nation is the matter of how to dispose of this produced water without causing further environmental damage. Recently, some oil producing companies in the United States, especially in California, had to cease their oil production as they could not find an effective method of disposal of produced water. Lately, a lot of oilfields in Texas, especially in West Texas, have also experienced the same problem and have urged that some research be carried out in this regard as soon as possible.

As of May 1994, there are about 55,000 oil and gas fields in Texas (RCT, 1994). These fields produce an enormous volume of undesired waste waters, requiring disposal every day. Since 1960, the RCT and the Petroleum Research Committee have been

spending large sums on numerous research activities on safe disposal of produced waters in the state of Texas.

Some research organizations, such as the Texas Energy and Natural Resources Advisory Council (TENRAC), have successfully experimented on some innovative techniques for managing oilfield produced waters, using salt-gradient solar pond technology in the oil-brine separation process. Swift and Golding have proposed that a salinity gradient solar pond may be used in oilfield waste brine reduction and hot water flood injection for secondary recovery projects (Swift, 1993). However, these innovative techniques are still in their rudimentary stages and may require some time before they may be applied commercially in oil and gas fields (Manning, 1983).

### **1.1 Sources and Types of Waters in Oilfields**

In a general way, water from different sources may be characterized according to its salinity (Muskat, 1981). Usually fresh-water is obtained from rivers, lakes, streams, or comparatively shallow water sands. Calcium, magnesium, and bicarbonate ions represent a greater percent of the dissolved ions in fresh waters than they do in waters in contact with oil. Table 1.1 shows the results of analysis of the Saskatchewan River water and an Alabama town-site water well in compare to other types of water (Ostroff, 1965). Both of these waters are extremely low in total dissolved solids (TDS) and suitable for human consumption.

TABLE 1.1 COMPOSITIONS OF SOME WATERS in mg/L (Ostroff, 1965)

Constituent	Saskth. River	Al. City Well	Sea Water	Marginulina Sand(TX)	Garner Sand(OK)
Carbonate	-	-	-	-	-
Bicarbonate	219	120	142	159	12
Sulfate	40	2	2,560	157	-
Chloride	20	11	18,980	29,573	101,479
Calcium	59	1	400	881	9,226
Magnesium	10	1	1,272	498	1,791
Na and K	30	51	10,840	17,258	46,000
Iron	0.1	0.4	0.02	135	35
Barium	-	-	-	-	127
TDS	378.1	186.4	34,194.02	46,661	158,670
pH	7.7	7.6	-	6.5	5.0

Almost all sedimentary rocks are deposited in water, one layer upon another. The water, which is deposited in sediment from the beginning, is called connate water (Drever, 1982). Connate water is a natural part of the sediments. As the sediment is buried and becomes an increasingly indurated sedimentary rock, much or all of its connate water is either altered in composition, diluted, or displaced by other waters, or expelled all together (Clarke, 1924). Since most of the



sedimentary rocks contain oil or gas, the oil or gas also displaced water that earlier occupied in the pore spaces of the sedimentary rocks. The water that the oil or gas is able to displace, is known as free water.

Much water resists displacement by invading hydrocarbons, because it occupies pore spaces too fine for the hydrocarbons to enter and may even adhere to the surfaces of the rock grains themselves. This water is known as interstitial water. The total water contained in an otherwise hydrocarbon-bearing reservoir rock is best called formation water or oilfield water (Drever, 1982).

Formation waters cause major problems in almost all the oilfields in the nation. Due to their high salinity and toxicity, most state prohibits the discharge of these waters into surface waters (RCT, 1994). A number of oil producing companies often join hands to dispose of their produced waters into one common underground formation although there is always the possibility for a midnight dumping while trucking these waters (TWC, 1989).

When pumped into water disposal wells, oilfield brines generally require some treatment in order to prevent corrosion of the disposal system or plugging of the interstices of the formation into which they are pumped (Shew, 1987).

## 1.2 Types and Constituents of Oilfield Brines

Oilfield brines may contain several times as much dissolved solids as sea water. Concentrations of 220,000 mg/L dissolved solids are not uncommon (Wiebe, 1930). Many reserve the term " Brine " for pure fluids having salinities in excess of 100,000 mg/L. However, Carpenter's classification of different types of salt water, based on the total dissolved solids (TDS), may be of interest here (Hanor, 1987).

TABLE 1.2 CLASSIFICATION OF OILFIELD WATER (Hanor, 1987)

Water Types	Total Dissolved Solids
Fresh Water	$\leq 1,000$ mg/L
Brackish Water	1,000 - 10,000 mg/L
Saline Water	10,000 - 100,000 mg/L
Brine	$\geq 100,000$ mg/L

However, for all practical purposes, oilfield brines may be considered as saline ground waters, usually 50,000 PPM of TDS (Giuliano, 1983). In general, brines contain high concentrations of chloride, arsenic, sulfate, sodium, and other constituents that are collected beneath the salt-waste storage pile with total dissolved solids levels up to 158,600 mg/L (Allu, 1992).

Some oilfield brines may associate with toxic chemicals, such as lead and barium. These brines, if disposed of arbitrarily, might cause hazardous effects on plants, fish, and other animals. Table 1.3 shows the typical composition of an oilfield brine (TWC, 1989). Determination of brine compositions of an oilfield is essential for its brine disposal system.

**TABLE 1.3 TYPICAL COMPOSITIONS OF OILFIELD BRINE (TWC, 1989)**

<b>ELEMENT</b>	<b>RANGE, PPM</b>	
Sodium	12,000	- 150,000
Potassium	30	- 4,000
Lithium	1	- 50
Rubidium	0.1	- 7
Cesium	0.01	- 3
Calcium	1,000	- 120,000
Magnesium	500	- 25,000
Strontium	5	- 5,000
Barium	0	- 1,000
Chloride	20,000	- 250,000
	(50,000 average)	
Bromine	50	- 5,000
Iodine	1	- 300

In addition to the elements listed in Table 1.3, there are other potential ground water contaminants which are inherent in oil and gas exploration and development activities. These include oil and gas, drilling fluids, chemicals used in treating wells, other additives, and corrosion inhibitors (Shew, 1987). Various additive chemicals, such as barium sulfate, are found in drilling fluids. Numerous acids are used in fracturing producing zones to improve permeability. These include hydrochloric, nitric, sulfuric, hydrofluoric, formic, and acetic (TWC, 1989). Corrosive inhibitors contain arsenic compounds. Certain oils contain mercury in concentrations exceeding the recommended standards set for potable water. Gases often contain hydrogen sulfide which may give ground water the odor of rotten eggs (Allu, 1992). Brines also contain (Table 1.3) an average chloride content of 50,000 PPM. Other brines contain toxic chemicals, such as lead and barium. All the above constituents have the potential to contaminate ground water when spilled on the surface, or if they leak to ground water, or if they move into fresh-water aquifers via inter-aquifer exchange.

### **1.3 Chemistry of Oilfield Waters**

The nature and quantity of the formation waters in an oil- or gas-bearing region are vital concerns to both exploration and exploitation of the region. Normal sea water contains about 3.5% of dissolved mineral matter, approximately

35,000 ppm (Enright, 1963). About 90% of this is sodium chloride.

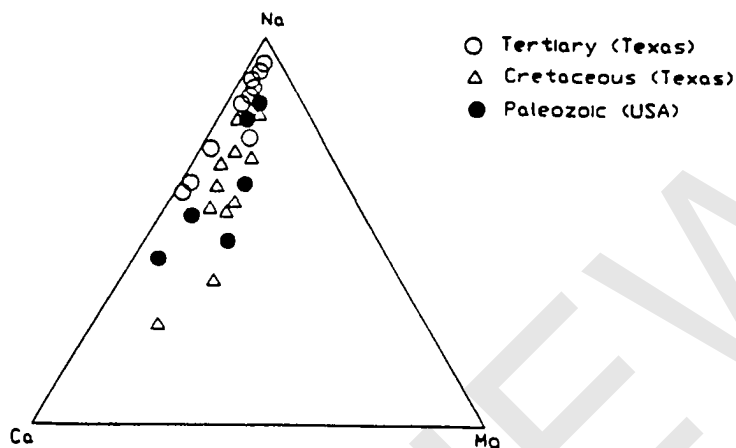
Many oilfield waters contain much more mineral matter in solution than this, up to 300,000 PPM or even more (North, 1987). The strongest brines occur in undeformed or little deformed basins like those overlying the stable interiors of shields, especially if the stratigraphic successions include evaporite formations. Waters in such basins not only become naturally concentrated with time, but also they are protected from dilution by meteoric waters entering the aquifers from the outcrop. In contrast, basins in which the reservoir rocks are close to the outcrop, or are strongly faulted, are characterized by oilfield waters deficient salinity. Dilution by invading waters reduces the mineral content to 1% or less. Generally, oilfield waters are classified according to the dominant mineral ions present in the solution. A widely used classification is that proposed by the Russian geochemist, V. Sulin, distinguishing four chemical types of water according to the distribution of three cations and three anions (North, 1987). These classifications are furnished in the Table 1.4.

TABLE 1.4 WATER CLASSIFICATION BASED ON IONS (NORTH, 1987)

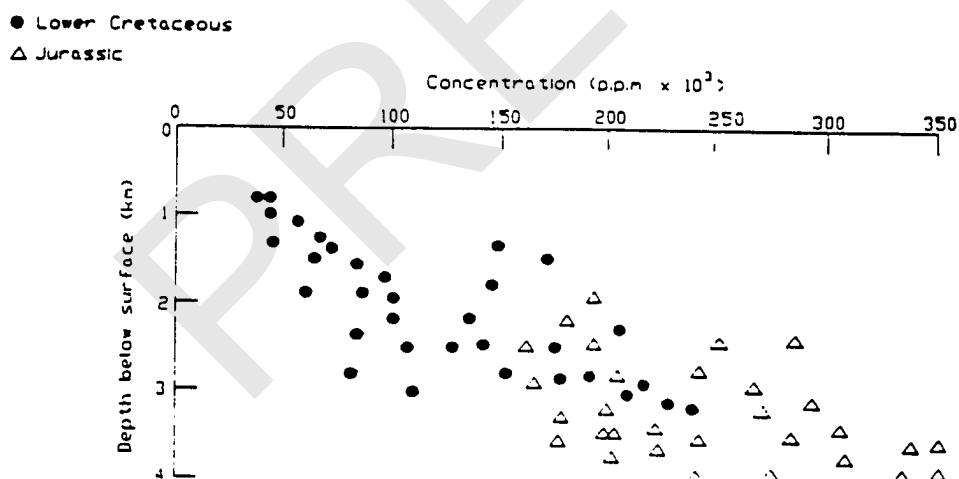
TYPE	ANION	CATION
A	sulfate	sodium waters
B	bicarbonate	sodium waters
C	chloride	magnesium waters
D	chloride	calcium waters

Type C and D also contain sodium to some extent. Most oilfield waters, including all typical " brines " fall into type D; sodium dominates the cations, but both magnesium and calcium are present in addition, the Ca : Mg ratio being about 5 : 1 (Figure 1.1). Chloride is almost the sole anion. Sulfate is notably absent.

Type C water takes the place of type D in many evaporite-bearing sequences. In both types, the concentrations of dissolved material tends to increase linearly with depth, in some basins of cratonic type as much as 10-15% per kilometer (Figure 1.2). This phenomenon, recognized since the early days of oil development, is probably due to reverse osmosis (Drever, 1982).



**Figure 1.1 Relative Amounts of Cations in typical concentrated Oilfield Brines of Connate type (Source: North, 1987).**



**Figure 1.2 Concentration of Oilfield Waters vs Depth in Lower Cretaceous and Jurassic Strata of the U.S. Gulf Coast Basin (Source: North, 1987).**

As water is expelled upwards through shales and other rocks impermeable to oils, the oil and the salt remain in the aquifer below, and this therefore becomes the reservoir formation for the oil (North, 1987). The water in the pore spaces of the shale, in contrast, acquires higher concentrations of sulfate and bicarbonate and lower concentrations of chloride. The solubility of salt increases with increasing temperature and pressure and so with increasing depth. Ultimately there must be a decrease in salinity with depth, as compaction releases the last water absorbed on clay mineral surfaces.

Water types A and B occur in near-surface artesian conditions (Figure 1.3). Bicarbonate is the dominant anion in meteoric waters. Waters containing it and/or sulfate are oxygen-bearing and very subsaline, in some basins almost fresh (North, 1987). Oils associated with them become oxidized, and the presence of sulfate, as in some of the much faulted Rocky Mountain basins of the western U.S.A. Combination of water types occur in basins in which shallow reservoirs, close to outcrop, are separated by unconformities from deeper reservoirs isolated from the outcrop.