1

FUNDAMENTALS OF CHEMISTRY

In order to deal intelligently with water systems and their problems one must be aware of the basic chemistry applying to water. This chapter summarizes pertinent fundamentals.

ELEMENTS AND COMPOUNDS

Matter is made up of elements and compounds. ***Elements*** are substances that can not be chemically decomposed to give two or more simpler substances. The names of elements are usually abbreviated in order to simplify chemical notations. For example:

TABLE 1.1

Examples of Chemical Symbols

Element	Chemical Symbol
Hydrogen	H
Calcium	Ca
Oxygen	O

A partial list of the 103 elements which have been discovered thus far is given in Appendix 1. This table contains certain other information in addition to the standard chemical symbols.(1.1)

A ***compound*** is a substance composed of two or more elements chemically combined in definite proportions by weight. The individual elements have lost their identity and no longer are recognizable unless you chemically separate the compound into its constituent elements.

For example, water (H_2O) is composed of hydrogen and oxygen, but you recognize water as a unique substance with its own peculiar properties. We seldom stop to consider that water is made up of hydrogen and oxygen. If you hold up a glass of water you certainly do not see hydrogen and oxygen. You see a clear liquid compound which we call water.

MIXTURES

A ***mixture*** is made up of two or more substances which retain their own properties. Thus, if you mix salt and pepper you can (with some effort) physically separate the two materials because you can readily identify them as individual species. Salt and pepper are both compounds. Salt (NaCl) is composed of sodium (Na) and chlorine (Cl), which are both elements.

ATOMS AND ATOMIC WEIGHTS

The fact that elements combine in fixed ratios by weight suggests that elements are made up of particles or pieces of matter. These units of matter, which are called ***atoms***, may be defined as the smallest particle of an element which can enter into chemical change.

Atoms are composed of ***electrons***, ***protons*** and ***neutrons***. The electrons and protons are charged particles and the mass of the atom is due almost entirely to the protons and neutrons in the nucleus. Electrons have negligible mass and are usually disregarded when calculating the mass of an atom. Their properties are summarized in Table 1.2.

TABLE 1.2

Properties of Subatomic Particles

Particle	Mass (Atomic Mass Units)	Electrical Charge
Electron	0.00055	–1
Proton	1.0	+1
Neutron	1.0	0

The ***atomic weight*** of each element is simply a way of comparing the mass of the atoms of that element with the mass of an arbitrary standard, the carbon atom. A scale of relative atomic weights based on the atomic mass unit (amu) has been established by the scientific community. The amu is defined as exactly 1/12 of the mass of an atom of carbon-12, which is a carbon atom with an atomic weight of 12.0000.

On this scale, the atomic weight of hydrogen (H) is 1.0 amu, that of helium (He) is 2.0 amu, and that of magnesium (Mg) is 24.3 amu. This tells us that He atoms have twice the mass of H atoms, while Mg atoms are about 24 times heavier than H atoms.

Figure 1.1 shows an idealized arrangement of the protons, neutrons and electrons in these atoms. The protons and neutrons reside in the nucleus, with electrons orbiting about the nucleus like a tiny solar system.

Appendix 1 gives the atomic weight of selected elements. Atomic weights are normally given to four decimal places, but they are rounded off to one decimal place for convenience in chemical calculations. This is sufficiently accurate for most purposes.

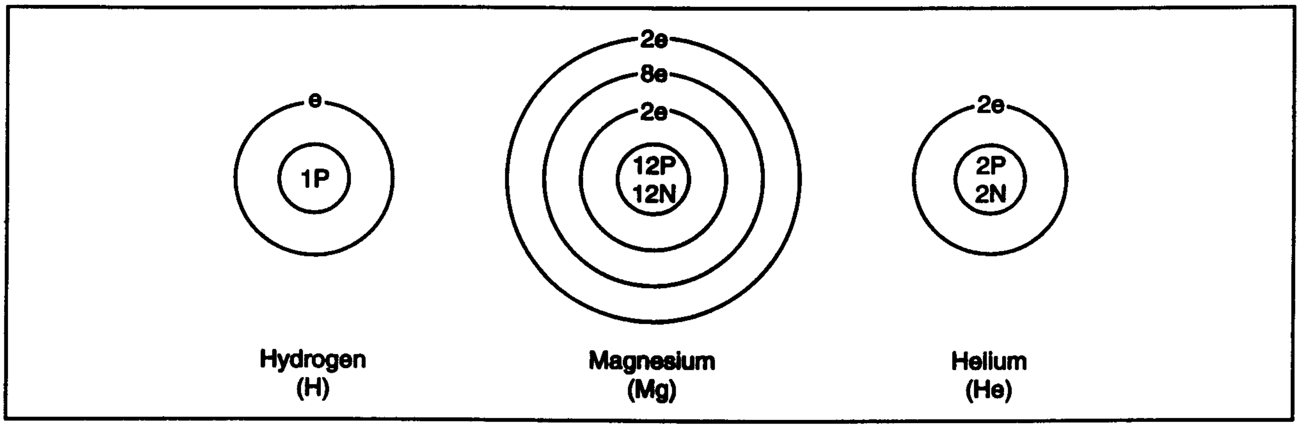

Figure 1.1 Hydrogen, Magnesium and Helium Atoms

Isotopes

As previously stated, electrons have a negligible weight as compared to protons and neutrons. Since protons and neutrons have unit mass, it follows that the atomic weights of atoms should be whole numbers if we neglect the very small mass due to the electrons. An examination of the atomic weights given in Appendix 1 shows that many of the elements have atomic weights which deviate considerably from whole numbers. For example, chlorine has an atomic weight of 35.5 and iron an atomic weight of 55.8.

Careful study has shown that most elements are actually mixtures of two or more forms of the element. Chlorine, for example, has been found to be made up of two kinds of chlorine, one of which has an atomic weight of 35 and the other of 37. In ordinary chlorine these two species are mixed in such a proportion as to give the average atomic weight of 35.5. The two kinds of chlorine have the same chemical properties but the mass of their atoms is different. They both have 17 electrons and 17 protons.

However, the atom of atomic weight 35 has 18 neutrons while the atom of atomic weight 37 contains 20 neutrons. In reality we have the same element, chlorine, in both instances. Elements with the same number of protons but different atomic weights are called ***isotopes***. Thus, ordinary chlorine is a mixture of two isotopes. Many other elements are also mixtures of isotopes, so their atomic weights are actually average weights based on the mixture of isotopes which normally exist in the naturally occurring element.

MOLECULES AND MOLECULAR WEIGHTS

Atoms combine to form ***molecules***, which can be defined as the smallest particle of a compound which can exist. Thus, atoms have the same relation to elements as molecules have to compounds.

A molecule of a compound is formed by the union of two or more atoms of the elements of which the compound is composed. The ***molecular weight*** (or formula weight) is the relative mass of a single molecule compared to the mass of the carbon-12 atom. Molecular weight is found by adding the atomic weights of the elements which form the molecule. An example calculation is shown in Table 1.3.

TABLE 1.3

Calculation of Molecular Weight

Compound	Constituent Elements	Number of Atoms	Atomic Weight	Wt. of Element Present
H_2O	H	2	1	2 amu
	O	1	16	16 amu
			Molecular Weight of H_2O = Total =	18 amu

Molecular weights, like atomic weights, are also relative weights. A molecular weight of 18 means that one molecule of water is 18 ÷ 12, or 1.5 times as heavy as one atom of carbon.

Another example: The chemical formula for sulfuric acid is H_2SO_4, which means that it contains 2 atoms of hydrogen, 1 atom of sulfur and 4 atoms of oxygen. Therefore, its molecular weight is:

$$(2\times1)+32+(4\times16)=98$$

Thus, a mole of H_2SO_4 contains 98 units of mass, of which two are hydrogen, 32 are sulfur and 64 are oxygen.

It should be noted that the traditional terms ***atomic weight*** and ***molecular weight*** are used herein even though they have been replaced by the terms ***relative atomic mass*** and ***relative molecular mass*** in the SI metric system of units.

The Mole

Attempts to measure the mass of an individual atom didn't work out too well because atoms are far too small to be seen or weighed individually; the smallest bit of matter that can be reliably measured contains an enormous number of atoms. We deal with large numbers of atoms in real situations, and a unit called the mole has been adopted as a standard unit of measurement.

A mole is defined as the amount of substance that contains as many ***elementary entities*** (atoms, molecules, or other particles) as there are atoms in 0.012 kg (12 g) of pure carbon-12 isotope. It is a fundamental SI unit and is abbreviated "mol" for use in equations.

$$1\,mol = 6.02 \times 10^{23}\,particles$$

According to this definition, one mole refers to 6.02×10^{23} "elementary entities" whose identities must be specified. We could have a mole of atoms or a mole of molecules (or a mole of ions, electrons, or other particles). For that matter we could have a mole of Lincoln Town Cars or BMW's.

The mass of one mole of atoms of a pure element is numerically equal to the atomic weight of that element (in amu's), expressed in grams. For example, 1 mole of elemental sodium contains 6.02×10^{23} sodium atoms and has a mass of 23.0 grams.

Similarly, one mole of ions contains 6.02×10^{23} ions, and this number of ions has a mass equal to the atomic or formula mass expressed in grams. Hence, one mole of Mg^{++} contains 6.02×10^{23} magnesium ions, and has a mass of 24.3 grams.

Another example: If you obtain a sample of pure gold, which has an atomic weight of 197 amu, and weigh out 197 grams, you will have one mole of gold, which contains 6.02×10^{23} atoms of gold. Thus, one atom of gold weighs:

$$\frac{197g}{6.02 \times 10^{23}} = 3.27 \times 10^{-23} g$$

which is 0.0000000000000000000000327 grams, an extremely small number!

When dealing with gases, you have to be careful, since some gases exist as atoms while others exist as molecules containing two atoms. Helium exists as discrete He atoms, so one mole of helium consists of 6.02×10^{23} atoms, and has a mass of 2.0 grams. Oxygen commonly exists as O_2 molecules (containing two atoms of oxygen), so one mole of oxygen has a mass of 32.0 grams contains 6.02×10^{23} molecules. This concept is further illustrated in Table 1.4.

Unless otherwise stated, the mass contained in a mole is expressed in grams. However, moles can also be expressed in other units, such as pounds, tons, or kilograms for the sake of convenience.

TABLE 1.4

Mass of One Mole of Atoms of Some Common Elements

Element	Sample Mass	Contains
Carbon	12.0 g of C	6.02×10^{23} or 1 mole of C atoms
Calcium	40.0 g of Ca	6.02×10^{23} Ca atoms or 1 mole of Ca atoms
Hydrogen	1.0 g of H_2	6.02×10^{23} H atoms or 1 mole of H atoms = 3.011×10^{23} H_2 molecules or 0.5 mole of H_2 molecules
Nitrogen	14.0 g of N_2	6.02×10^{23} N atoms or 1 mole of N atoms = 3.011×10^{23} N_2 molecules or 0.5 mole of N_2 molecules
Sulfur	32.0 g of S_8	6.02×10^{23} S atoms or 1 mole of S atoms = 0.753×10^{23} S_8 molecules or 0.125 mole of S_8 molecules

Using carbon as an example:

- 1 mol C = 12 g
- 1 lb-mole C = 12 lb. 12 lb = 5448 g which equals 454 g-mol
- 1 ton-mole C = 12 tons. 12 tons = 24000 lb which is 2000 lb-mol or 908000 g-mol

Although grams are convenient for a laboratory chemist, we often use larger units in industrial process calculations because of the large quantities involved.

IONS AND VALENCE

As previously stated, atoms are made up of protons, neutrons, and electrons. Each atom has an equal number of protons and electrons, so their charges balance out and the net charge is zero. If, however, an atom should lose or gain electrons, an imbalance in charge will result since the number of protons in the nucleus stays constant. Therefore, if an atom gains electrons it will have a net negative charge. If it loses electrons it will have a net positive charge. Whenever this happens, the atom is no longer called an atom. It becomes an ***ion*** which may be defined as an atom or group of atoms containing an electric charge. A positively charged ion is called a ***cation*** while a negatively charged ion is called an ***anion***.

The amount of charge is called the ***valence*** and is a measure of the element's chemical combining power. When hydrogen ionizes it loses its electron and has a net positive charge or valence of +1.

$$H - e \rightarrow H^+$$

Calcium ionizes by losing 2 electrons and thus the calcium ion has a valence of +2.

$$Ca - 2e \rightarrow Ca^{++}$$

Chlorine ionizes by gaining 1 electron and the chlorine ion has a valence of –1.

$$Cl + e \rightarrow Cl^-$$

Hydrogen is taken as the standard with a valence of +1. Any atom or group of atoms that combines with hydrogen on a one-to-one basis will also have a valence of one. The formula of hydrochloric acid, HCl, tells us that one atom of hydrogen combines with one atom of chlorine. Thus the valence of chlorine is also one; although it is a negative 1 (–1). The sum of the valences must be zero since compounds have a net charge of zero.

$$H^{+} + Cl^{-} \rightarrow HCl$$
$$(+1) + (-1) = 0$$

Similarly, for table salt:

$$Na^{+} + Cl^{-} \rightarrow NaCl$$
$$(+1) + (-1) = 0$$

Radicals

A ***radical*** is a group of atoms found in certain compounds which reacts as a unit, i.e., as if it were a single atom or ion. The radicals in the compounds following are enclosed in parentheses. Each radical shown has a valence of –2.

$H_2(SO_4)$	$Ca(CO_3)$	$Ba(SO_4)$
Sulfuric Acid	Calcium Carbonate	Barium Sulfate

If these compounds were ionized we would find that the radicals behave as polyatomic anions:

$SO_4^{=}$	$CO_3^{=}$
Sulfate ion	Carbonate ion

EQUIVALENT WEIGHTS

When elements combine to form a given compound they do so in a fixed and invariable ratio by weight. This ratio can be predicted by means of equivalent weights. For an ***element*** or ***ion***:

$$Equivalent\ Weight = \frac{Atomic\ Weight}{Valence} \tag{1.1}$$

Since equivalent weights are positive, the equivalent weight of an anion is calculated by dividing the atomic weight by the absolute value of the valence.

It should be remembered that an atom of an element exhibits no charge. Therefore, the valence of an element is actually the charge it exhibits when it is ionized.

Some elements, such as iron, have more than one equivalent weight because it can exist in more than one valence state. For example, iron has two different equivalent weights because it can exist as either ferrous ions (Fe^{++}) or ferric ions (Fe^{+++}).

The equivalent weight of a ***compound*** is:

$$Equivalent\ Weight = \frac{Molecular\ Weight}{Net\ Positive\ Valence} \tag{1.2}$$

A compound has no charge. The net positive valence of a compound is the total number of positive charges that would result if the compound were ionized in an aqueous solution.

Example 1.1: Determine the net positive valence of the following compounds: NaCl, K_2CO_3, $CaSO_4$ and $Fe_2(SO_4)_3$.

To determine the net positive charge, first write down the formulas of the compounds. Then assume that the compound has ionized in water. Split the cations from the anions as follows:

$$Na^+ \,\big|\, Cl^- \qquad (K^+)_2 \,\big|\, CO_3^= \qquad Ca^{++} \,\big|\, SO_4^= \qquad (Fe^{+++})_2 \,\big|\, (SO_4^=)_3$$

Then consider the positive (left) part of the formula. Multiply the valence of the positive part times the number of ions to obtain the net positive valence.

$Na^+ \mid Cl^-$	$2K^+ \mid CO_3^=$	$Ca^{++} \mid SO_4^=$	$2Fe^{+++} \mid 3SO_4^=$
$1 \times 1 = 2$	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 \times 3 = 6$

Net Positive Valence = Valence of positive element multiplied by the number of ions

Using Equivalent Weights

One of the main uses of equivalent weights is to permit us to easily determine the quantity of reactants and products in a chemical reaction.

If two elements, A and B, combine to form compound C, they will do so on an equivalent basis. One equivalent of A will combine with one equivalent of B to form one equivalent of C.

For example:

$$1\ \text{Equivalent Weight } Ca^{++} + 1\ \text{Equivalent Weight } CO_3^= = 1\ \text{Equivalent Weight } CaCO_3$$

$$20 \quad + \quad 30 \quad = \quad 50$$

Similarly, for ferric chloride:

	Fe^{+++}	$+\ 3Cl^-$	$= FeCl_3$
Weight Reacting:	56	+ 3(35.5) =	162.5
Equivalent Wt.:	18.7	35.5	54.2
No. of Equivalents:	3	3	3

We see that one atomic weight of iron has combined with three atomic weights of chlorine to give one mole of $FeCl_3$. More important, however, 3 equivalents of iron have combined with 3 equivalents of chlorine to give 3 equivalents of ferric chloride. Equivalents always combine on a one-to-one basis. That is the reason we use them.

Some examples of equivalent weights are given in Table 1.5.

A more complete list of equivalent weights of selected ions and compounds is given in Appendix 2.

TABLE 1.5

Equivalent Weights

Element, Ion or Compound	Atomic or Molecular Weight	Valence	Equivalent Weight
H	1	+1	1
O	16	–2	8
$CO_3^=$	60	–2	30
$SO_4^=$	96	–2	48
Ca^{++}	40	+2	20
Fe^{++} (Ferrous ion)	56	+2	28
Fe^{+++} (Ferric ion)	56	+3	18.7
$CaCO_3$	100	+2*	50
HCl	36.5	+1*	36.5
Cl	35.5	–1	35.5

* The compound itself has no valence. This is the total valence of the cations if the compound were ionized in an aqueous solution.

ACIDS, BASES AND SALTS

Acids

An acid is any substance that is capable of giving up hydrogen ions. Acids neutralize bases to yield salts and water, and they ionize or dissociate in water. The ionization of nitric acid in water is given as follows:

$$HNO_3 \rightarrow H^+ + NO_3^-$$

Some common acids are listed in Table 1.6.

TABLE 1.6

Common Acids

Acid	Symbol
Hydrochloric	HCl
Carbonic	H_2CO_3
Sulfuric	H_2SO_4
Nitric	HNO_3
Phosphoric	H_3PO_4

Bases

Bases are substances which accept hydrogen ions in a chemical reaction. A base is commonly defined as being a substance that dissociates when dissolved in water to yield hydroxyl ions. For example:

$$\underset{\text{Sodium Hydroxide}}{NaOH} \rightarrow \underset{\text{Sodium ion}}{Na^+} + \underset{\text{Hydroxyl ion}}{OH^-}$$

Salts

A salt is an ionic compound containing a positive ion other than the hydrogen ion and a negative ion other than the hydroxyl or the oxide ion.

SOLUTIONS

Solutions are homogeneous mixtures of two or more substances. They are like compounds in that they are homogeneous and like mixtures in that the relative proportions of the constituents are variable.

A solution is formed when sugar is dissolved in water. It is perfectly uniform or homogeneous; if we should taste samples taken from various parts of the solution, we would find that each part has the same degree of sweetness. The amount of sugar we can dissolve in 100 milliliters of water is variable; we may dissolve one gram, ten grams, or sixty grams of sugar in the water. There is a limit, though, to the amount of sugar we can dissolve in a given amount of water at a certain temperature. This limiting amount is termed the ***solubility*** of sugar in water at that temperature.

TABLE 1.7

Properties of Mixtures, Solutions and Compounds

Mixtures	Solutions	Compounds
Not always homogeneous	Homogeneous	Homogeneous
Variable proportions of constituents	Variable proportions of constituents	Fixed proportions of elements

The dissolved material in a solution (in this case sugar) is called the ***solute***. The water is the dissolving medium in this particular example and is called the ***solvent***. Likewise, if we dissolve salt in water, we create a solution called ***brine*** — salt is the solute and water is the solvent.

It should be realized that there are several types of solutions which may be formed when different materials are added to water.

The dissolving of sugar in water is an illustration of a solution where the individual solute molecules disperse themselves uniformly throughout the solvent. The solid sugar is said to be ***molecularly dispersed***.

Most of the materials of interest to us in water chemistry are materials which ***ionize*** when added to water. Thus when table salt is added to distilled water, the solid crystals of NaCl dissolve and break up into sodium (Na^+) and chloride (Cl^-) ions.

Most water contains considerable quantities of different dissolved impurities which exist as ions. Thus, a water analysis is really just a list of the types and amounts of the different ions which are present in the water of interest. Remember ... pure water contains only hydrogen and oxygen.

One other very important type of solution in industrial water chemistry is one where a gas is dissolved in water. The three gases of greatest interest in the oilfield are oxygen, carbon dioxide, and hydrogen sulfide. The primary problem associated with these gases is that they tend to make the water more corrosive. Thus, we are usually quite interested in knowing the amount of dissolved gases, as well as the amount of other impurities, present in a given water sample.

Oxygen dissolves in water as an oxygen molecule, O_2. Carbon dioxide (CO_2) and hydrogen sulfide (H_2S) partially ionize when they dissolve in water, resulting in a mixture of dissolved gas molecules and ions.

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$$

$$H_2S + H_2O \rightarrow H^+ + HS^- + H_2S$$

The relative amounts of CO_2 and HCO_3^-, or H_2S and HS^- in the water are dictated by the pH of the water.

Carbon dioxide (CO_2) and hydrogen sulfide (H_2S) are also known as ***acid gases*** because they create hydrogen ions (H^+) when they dissolve in water, thus making the water more acid.

Methods of Expressing Concentrations

When discussing solutions it is necessary to define the quantity of the different solutes present in the solvent. The amount of solute present is expressed as some fraction of the amount of solvent or total solution. It is called the ***concentration*** and may be expressed in a number of ways.

Weight of Solute per Volume of Solution

Most solutes in water are present in rather small quantities and so concentrations are usually expressed in milligrams of solute per liter of solution (mg/L).

Parts per Million

A dimensionless concentration term which expresses the number of unit weights of solute per million unit weights of solution (ppm).

One ppm is equivalent to 1.0 mg of solute per 1 000 000 mg (1000 g) of solution.

$$ppm = \frac{mg/L}{S.G.} \qquad (1.3)$$

Where: S.G. = specific gravity (relative density)

Molarity

A one molar solution contains one gram-molecular weight of solute in a liter of solution. The molecular weight of table salt (NaCl) is 58.4 g. A one molar solution of table salt in water contains 58.4 grams of NaCl per liter of solution.

$$\frac{Moles}{Liter} = \frac{mg/L}{1000 \times MW} \qquad (1.4)$$

Where: MW = g-molecular wt

Molality

A one molal solution contains one gram-molecular weight of solute in 1000 g (1.0 kg) of solvent. A one molal solution of table salt contains 58.4 g of NaCl in 1000 g of water.

$$Molality = \frac{Moles}{1000gH_2O} = \frac{mg/L}{1000(1000 \times S.G.-TDS \div 1000)} \qquad (1.5)$$

Where:

TDS = Total dissolved solids (See Chapter 2.)
S.G. = Specific gravity (relative density).

Normality

A one normal solution contains one gram equivalent weight of solute in a liter of solution. Since the molecular weight and the equivalent weight of table salt are the same, a one normal solution is the same as a one molar solution. It contains 58.4 grams of salt per liter of solution. If the solute were sulfuric acid (H_2SO_4), however, a one normal solution would contain 49 g of H_2SO_4 per liter of solution. This results from the fact that the molecular weight of H_2SO_4 is 98 and its equivalent weight is 98 ÷ 2 = 49. In this case a one-molar solution would contain one gram molecular weight of H_2SO_4 (98 g), while a one-normal solution would contain one gram-equivalent weight (49 g).

Standard Solutions

Standard solutions are simply solutions of known composition.

pH

The pH of a water is the logarithm of the reciprocal of the hydrogen ion concentration expressed in moles per liter.

$$pH = \cancel{\frac{1}{[H^+]}} \qquad pH = \log \frac{1}{[H^+]} \qquad (1.6)$$

It is also a number between 0 and 14, indicating the degree of acidity or alkalinity. The pH scale is similar to that of a thermometer. Just as a thermometer measures heat intensity, the magnitude of the pH indicates the intensity of acidity or alkalinity.

The midpoint of the pH scale is 7; a solution with this pH is neutral. Numbers below 7 denote acidity; those above alkalinity. Since pH is a logarithmic function, solutions having a pH of 6.0, 5.0, and 4.0 are 10, 100 and 1000 times more acid than one with a pH of 7.0. Just remember that hydrogen ions (H^+) make a solution acid and therefore force the pH toward zero. Hydroxyl ions (OH^-) make a solution basic or alkaline and push the pH upward.

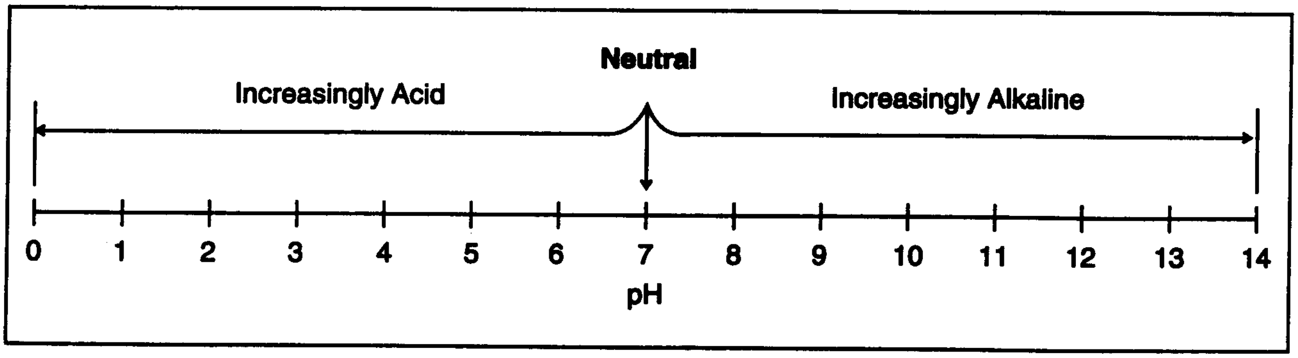

Figure 1.2 pH Scale

SYSTEM OF MEASUREMENT

Chemical calculations traditionally have used the metric system because it is relatively simple; all measures are expressed in multiples of ten. However, several years ago the international scientific community switched from traditional metric to the Systeme Internationale, or SI metric. The basic units are given in Table 1.8.

TABLE 1.8

Basic SI Units

Quantity	Traditional Metric	SI Metric
Mass	gram (g)	kilogram (kg)
Length	centimeter (cm)	meter (m)
Time	second (s)	second (s)
Volume	cubic centimeter (cm^3) or liter (L)	cubic meter (m^3)

There also is a clarification of the words "weight" and "mass" which have been used traditionally as synonyms (incorrectly). In addition, there is clarification of the term "mole," expressed in symbol form as "mol," as noted in a previous section.

Prefixes

A system of prefixes is used to denote the size of a unit as shown in Table 1.9.

TABLE 1.9

SI Prefixes

Multiplication Factor	SI Prefix	SI Prefix Symbol	Meaning (USA)	Meaning (Some Other Countries)
1 000 000 000 000 000 000 = 10^{18}	exa	E	one quintillion times	trillion
1 000 000 000 000 000 = 10^{15}	peta	P	one quadrillion times	thousand billion
1 000 000 000 000 = 10^{12}	tera	T	one trillion times	milliard
1 000 000 000 = 10^9	giga	G	one billion times	
1 000 000 = 10^6	mega	M	one million times	
1 000 = 10^3	kilo	k	one thousand times	
100 = 10^2	hecto	h	one hundred times	
10 = 10	deka	da	ten times	
0.1= 10^{-1}	deci	d	one tenth of	
0.01= 10^{-2}	centi	c	one hundredth of	
0.001= 10^{-3}	milli	m	one thousandth of	
0.000 001= 10^{-6}	micro	μ	one millionth of	
0.000 000 001= 10^{-9}	nano	n	one billionth of	milliardth
0.000 000 000 001= 10^{-12}	pico	p	one trillionth of	billionth
0.000 000 000 000 001= 10^{-15}	femto	f	one quadrillionth of	thousand billionth
0.000 000 000 000 000 001= 10^{-18}	atto	a	one quintillionth of	trillionth

Length (Distance)

These prefixes normally are shown in front of the meter, the standard length unit. So,

1 millimeter (mm) = 0.001 meter (m)

1 centimeter (cm) = 0.01 m

1 decimeter (dm) = 0.1 m

Common conversions are:

1 inch = 2.54 cm = 0.0254 m

1 mil = 0.001 inch = 25.4 micrometer (µm) = 25.4 microns

1 meter = 39.37 inches

Volume

The term liter (or litre) is not an official part of the SI system but is acceptable as a term for the cubic decimeter (dm^3). It is abbreviated as "L" rather than the lower case "l" to prevent confusion with the numeral "1".

1 cubic meter (m^3) = 1000 dm^3 = 1000 L

1 liter (L) = 1000 milliliters (mL) = 1.06 quarts

The term "cc" or cubic centimeters is discouraged; use mL instead. They are equivalent for ordinary usage.

Mass

Some multiple of a gram (g) is used as the most common mass unit. A very common concentration term is milligrams per liter (mg/L).

1 kg = 1000 g = 2.205 lb

1 lb = 453.5 g

The term ***specific gravity*** (or ***relative density***) is the density of a material in mass per unit volume divided by the of pure water at the same conditions. The SI metric system uses "relative density" instead of the more traditional "specific gravity." The most common abbreviations are S.G. or @.

Temperature

The temperature normally is expressed in degrees centigrade or degrees Celsius (°C) when the metric system is employed. This may be compared to degrees Fahrenheit (°F) as shown in Figure 1.3.

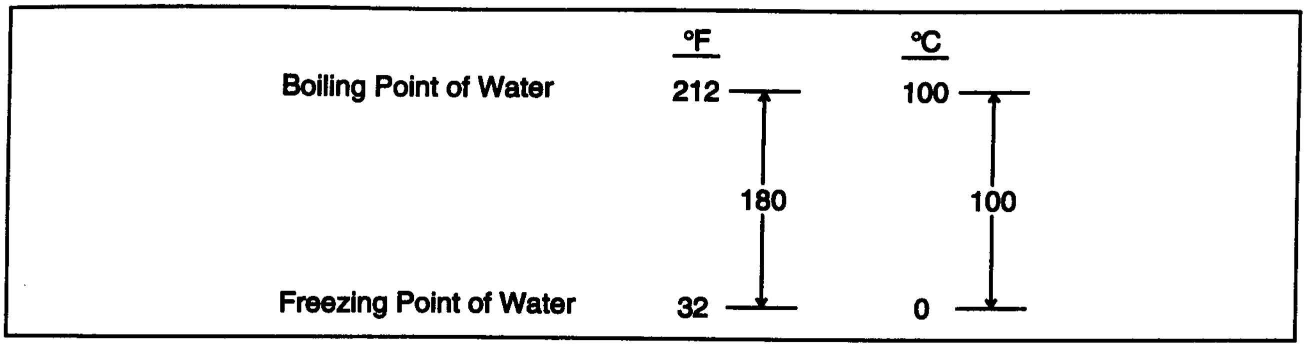

Figure 1.3 Comparison of Fahrenheit and Centigrade

Formulas for converting temperatures from one scale to the other are:

$$^{\circ}F = (1.8 \times {}^{\circ}C) + 32 \tag{1.7}$$

$$^{\circ}C = \frac{1}{1.8} \times ({}^{\circ}F - 32) \tag{1.8}$$

A conversion chart is given in Appendix 4.

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2

WATER SAMPLING AND ANALYSIS

Many profound statements can be made about water and its importance in our lives. Its beneficial qualities are many. However, routinely handling large quantities of waters of vastly differing compositions at minimum cost and with a minimum of operating problems often presents some tremendous problems.

CHEMICAL AND PHYSICAL PROPERTIES

Water is often called the universal solvent because it has the power to dissolve virtually all inorganic substances to some extent. In its pure state it has the following physical properties:

TABLE 2.1

Physical Properties of Water

Property	Value
Molecular Weight	18
Density @ 4°C	1 g/mL
Freezing Point	32°F [0°C]
Boiling Point	212°F [100°C]

Most water handling problems in the oilfield arise from the fact that water is such a superb solvent. Both produced waters and surface waters contain considerable quantities of impurities. It has had ample contact with soil and rock formations and has dissolved certain compounds. In addition, it usually contains some suspended solids and dissolved gases. Water will dissolve metal. Microbiological growths often proceed very readily in water. As conditions of temperature and pressure change, many of the dissolved compounds may become insoluble to some degree, precipitate from the water and form scale. The number and combination of difficulties which may arise in water handling are enormous.

In the oilfield we use water for many purposes. The most common are:

- Injection into subsurface formations to increase oil recovery and/or maintain reservoir pressure.
- Injection into subsurface formations to dispose of waste waters.
- Disposal of waste waters into surface waters.

- Cooling of natural gas engine jackets, compressor cylinders, natural gas and other process streams.
- Feedwater for boilers and steam generators.

Regardless of the application, we have two primary goals from an operational standpoint:

- Avoid plugging and deposition of solids in lines, vessels and wells.
- Prevent corrosion of surface and downhole equipment.

WATER SAMPLING

One of the first items of interest in water handling is to sample it and determine its composition. This is our primary means of detecting present and potential problems. However, the water sample must be representative of the water of interest or our analysis will lead to false conclusions. The importance of good sampling practices cannot be overemphasized. An extremely accurate chemical analysis of a water sample, followed by a brilliant assessment of the problems indicated by the analysis, is worthless if the sample does not represent the water in your system.

Sample Containers

Clean (preferably new) plastic bottles with tightly fitting plastic caps are recommended for routine water samples. Pint or quart (500 mL or one liter) bottles are commonly used. Several different types of plastic and different cap designs are available. Once you have selected a particular bottle and cap combination, fill it with water, cap it, and squeeze it to make sure that the cap will not pop off or leak. Wide-mouth bottles are usually easier to fill, but often have less dependable caps.

Label the bottle (not the cap) so that the sample can be identified. Cardboard mailing tubes or cartons should be obtained if the samples are to be shipped to a laboratory or carried a considerable distance.

If the sample is to be analyzed for oil content or for the concentration of any other organic constituent, a glass bottle should be used. Oil or other organic materials will adhere to the walls of a plastic container or be absorbed by it. Extra precautions are necessary in packing the sample for shipment. Freezing can be a problem. Use a plastic cap with a plastic liner.

Never use a metal container or a metal cap. The water will corrode them and become contaminated with corrosion products.

Sample Volume

A minimum sample volume of one pint (500 mL) is recommended for routine analysis.

If you are going to personally perform on-site analyses, you can take as much as you think you need. If only one or two analyses are to be performed, only a few hundred milliliters may be necessary. Also, since you are on site, you can run back to the sampling point and obtain some more water (provided the water system is not changing composition rapidly). But remember that if you send water samples to a laboratory several miles away and you don't send enough to permit them to perform all of the analyses you want, you are simply out of luck. Always send more than enough if there is any doubt in your mind as to the minimum volume required.

Sampling Procedure

If a sampling valve is available, connect a piece of plastic tubing to the end of the valve. A small nipple or hose connector is handy for this purpose. Open the valve and let the water run for at least one minute. Watch to see if the color of the water is changing. If it is, wait until the color becomes constant. Remember that there is probably some debris in the valve or in the bottom of the line and this will have to be flushed out before you can get a good sample.

Once you have a representative water flow, the following sampling procedures are recommended:

- Sample for Routine Analysis — Rinse the bottle out three times, then place the end of the hose in the bottom of the bottle and let the bottle overflow for an estimated 10 volumes. Then slowly pull out the hose and quickly cap it to minimize (1) oxygen contamination and (2) the escape of dissolved gases.
- Sample for Oil-in-Water Analysis — Fill a clean glass bottle to the neck directly from the sample point and cap quickly. Do not rinse or overflow the bottle with the water to be sampled as in the case of the sampling procedure given for routine analyses. Oil will tend to adhere to the bottle wall and separate from the water. If the bottle is filled more than once, oil from each filling is likely to stay in the bottle, giving erroneously high results. Alternately, free oil may be carried out of the bottle by overflowing, giving low results.
- Sample for Bacterial Analysis — This procedure is covered in detail in Chapter 5.

Once the sample is capped, prepare a label immediately and attach it to the bottle or label the bottle with an indelible, smear-proof marking pen. Make sure the label is securely glued to the bottle. You can mark the cap for convenience if you wish, but remember that caps can be inadvertently switched!

If the sample is to be sent to a laboratory for analysis it should be accompanied by a Water Sample Description Form detailing the sampling conditions. A typical example is given in Appendix 5.

Some other hints:

1. Take wellhead samples at the wellhead, not at the heater-treater or at the tank.
2. If a tank is to be sampled, sample it at several levels, preferably top, middle and bottom. This can require special equipment. You may be able to borrow a "thief" from a gauger and clean it thoroughly before use in order to obtain a sample from the center of a conventional tank.
3. Take samples from the system when it is operating normally. It is often most convenient to take samples when the system is shut down. Needless to say, this type of sample is of questionable value. Make sure the flow rate is "normal" and that nothing unusual is going on upstream of the sampling point.
4. If you are sampling a surface water as a possible source for a waterflood remember that the water composition (especially the turbidity, oxygen concentration and microbial population) may change considerably with the time of the year. It is advisable to sample at several points over a period of several months.
5. Waters for disposal may change considerably with time. Plant waste waters may show a cyclic change in composition due to ion exchange regeneration, cooling tower blowdown cycles, or plant cleaning operations. Once again, a series of samples over a period of time is recommended. Conversations with plant personnel may enrich your intuition as to when to take samples which will reflect the greatest variations in disposal water composition. This can influence your water treating procedure.

QUANTITATIVE ANALYSIS OF OILFIELD WATERS

Water analyses are routinely carried out in laboratories by skilled chemists. They are capable of making extremely accurate measurements on the water sample provided. However, many water properties can change very quickly after sampling. Typical are pH, temperature, dissolved gas content, suspended solids and bacterial population. This means that many of the properties which are of greatest concern to us can be determined accurately only by measuring them on-site. Therefore, a thorough analysis of any water usually involves both laboratory and field analyses.

It is extremely important that any person involved in a water injection or disposal project have an understanding of:

- The constituents and properties of water of greatest importance in water systems
- The significance of each
- The analytical methods typically used, along with their strengths and weaknesses

If these items are understood, then it is possible to specify which analyses are needed and to understand the significance of the results.

Primary Constituents and Properties

In water handling operations we are primarily concerned with those ions and physical properties which are important from the standpoint of plugging or corrosion. Table 2.2 is a list of the most important.

It may also be desirable to measure the amount of chlorine (a bactericide) or the concentration of treating chemicals present in order to monitor their effectiveness.

In steam operations and cooling water systems the amount of silica (SiO_2) in the water is also important, as it can form deposits.

TABLE 2.2

Primary Constituents and Properties of Oilfield Waters

Cations	Anions	Other Properties
Sodium (Na^+)	Chloride (Cl^-)	pH
Calcium (Ca^{++})	Sulfate ($SO_4^=$)	Bacterial Population
Magnesium (Mg^{++})	Bicarbonate (HCO_3^-)	Suspended Solids: Amount, size, shape, composition
Iron (Fe^{+++} & Fe^{++})	Carbonate ($CO_3^=$)	Turbidity
Barium (Ba^{++})		Water Quality
Strontium (Sr^{++})		Dissolved Oxygen
		Dissolved Carbon Dioxide
		Total Sulfides as H_2S
		Oil Content
		Temperature
		Total Dissolved Solids (TDS)
		Specific Gravity
		Resistivity (Conductivity)
		Silica

Significance of Constituents and Properties$^{(2.1)}$

Cations

a. ***Sodium*** is a major constituent in oilffield waters, but does not normally cause any problems. About the only exception is the precipitation of NaCl from extremely salty brines.

b. The ***calcium*** ion is a major constituent of oilfield brines and may run as high as 30 000 mg/L although its concentration is normally considerably lower. The calcium ion is of major importance because it readily combines with bicarbonate, carbonate or sulfate ions and precipitates to form adherent scales or suspended solids.

c. ***Magnesium*** ions are usually present in much lower concentrations than calcium. They tend to ***add*** to $CaCO_3$ scaling problems by co-precipitating with the calcium ion. It is very common to find magnesium in calcium carbonate scales.

   Magnesium ions ***decrease*** the amount of $CaSO_4$, $CaSO_4$ and $CaSO_4$ scales. They do so by forming "ion pairs" with the sulfate ion. Essentially, the magnesium ion has the ability to form a compound which remains in solution. The sulfate ions which are tied up with magnesium are not available to form sulfate scales.

d. The natural ***iron*** content of formation waters normally is quite low and its presence is usually indicative of corrosion. It may be present in solution as ferric (Fe^{+++}) or ferrous (Fe^{++}) ions, or it may be in suspension as a precipitated iron compound. "Iron counts" are often used to detect and monitor corrosion in a water system. The presence of precipitated iron compounds is one of the major causes of formation plugging.

e. ***Barium*** is of importance primarily because of its ability to combine with the sulfate ion to form barium sulfate, which is extremely insoluble. Even small quantities can present severe problems.

f. ***Strontium***, like barium and calcium, can combine with the sulfate ion to form insoluble strontium sulfate. Although more soluble than barium sulfate, it is often found in scales mixed with barium sulfate.

Anions

a. The ***chloride*** ion is nearly always the major anion in produced brines and is usually present as a major constituent in fresh waters. The major source of the chloride ion is NaCl, so the chloride ion concentration is used as a measure of water salinity.

   Although salt deposition can be a problem, it is normally of little consequence. The primary problem associated with the chloride ion is that the corrosivity of the water increases as it gets saltier. Therefore, high chloride concentrations make corrosion more likely. Also, the chloride ion is a stable constituent and its concentration is one of the easier ways of identifying a water.

b. The ***sulfate*** ion is a problem because of its ability to react with calcium, barium or strontium to form insoluble scales. It also serves as a "food substance" for sulfate reducing bacteria.

c. The ***bicarbonate*** ion can react with calcium, magnesium, iron, barium and strontium ions to form insoluble scales. It is present in virtually all waters. Bicarbonate ion concentration is sometimes called methyl orange alkalinity.

d. Like the bicarbonate ion, the ***carbonate*** ion can also react with calcium, magnesium, iron, barium and strontium ions to form insoluble scales. Carbonate ions are rarely present in produced waters because the pH is usually too low (< 8.3). Carbonate ion concentration is sometimes called phenophthalein alkalinity.

Other Properties

a. The ***pH*** is extremely important for several reasons. The solubility of $CaCO_3$ and iron compounds is highly dependent on pH. The higher the pH, the greater the tendency for precipitation.

   As the pH decreases (becomes more acidic) the scaling tendency of the water is decreased, but its corrosivity is increased. Most oilfield waters have a pH between 4 and 8.

   Both H_2S and CO_2 are "acid" gases as they tend to lower the pH of water (make it more acid) when they dissolve in water. They partially ionize when they dissolve and the degree of ionization is reflected by the pH. This is important in predicting their effect on corrosion and suspended solids.

   Since pH values usually change rapidly after a sample is withdrawn from a pressurized system (due to the escape of dissolved acid gases), pH values should be measured immediately after the sample is taken.

b. The presence of ***bacteria*** may result in corrosion and/or plugging. A more detailed treatment of this subject is given in Chapter 5.

c. The quantity of ***suspended solids*** which can be filtered from a given volume of water using a membrane filter is one basis for estimating the plugging tendency of a water. A 0.45 μm pore-size filter is commonly used.

d. It is possible to estimate the ***particle size distribution*** of the suspended solids in a water sample by various techniques. A knowledge of the particle size distribution can be very helpful in determining the need for filtration and in filter selection. It is also useful in monitoring filter performance.

e. Determination of ***particle shape*** by visual or scanning electron microscopy is very helpful in the determination of filtration needs. It is usually used in conjunction with particle size distributions.

f. Determination of the ***composition of the suspended solids*** makes it possible to ascertain their origin (corrosion products, scale particles, formation sand, etc.) so that proper remedial action can be taken. Knowledge of their chemical composition is also important from the standpoint of designing a cleanout procedure should plugging occur.

g. ***Turbidity*** simply means that the water is not "clear" and that it contains undissolved matter such as suspended solids, dispersed oil or gas bubbles. It is a measure of the degree of "cloudiness" of the water. Turbidity indicates the possibility of formation plugging in injection operations. Turbidity measurements are often used to monitor filter performance.

h. ***Water quality*** is a measure of the relative degree of plugging which occurs when a given volume of water is passed through a membrane filter of a given pore size. A pore size of 0.45 μm is most commonly used. The utility of water quality testing lies largely in its use as a comparative measurement.

i. ***Dissolved oxygen*** contributes significantly to the corrosivity of a water. Also, if dissolved iron is present in a water, the entry of oxygen into the system can result in the precipitation of dissolved iron as insoluble iron oxides which may result in plugging. Oxygen also facilitates the growth of aerobic bacteria.

j. ***Dissolved carbon dioxide*** influences the pH, corrosivity and $CaCO_3$ scaling tendency of a water.

k. The presence of ***sulfides*** in water will increase its corrosivity. Dissolved sulfides exist in water as a mixture of HS^- ions and dissolved H_2S gas at the pH values normally found in oilfield waters, and the total concentration of both species is usually measured and referred to as "total sulfides". It may be present naturally in the water or it may be generated by sulfate-reducing bacteria. If a normally sweet (free of H_2S) water begins to show traces of H_2S, this indicates that sulfate-reducing bacteria are probably at work somewhere in the system busily corroding holes in your piping and vessels. In addition, iron sulfide will be generated as a corrosion product, and it is a very efficient plugging agent.

l. The presence of dispersed or emulsified ***oil*** in water often presents problems when injecting produced waters.

Oil in water can cause decreased injectivity in several ways. It can cause "emulsion blocks" in the formation. It serves as an excellent glue for certain solids, such as iron sulfide, thereby increasing their plugging efficiency.

When water is being injected into an aquifer with no initial oil saturation, oil in the water can be trapped in the pores of the formation rock around the wellbore. This creates an oil saturation, which can reduce injectivity.

An analysis for oil content should be conducted on any water, regardless of origin. There are many ways in which water can become contaminated with oil.

When produced water is disposed into surface waters, the concentration of oil in the water is usually limited by government regulation.

m. The ***temperature*** of the water affects the scaling tendency, the pH and the solubility of gases in water. The specific gravity of water is also a function of temperature.

n. The ***total dissolved solids*** is simply the total amount of matter dissolved in a given volume of water. It can be calculated by taking the sum of the concentrations of all cations and anions shown on the water analysis report, or it can be measured by evaporating a sample of water to dryness and weighing the residue.

o. ***Specific Gravity***

$$\textit{Specific Gravity} = \frac{\textit{Density of Water Sample}}{\textit{Density of Pure Water}} \tag{2.1}$$

Density is simply weight per unit volume. Pure water weighs 1 g/mL or 1000 kg/m^3. Thus, a specific gravity greater than 1.0 means that the water sample of interest is more dense, or weighs more than an equal volume of pure water. Since the waters we are interested in contain dissolved solids, they are always more dense than pure water and therefore have a specific gravity greater than 1.0.

The magnitude of the specific gravity is a direct indicator of the total amount of solids dissolved in the water. Therefore, comparison of the specific gravity of several waters gives a rapid estimate of the relative amounts of solids dissolved in the waters.

A graph of total dissolved solids as a function of specific gravity is given in Appendix 6. This is an empirical correlation based on actual density measurements of oilfield waters.

Specific gravity is also a useful check on the accuracy of laboratory water analyses. If the quantity of dissolved solids calculated from the laboratory analysis drastically disagrees with the amount estimated from the specific gravity correlation, there is a good chance that the analysis is in error.

p. The ***resistance*** to electrical current flow is a function of the number of ions dissolved in the water. The lower the resistance the higher the concentration of ions dissolved in the water. It is a method of estimating total dissolved solids which is primarily applied to fresh, low TDS waters. Resistivity measurements are much more sensitive to small changes in TDS in fresh waters than specific gravity.

A chart showing the resistivities of sodium chloride solutions as a function of temperature is given in Appendix 7.

q. ***Conductivity*** values are measured by some laboratories instead of resistivity. Conductivity is the reciprocal of resistivity and can be derived from resistivity values using the following formula:

$$Conductivity\,(\mu mho\,/\,cm) = \frac{1000}{Resistivity\,(ohm - m)} \tag{2.2}$$

r. ***Silica*** occurs in most well waters and can be a serious source of scale deposition in cooling waters and in steam boilers. It normally does not present any problems in water injection operations.

Water Analysis Techniques

Summary of Methods Used

Recommended techniques for measuring the concentration of the ions of interest are given in *API RP 45, Analysis of Oilfield Waters.*(2.2) In addition, meters may be used to determine dissolved oxygen or pH; membrane filter analysis will be used to measure the suspended solids.(2.3)

The types of techniques normally used to analyze an oilfield water sample are summarized in Table 2.3.

Chemical Quantitative Analysis

Quantitative analysis is simply the determination of how much of each of the individual constituents are present in a given sample. Three basic types of methods are commonly used to analyze water samples in the field. More sophisticated instrumental techniques may be used in an analytical laboratory.

Titration

An "indicator" is added to the water sample and a standard solution is then added drop-by-drop from a calibrated dispenser until the solution changes color. The point at which the solution changes color is called the ***endpoint***. This simply means that you are finished titrating. The volume of standard solution used to reach the endpoint is noted and the amount of the unknown species present is calculated.

A titration is simply a method of determining the concentration of a particular substance in solution by reacting it with a known material. Reactions are used which are known to be complete at a given pH. A pH meter is normally used to detect the end point in the laboratory. However, color indicators (substances that change color at a specific pH value) are used for analyses carried out in the field.

TABLE 2.3

Summary of Analysis Methods

Determination	Analysis Method
Sodium	Calculation, spectroscopic, gravimetric
Calcium	Titration, gravimetric, spectroscopic
Magnesium	Titration, gravimetric, spectroscopic
Iron	Colorimetric, titration, spectroscopic
Barium	Turbidimetric, spectroscopic
Strontium	Spectroscopic
Chloride	Titration
Sulfate	Turbidimetric, gravimetric
Bicarbonate	Titration
Carbonate	Titration
pH	pH Meter, colorimetric, pH paper
Bacterial Population	Culturing, microscopic, others
Suspended Solids Concentration	Gravimetric
Particle Size	Coulter Counter, light scattering, microscopy
Particle Shape	Microscopy
Suspended Solids Composition	Chemical analyses
Turbidity	Turbidimetric
Water Quality	Membrane filter test
Dissolved Oxygen	Oxygen meter, titration, colorimetric
Carbon Dioxide	Titration
Total Sulfides	Alkaseltzer test, colorimetric, titration
Oil-in-water	Colorimetric, spectroscopic, gravimetric
Temperature	Thermometer
Total Dissolved Solids	Calculation, gravimetric, conductivity
Specific Gravity	Hydrometer
Resistivity	Resistivity cell, calculation
Silica	Gravimetric, colorimetric, spectroscopic

The colors of some commonly used indicators are shown in Table 2.4 as a function of pH. The pH value at which the color change occurs is designated with a "T."

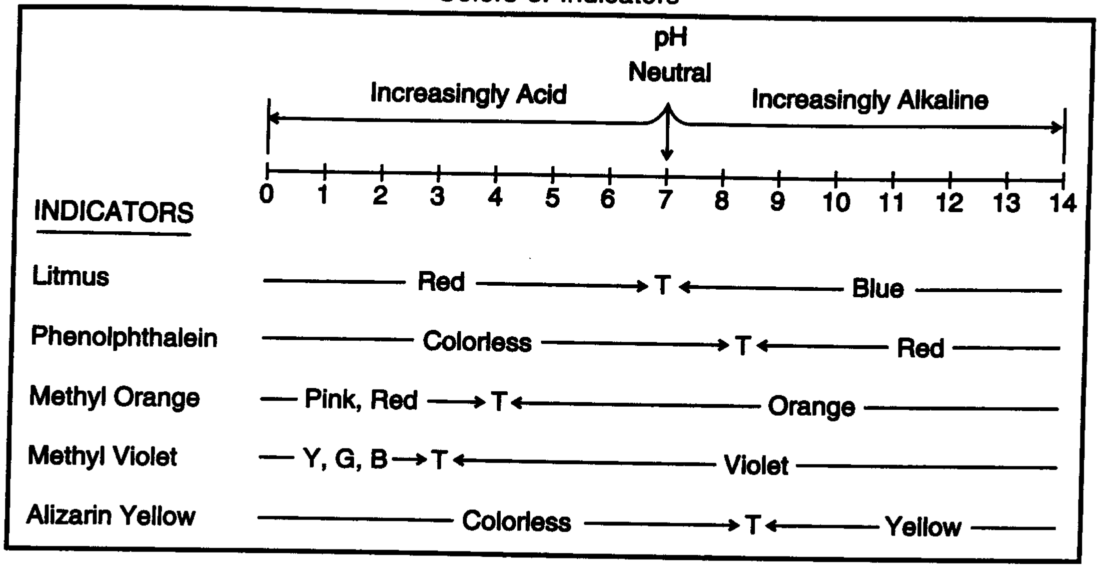
An example of a titration is the determination of bicarbonate ion (HCO_3^-) concentration by titration with HCl:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$

The reaction is complete at a pH of 4.5, so methyl orange is used as the indicator.

TABLE 2.4

Colors of Indicators



The concentration of the ion of interest is calculated based on the fact that one equivalent weight of the known, or standard solution, will react with one equivalent weight of the ion in the water sample.

$$E_{standard} = E_{sample}$$

Where: $E_{standard}$ = number of equivalent weights of titrant (standard solution) added to water sample to reach end-point

E_{sample} = number of equivalent weights of ion of interest in water sample

By definition:

$$Normality(N) = \frac{Number\ of\ Gram\ Equivalent\ Weights\ of\ Ion\ (E)}{Liters\ of\ Solution\ (L)} \tag{2.3}$$

So:

$$[E = N \times L]_{standard} \quad \text{and} \quad [E = N \times L]_{sample}$$

Setting them equal to each other:

$$[N \times L]_{standard} = [N \times L]_{sample}$$

$$\left[N \times L \times \frac{1000ml}{L}\right]_{standard} = \left[N \times L \times \frac{1000ml}{L}\right]_{sample}$$

$$[N \times mL]_{standard} = [N \times mL]_{sample}$$

$$[N \times mL]_{standard} \times \left[\frac{1}{mL}\right]_{sample} = N_{sample}$$

The normality of the standard solution is known. The volume of the standard solution required to reach the endpoint and the volume of the water sample is measured. The equation can then be solved for the normality of the ion of interest in the water sample. Substituting:

$$\left[\frac{E}{L}\right]_{sample} = N_{sample}$$

$$[N \times mL]_{standard} \times \left[\frac{1}{mL}\right]_{sample} = \left[\frac{E}{L}\right]_{sample}$$

This enables us to calculate the number of equivalent weights of the ion of interest per liter of water. In order to determine the weight of the ion present in a liter, it is necessary to multiply both sides of the equation by the gram equivalent weight of the ion and convert grams to milligrams.

$$[N \times mL]_{standard} \times \left[\frac{1}{mL}\right]_{sample} \times EW(g) \times \frac{1000mg}{g} = \left[\frac{E}{L}\right]_{sample} \times EW(g) \times \frac{1000mg}{g}$$

All of this is the long way to arrive at the final formula which we use to calculate the results from a titration:

$$\frac{[N \times mL]_{standard} \times EW\ of\ ion \times 1000}{mL\ of\ sample} = \frac{mg}{L} \tag{2.4}$$

The API recommends the use of mg/L as the unit of concentration for water analyses. Therefore, it is suggested that all titration results be reported as mg/liter of the substance determined.

Sometimes ppm are used interchangeably with mg/L. This is correct only when the specific gravity of the water is very near 1.0, since:

$$mg/L = ppm \times S.G. \tag{2.5}$$

In most titrations certain ions other than the ion of interest will react with the standard solution. This can be a serious problem if the interfering ions are present in significant quantities relative to the amount of the ion of interest present. Table 2.5 lists some common titrations and the interferences for each.

TABLE 2.5

Common Titrations and Interferences$^{(2.2)}$

Ion	Titrant	Indicator	Interferences
$CO_3^=$	H_2SO_4 or HCl	Phenolphthalein	Borate, silicate, sulfide and phosphate will be included in the values for carbonate and bicarbonate as are volatile fatty acid anions.
HCO_3^-	H_2SO_4 or HCl	Methyl Purple or Methyl Orange	
Ca^{++}	EDTA	Cal-Red, Calcon or Murexide	Barium and strontium are included with the calcium determination. Iron also interferes. Can be masked by triethanolamine when more than 20 mg/L is present.
Mg^{++}	EDTA	Eriochrome Black T	
Cl^-	Silver Nitrate	Potassium Chromate (K_2CrO_4)	Bromides, iodides, thiocyanates, phosphates, carbonates and sulfides precipitate silver ions. Iron, barium , lead, and bismuth precipitate chromate indicator.

Colorimetric Analysis

Colorimetric methods are widely used because of their simplicity. This type of test is based on addition of a material to the water sample which will react specifically with the species in question and produce a colored solution. The intensity of the color is proportional to the amount of the species present. The concentration of the substance in the water is found by comparing the color of the sample with the color standards of known concentration.

For example:

$$Fe^{++} + ortho - phenananthroline \rightarrow Orange\ red$$

$$pH + various\ indictors \rightarrow Spectrum\ of\ color$$

Battery-powered spectrophotometers or colorimeters are also available and can be used for many test procedures. The color-developing reagents are available in pre-weighed packets which are extremely convenient for field use.

One of the most convenient colorimetric analysis procedures employs an extremely clever unitized reagent and sampling system called a CHEMet® (CHEMetrics, Inc., Rt. 28, Calverton, VA 22016). Each CHEMet is a 7-mm diameter glass ampoule with a tapered, prescored tip. Color-forming reagents are sealed inside the ampoule under vacuum. When the user snaps the tapered tip of the ampoule in the sample, vacuum pulls the sample in automatically.

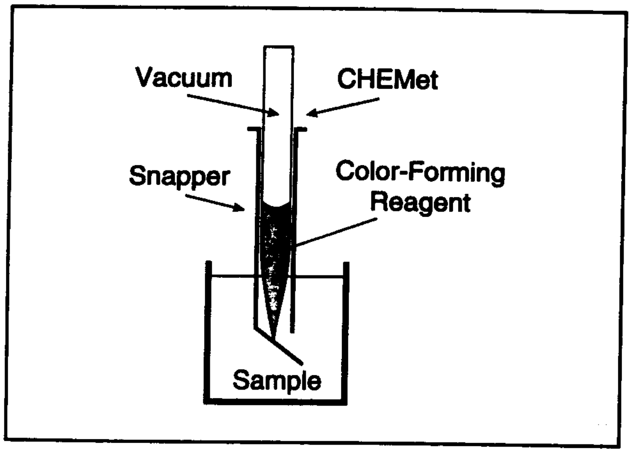


Figure 2.1 Using a CHEMet

Filling is instantaneous and complete except for a small bubble of inert gas. Sample and reagent are mixed by tilting the ampoule and allowing the bubble to travel from end to end several times. After waiting a specified period for color development (usually two minutes or less) the analyst quantifies the result using a color comparator supplied with the kit.

Although CHEMets are available for a fairly wide range of analyses, they have proven to be invaluable for the detection of low levels of dissolved oxygen. Test kits are available with ranges as low as 0-20 ppb (0-0.02 ppm). The results are expressed as mg/L O_2.

The results are not affected by temperature, salinity, other dissolved gases (including H_2S), or the presence of sulfite oxygen scavengers.

Oxidizing agents, such as chlorine, can cause high results unless a special formulation of the reagent is used.

Turbidimetric Analysis

In this type of analysis, a reagent is added to the water which will react with the ion of interest to form a finely divided precipitated solid. The precipitate creates a cloudy solution and the degree of cloudiness, or turbidity, is proportional to the amount of the ion present.

For example, turbidimetric analysis can be used to determine sulfate concentration.

$$SO_4^{=} + Ba^{++} \rightarrow BaSO_4$$

Of the three analytical methods,

- Titration is the most accurate.
- Colorimetric techniques are the most sensitive (can detect the smallest quantities).
- Turbidimetric analyses are the least accurate.

Expression of Results

The concentration of different species in a water can be expressed in several different ways.

1. Milligrams per Liter (mg/L)

   This is the unit of concentration recommended by the API for oilfield waters.

2. Milliequivalents per Liter (meq/L)

   Some laboratories also report results in milliequivalents per liter.

$$meq/L = \frac{mg/L}{Equivalent\ weight} \qquad (2.6)$$

3. Parts per Million (ppm)

   If the water is very fresh, the specific gravity is essentially 1.0, and ppm and mg/L are equal. However, as the TDS of the water increases, the specific gravity increases and the units become increasingly different.

$$ppm = \frac{mg/L}{S.G.} \qquad (2.7)$$

4. Equivalents per Million (epm)

   This unit of concentration is calculated as follows:

$$epm = \frac{ppm}{Equivalent\ weight} \qquad (2.8)$$

5. Grains/U.S. Gallon

   Grains/gallon (gr/gal.) are units which are seldom used in routine oilfield water analysis work. However, they are used in calculations involving water softening by ion exchange.

$$gr/U.S.\,gal. = \frac{mg/L}{17.1} \qquad (2.9)$$

6. ppm as $CaCO_3$

   Watch out for this unit system as it is frequently used in cooling water and boiler water work. When the concentration of an ion is expressed in ppm as $CaCO_3$ this means that its concentration has been calculated using the equivalent weight of $CaCO_3$ (50) instead of the equivalent weight of the ion in question. This is done by multiplying the concentration of the ion by the ratio of the equivalent weight of $CaCO_3$ to the equivalent weight of the ion of interest.

For example:

$$ppm\ Ca^{++}\ as\ CaCO_3 = ppm\ Ca^{++} \times \frac{50}{20} \tag{2.10}$$
$$= 2.5 \times ppm\ Ca^{++}$$

In our work we are usually interested in just the reverse of the above procedure, i.e., converting results reported to us in ppm as $CaCO_3$ to ppm of the ion. Therefore, we do just the reverse of the above.

$$ppm\ Ca^{++} = ppm\ Ca^{++}\ as\ CaCO_3 \times \frac{20}{50} \tag{2.11}$$
$$= 0.4 \times ppm\ Ca^{++}\ as\ CaCO_3$$

A conversion table for converting ppm as $CaCO_3$ to ppm of the ion is given in Appendix 8.

Calcium carbonate equivalent concentration units are used in water softening calculations and is the standard method of expressing hardness and alkalinity.

7. Hypothetical Salt Combinations

   Sometimes the reported results are expressed in ppm of hypothetical salts. The chemist may assume that all of the Ca^{++} present will be present as calcium bicarbonate, $Ca(HCO_3)_2$, for instance. This is not true, since the calcium is present in solution as the calcium ion, not as a salt. Many hypothetical combinations of ions are possible from a single ionic analysis. This unit system is not recommended.

8. Hardness

   Total hardness is normally the sum of the calcium and magnesium concentrations expressed as equivalent $CaCO_3$.

$$\left(ppm\ Ca^{++} \times 2.5\right) + \left(ppm\ Mg^{++} \times 4.1\right) = Total\ Hardness,\ ppm\ as\ CaCO_3 \tag{2.12}$$

9. Alkalinity

   Alkalinity in waters is usually attributed to the presence of bicarbonate, carbonate, and hydroxyl ions. However, each of these ions exists only in a given pH range. A general idea of the ions contributing to alkalinity as a function of the pH of the water is as follows:

TABLE 2.6

Ions Causing Alkalinity

pH	Ions Causing Alkalinity
9.6-14.0	OH^- and $CO_3^=$
8.3-9.6	HCO_3^- and $CO_3^=$
4.5-8.3	HCO_3^-

These relationships are not exact, and alkalinity is defined as the capacity of a water to react with hydrogen ions. The distribution of HCO_3^- and $CO_3^=$ ions as a function of pH is shown in Figure 3.1.

Alkalinity is determined by titrating with a standard acid to two different endpoints or pH values.

- ***P Alkalinity***: A measure of the number of equivalents of acid required to lower the pH of the water to approximately 8.3 (the phenolphthalein, or "P" endpoint).
- ***M Alkalinity***: A measure of the number of equivalents of acid required to lower the pH to approximately 4.5 (the methyl orange or "M" endpoint).

Most natural waters have a pH less than 8.3, and hence have a P alkalinity of zero and contain no $CO_3^=$. This means that they show only M alkalinity, which is attributed solely to HCO_3^-.

Alkalinity and acidity as a function of pH is shown in Figure 2.2.

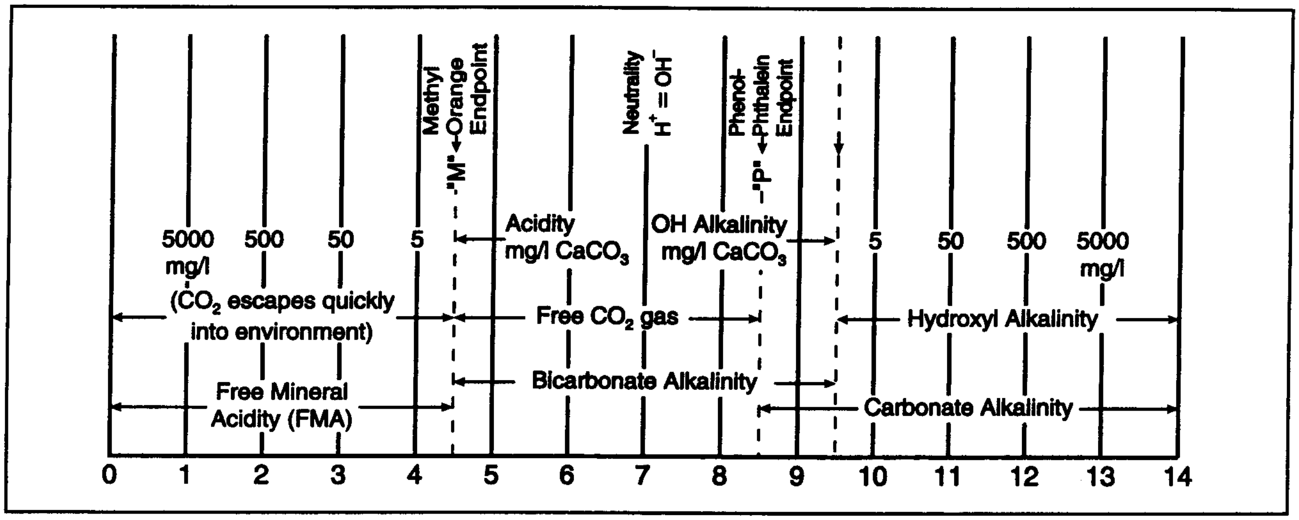


Figure 2.2 Alkalinity and Acidity Ranges

Although absent from surface waters and most aquifer waters, ***carboxylic acids*** are commonly present in produced waters (water produced with oil and/or gas) and are usually referred to as volatile fatty acids (VFA's). Even though they are classified as acids they are not actually present as acids in produced water because they have ionized to yield a hydrogen ion and a volatile fatty acid anion ("VFA anion").(2.4) For example, in the case of acetic acid:

$$CH_3COOH \rightarrow H^+ + CH_3COO^-$$

Acetic Acid Acetate Ion

The VFA anions commonly found in produced water contribute to alkalinity and are listed in Table 2.7.

TABLE 2.7

Volatile Fatty Acid Anions

VFA Anions	Formula
Acetate Ion	CH_3COO^-
Propionate Ion	$CH_3CH_2COO^-$
Butyrate Ion	$CH_3CH_2CH_2COO^-$

Alkalinity in produced waters is the sum of the concentrations of the bicarbonate ion and the VFA anions.

$$Alkalinity = HCO_3^- + Acetate + Propionate + Butyrate \tag{2.13}$$

The acetate ion usually comprises the major portion of the VFA anions in produced waters with considerably smaller quantities of propionate and even smaller concentrations of butyrate ions.

The concentration of the VFA anions in produced water can be substantial relative to the bicarbonate concentration. When this occurs, the bicarbonate ion concentration determined by titration with acid will be significantly in error.

Accurate determination of the HCO_3^- concentration in these types of waters requires the measurement of the VFA anion concentration so that it can be subtracted from the total alkalinity. This measurement is not routinely performed and must be requested if desired. This can be quite important when making calcium carbonate scaling calculations.

Graphical Presentation of Results — Water Patterns

Water analyses are often expressed graphically. The diagram, or pattern, obtained by graphically plotting the results of a water analysis will often highlight important points about the analysis that might be missed by simply reading the report. Pattern comparison is also an easy way to quickly spot differences in two or more waters.

There are many different water analysis diagrams in use. However, the Stiff Method(2.5) has been adopted by the API and is probably the most universally used method in the oilfield. It is the only one presented here. A logarithmic plot of meq/liter of the various ions is most often used, although linear plots are also used. The concentrations of Na^+, Ca^{++}, Mg^{++}, Fe (total), Cl^-, HCO_3^-, $SO_4^=$ and $CO_3^=$ given in Table 2.8 are plotted as shown in Figure 2.3.

TABLE 2.8

Water Analysis

Ion	mg/L	meq/L
Na^+	93230	4053
Ca^{++}	5173	258
Mg^{++}	620	51
Fe (Total)	12	0.6
Cl^-	153175	4320
HCO_3^-	195	3
$SO_4^=$	1910	40
$CO_3^=$	0	0

The concentrations of the cations are plotted to the left of the center line, while the anion concentrations are plotted to the right of the center line.

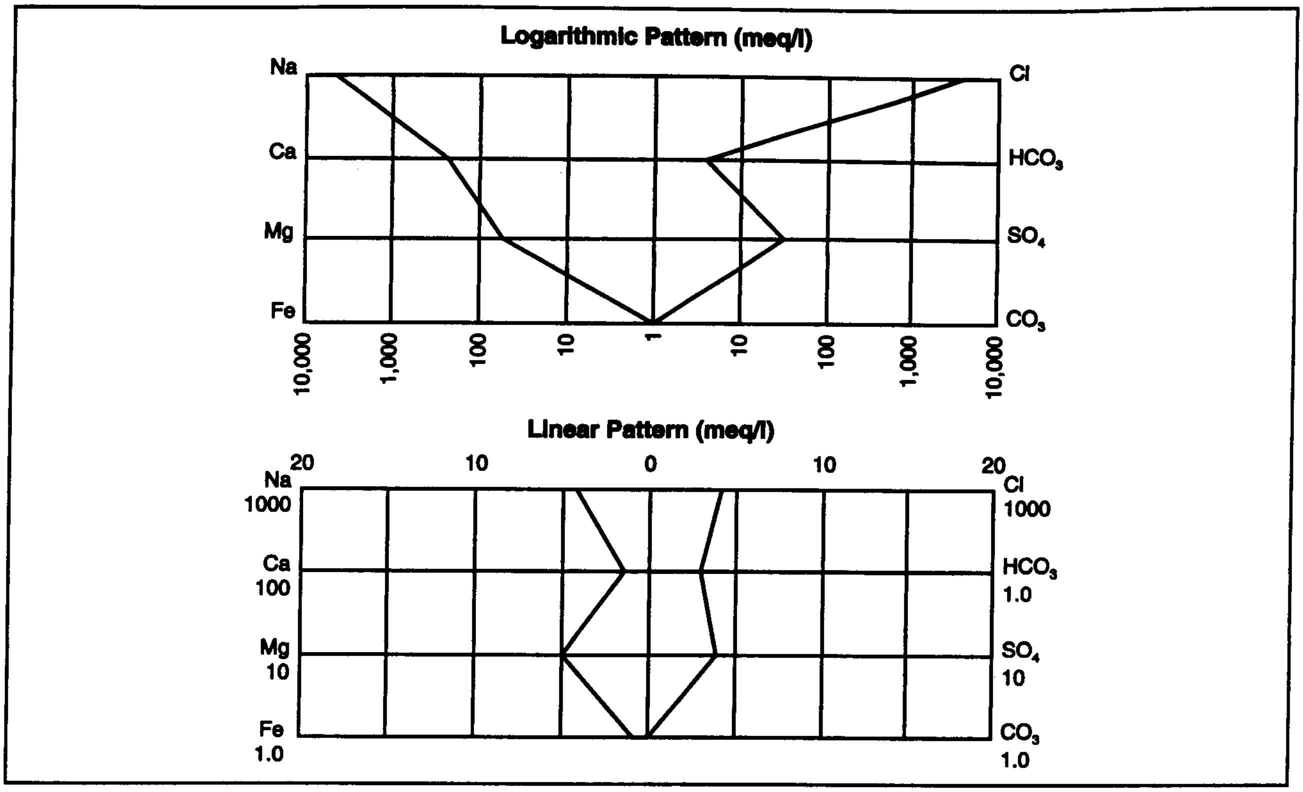


Figure 2.3 Graphical Presentation of Water Analysis — Stiff Method

Water Analysis Reports

Appendix 9 contains examples of two water analysis reports. The first is presented on a modified API Water Analysis Report form. The second report presents the same data in a slightly different format used by a commercial water analysis laboratory.

Both reports contain the following:

- Sample identification information.
- Quantitative analysis of water sample. The degree of detail will vary.
- A graphical representation of the analysis — a water pattern.

The Stiff Method is used in both cases, although the logarithmic pattern is used in the first form while the linear pattern is used in the second.

The API report form is recommended for your own field analysis work. You may find it desirable to eventually modify the form to contain space for reporting additional information pertinent to your own operation.

Oil-in-Water Analysis

The oil content of a water depends on how it is measured. There is no absolute value.

Produced water contains both dispersed oil and "dissolved oil". The dissolved oil consists of hydrocarbons, phenols, organic acids, and low molecular weight aromatic compounds such as benzene and toluene.

Normal oil/water separation equipment cannot remove dissolved organic compounds. However, values of "oil and grease" include ***both*** the dispersed oil and dissolved organic compounds. Hence, equipment performance should not be judged by "oil and grease" values.

Oil and Grease

In the determination of oil and grease, an absolute quantity of a specific substance is not measured. Rather, the amount of substances with similar physical characteristics are determined quantitatively on the basis of their common solubility in freon. Oil and grease may include hydrocarbons, fatty acids, soaps, fats, waxes, oils, and any other material that is extracted by the solvent from an acidified sample unless it evaporates during the test procedure. Oil and grease is defined by the method used for its determination.

Gravimetric: EPA Method 413.1

The water sample is acidified to a low pH (< 2). The acidified water sample is then poured into a glass container along with freon (fluorocarbon-113) and shaken vigorously. Any oil and grease present is extracted from the water into the freon. The freon is then evaporated from the extract at 70°C, and the residue (oil and grease) is weighed. The results obtained include both dispersed oil and dissolved organic compounds. Any hydrocarbons which will evaporate at this temperature are lost.

Infrared: EPA Method 413.2

The water sample is acidified to a low pH (< 2) and extracted with freon (fluorocarbon-113) as in the gravimetric technique. The freon extract is then placed in an infrared spectrophotometer and the infrared absorption is measured at a wavelength of 2930 cm^{-1}. This wavelength is characteristic of the carbon-hydrogen bond. The oil and grease content of the sample is obtained by comparing the measured value with standards prepared using the same oil. The results obtained include both dispersed oil and dissolved organic compounds.

Results obtained by this method are usually considered to be a more accurate reflection of the true oil and grease content of the water than gravimetric results since the sample is not heated and the loss of light ends is minimized.*(2.6)*

Petroleum Hydrocarbons

Petroleum Hydrocarbons: EPA Method 502 E

The water sample is acidified to a low pH (< 2) and extracted with freon (fluorocarbon-113) as in the gravimetric technique. The freon extract is then mixed with silica gel. Water soluble polar organic materials are removed from the freon by adsorption on the silica gel. Petroleum hydrocarbons remain in the freon and can be determined by either the gravimetric or infrared methods.

Oil Content by Colorimetric Analysis

The water sample is ***not*** acidified. Oil is extracted from a water sample using a dense solvent such as trichloroethane. The color intensity of the extract is compared with standards prepared with the same oil to determine the concentration.

This is a very useful field technique and is commonly used to assess equipment performance; however, the sensitivity of the method is limited with light colored oils such as condensates.

Suspended Solids Analysis

Techniques for suspended solids determination and characterization are not covered in API RP 45.(2.2) Because of the extreme importance of suspended solids control in water handling operations, a brief summary of techniques used to determine the amount and nature of suspended solids in a water is presented in the following sections.

Suspended Solids Concentration

The concentration of suspended solids in a water is determined by passing a known quantity of water through a membrane filter and determining the weight of solids collected on the filter. The weight of solids collected (mg) divided by the quantity of water passed through the filter (liters) gives the suspended solids concentration in mg/L. Standard methods for this test are given in NACE Standard TM0173-92 published by the National Association of Corrosion Engineers.(2.7)

It is strongly recommended that water be flowed ***directly from the system*** through the membrane, when possible, as shown in Figure 2.4. This approach eliminates problems of secondary precipitation associated with sample aging and contact with atmospheric oxygen.

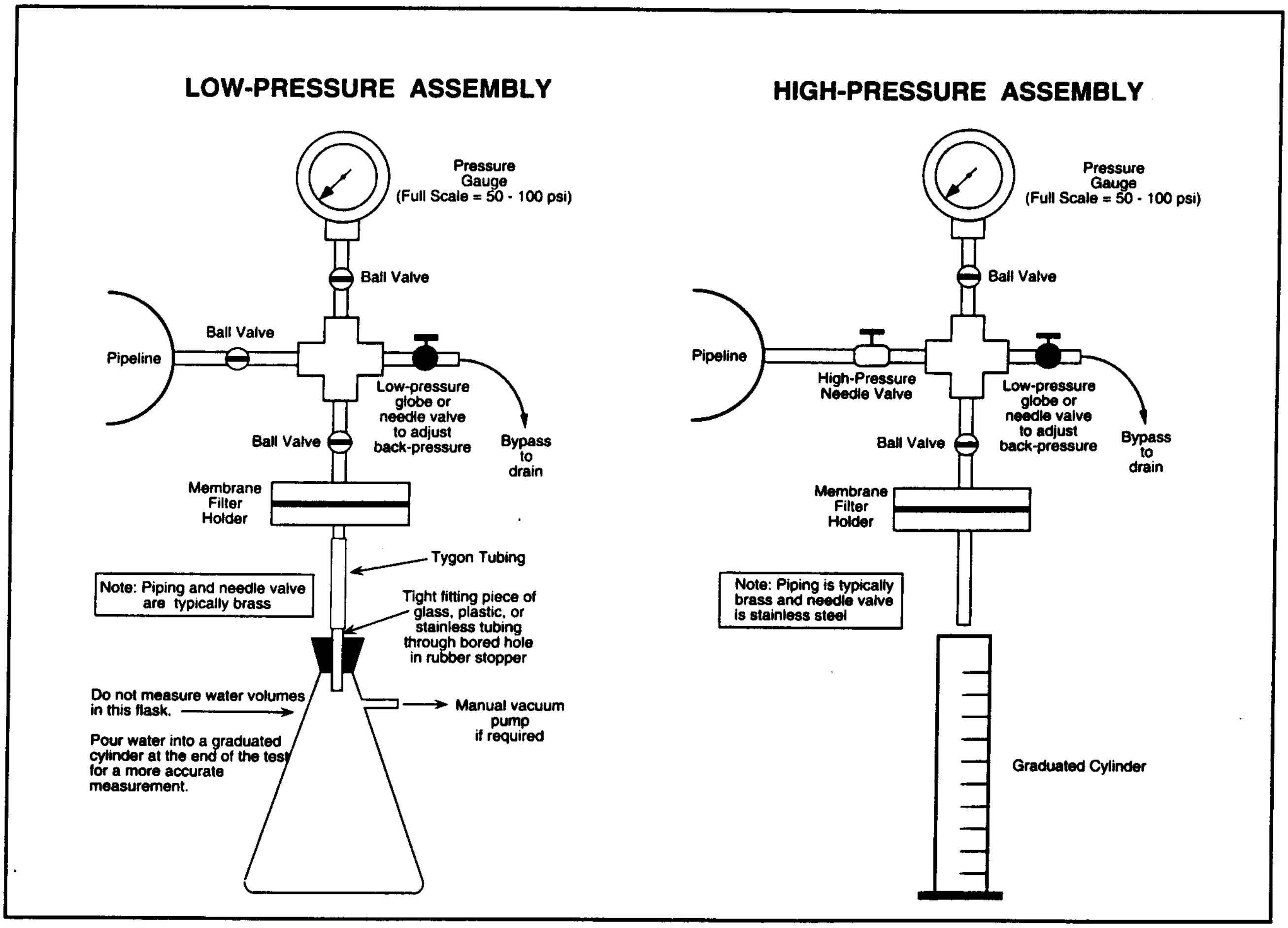


Figure 2.4 Membrane Filter Test Apparatus

Suspended solids are sometimes collected by flowing a water sample from the system into a clear plastic cylinder which has been purged with nitrogen or some other inert gas. Water is then displaced from the cylinder through a 0.45 μm membrane filter by applying approximately 20 psi pressure to the cylinder with a nitrogen bottle. This method is often used at low-pressure sample points although it is sometimes used at high-pressure sample points as well.

The use of a pressurized plastic cylinder may give acceptable results in some waters but it is not recommended for general use. It is particularly unreliable for produced waters. The basic problem arises from the fact that a large volume of water is transferred from the system into the plastic cylinder (typically several liters) but only a small portion of the water (often a few hundred milliliters in poor quality waters) passes through the membrane filter before it plugs and flow ceases. Two things typically occur:

1. Oil tends to rise to the surface of the water and to coat the walls of the plastic cylinder. The net result is that the amount of oil passing through the membrane filter is less than occurs when the sample is drawn directly from the system. This effects the permeability of the filter cake and hence the volume of water which will flow through the cake at a given pressure drop.
2. Suspended solids tend to segregate in the cylinder, with the larger particles settling to the bottom. This gives a non-representative sample.

Although this technique is widely used, and is indeed a NACE-recommended ***alternate*** method, we strongly recommend that suspended solids be collected directly from the system using an apparatus such as one of those shown in Figure 2.4.

The most common reason for using the pressurized cylinder method is that system pressure becomes irrelevant. Furthermore, the pressure drop across the membrane filter is always the same, which is very handy when water quality testing (flow rate vs. cumulative volume at a constant ΔP) is performed. A pressure drop of 20 psi is typically chosen because it is the value recommended by NACE for water quality testing.

However, the pressure drop across the membrane filter is not important when the sole purpose is to determine the suspended solids concentration in the water. If the pressure at the sample point is low, the pressure drop across the membrane filter can be increased by using a hand-operated vacuum pump as shown in Figure 2.4.

The test is normally conducted using a single pre-weighed membrane filter when the suspended solids content is 1 mg/L or greater. When the concentration is less than 1.0 mg/L, matched weight membranes or pre-weighed pairs are preferred.

It is critical that the increase in weight of the membrane filter due to solids filtered from the water be sufficient to provide analytical accuracy. For example, a 47-mm diameter, 0.45 μm pore size, membrane filter weighs about 100 mg. At least 2 mg of solids should be filtered from the water so that the weight gain will be at least 2%. This means that the suspended solids concentration determines the amount of water which must be filtered to provide the minimum weight gain required.

Elution Loss

There is one complicating factor when large quantities of water are passed through the standard cellulose acetate/cellulose nitrate membrane filter: the water dissolves a small amount of the filter, resulting in a small loss of weight. This weight loss is referred to as ***elution loss***. This loss is not significant when the amount of solids collected on the filter is large. However, elution loss can be quite significant in waters containing low levels of suspended solids.

It has been common practice to deal with this problem by running matched-weight filters. Filtration through two matched-weight membrane filters mounted in series subjects both filters to the same elution loss but all solids are collected on the top filter. Therefore, the differential weight is the suspended solids corrected for elution loss.

However, it is not necessary that the two filters be matched in weight. If both are pre-weighed, the elution loss correction can be determined from the bottom filter and applied to the top filter.

Another option is to use a different membrane material, such as polyvinylidene difluoride (PVDF) which is not subject to elution loss.

Chemical Composition of Suspended Solids

An analysis procedure for the determination of solids composition is given in TM0173-92.(2.7) Determination of hydrocarbon solubles, acid solubles, organics and insoluble residue should be supplemented by chemical analyses to identify the major components of each fraction. Of specific interest is iron, sulfate and carbonate, supplemented by determinations of calcium, barium, and strontium as deemed necessary. Analysis for silica and protein may also be of interest.

When membrane filters are used in brines, the membrane must first be washed with deionized water prior to weighing and analysis. The purpose of the wash is to remove water-soluble salts which precipitated in the filter when the water evaporated from the wet membrane during drying. They are not a part of the suspended solids.

A typical analysis format for suspended solids is shown in Table 2.9.

TABLE 2.9

Analysis of Suspended Solids

Component	mg/L	mg/L
Total Acid Solubles		1.50
Calcium as $CaCO_3$	0.13	
Iron as FeS	0.40	
Unidentified	0.97	
Total Organics		3.55
Solvent Soluble (Oil)	1.70	
Ignition Loss	1.85	
Total Acid Insolubles		0
Total Suspended Solids		5.05

Water Quality

In water injection systems, water quality is a measure of the relative degree of plugging which occurs when a given volume of water is passed through a membrane filter of a given pore size. A pore size of 0.45 μm is most commonly used.

The National Association of Corrosion Engineers has approved a standard method for running the test.(2.7) Several modified methods are used. However, the basic test consists of forcing a given volume of water through a filter under constant pressure. The cumulative volume through the filter is recorded as a function of time, and the flow rate for each time increment is calculated from the data. Flow rate is plotted versus cumulative volume throughput on a semi-log plot. The slope of the line indicates the "quality," or degree of plugging which occurred with that particular water sample, as illustrated in Figure 2.5.

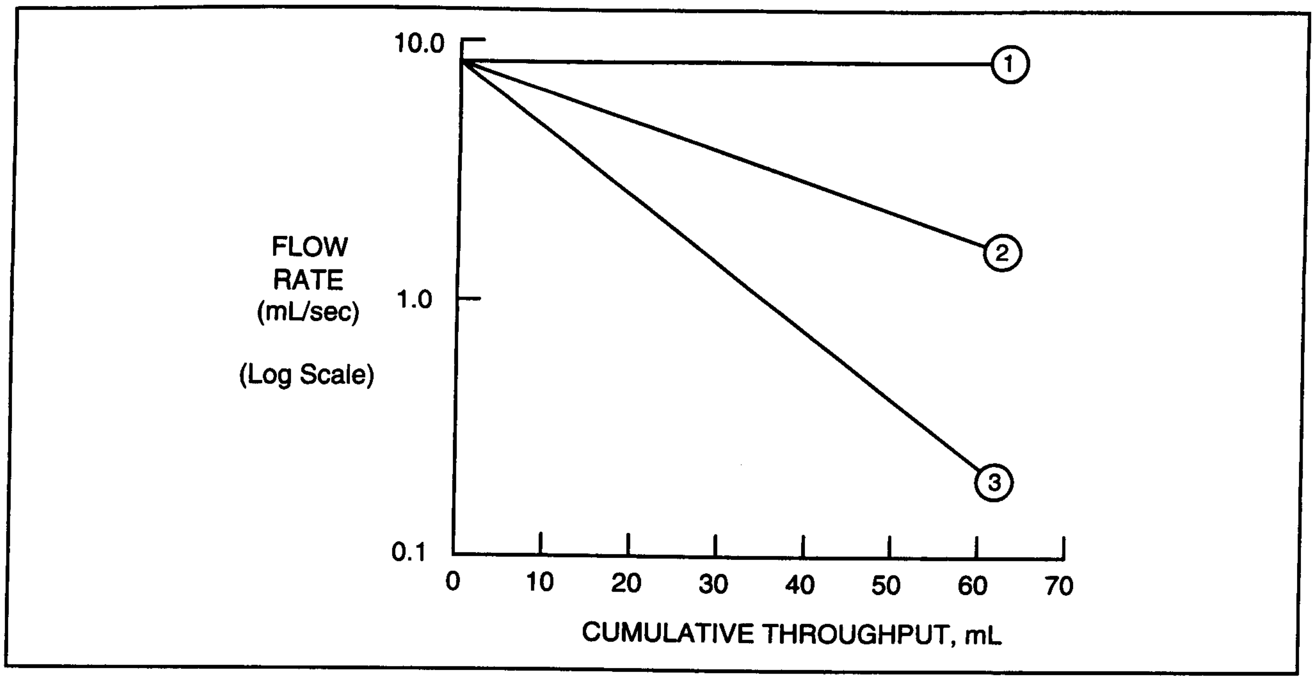


Figure 2.5 Water Quality Plot

It is also a measure of the permeability of the filter cake formed on the membrane. The steeper the slope, the less permeable the cake formed by the solids.

The important point to be made about water quality testing is that it is a way of comparing the relative tendency of different waters to plug a membrane filter. It does not necessarily have any correlation with the tendency of a water to plug the formation.

TABLE 2.10

Interpretation of Water Quality Curves in Figure 2.5

Curve	Quality
1	Excellent. No plugging occurred since the flow rate remained constant throughout the test.
2	Poorer than Curve 1. The flow rate decreased as the cumulative volume throughput increased indicating plugging of the filter.
3	Poorest of the three curves. The flow rate dropped much more rapidly indicating faster plugging.

The utility of water quality testing lies largely in its use as a comparative test.

- Water quality testing can be used to detect changes in a single water at a given point in a system over a period of time.
- Tests can be run at various points through a system to detect changes which may be occurring between the water source and the injection wells.
- Different waters can be compared.
- Through experience, minimum water quality standards may be set for a specific area. Careful correlation of water quality measurements with injectivity data can be very helpful in determining filtration requirements.

Any insoluble material in a water will reduce its quality. Corrosion products, water-formed scales, clay, silt, oil, insoluble treating chemicals, bacterial growths or algae will all contribute to decreased quality.

It should be obvious that the quality required will be largely determined by the reservoir permeability. Tight, low permeability zones will require better water than a high permeability reservoir. What is considered acceptable quality in one area (or zone) might quickly plug a different formation.

Cerini Slope Measurements

In 1953, William F. Cerini proposed a novel means of measuring the slope of water quality curves.(2.8) Although he used a sintered glass disc rather than membrane filters for his test work, his slope measurement technique is still widely used in water-quality work.

The water quality data is plotted in the normal way on two cycle semi-log graph paper. A best fit straight line is drawn through the points, and the slope is then measured as though it were a linear Cartesian plot.

Both the vertical and horizontal components of the slope are measured using the same linear scale. The slope value is then calculated by dividing the vertical component (y) by the horizontal distance (x). As long as the curve slopes downward to the right, the slope value is always negative, and is commonly called the Cerini Slope.

The Cerini Slope of the curve shown in Figure 2.6 is $-2.4/1.5 = -1.6$.

Cerini Slope values are a function of scales used on both the ordinate and the abscissa. Therefore, slope values can be compared only when the scales are fixed.

Relative Plugging Index

Amoco developed a method of rating water quality called the Relative Plugging Index, or RPI.(2.9)

$$RPI = TSS - MTSN \tag{2.14}$$

Where: TSS = Total suspended solids, ppm
MTSN = Millipore test slope number

Millipore Test Slope Number (MTSN)

The MTSN is the Cerini Slope of a conventional water quality curve, with fixed ordinate and abscissa scales:

Vertical "y" axis (Ordinate): 1 cycle/5 inches

Horizontal "x" axis (Abscissa): 500 mL/inch

The MTSN is determined as follows:

1. Plot the water quality data, log flow rate (mL/sec) vs cumulative volume (mL), on 2-cycle semi-log graph paper.
2. Draw a best fit straight line through the data points in the latter portion of the curve as illustrated in Figure 2.6.
3. Select two points on the curve. The coordinates of the selected points are designated as (Q_a, V_a) and (Q_b, V_b).
4. Calculate MTSN directly from the data or determine it graphically.

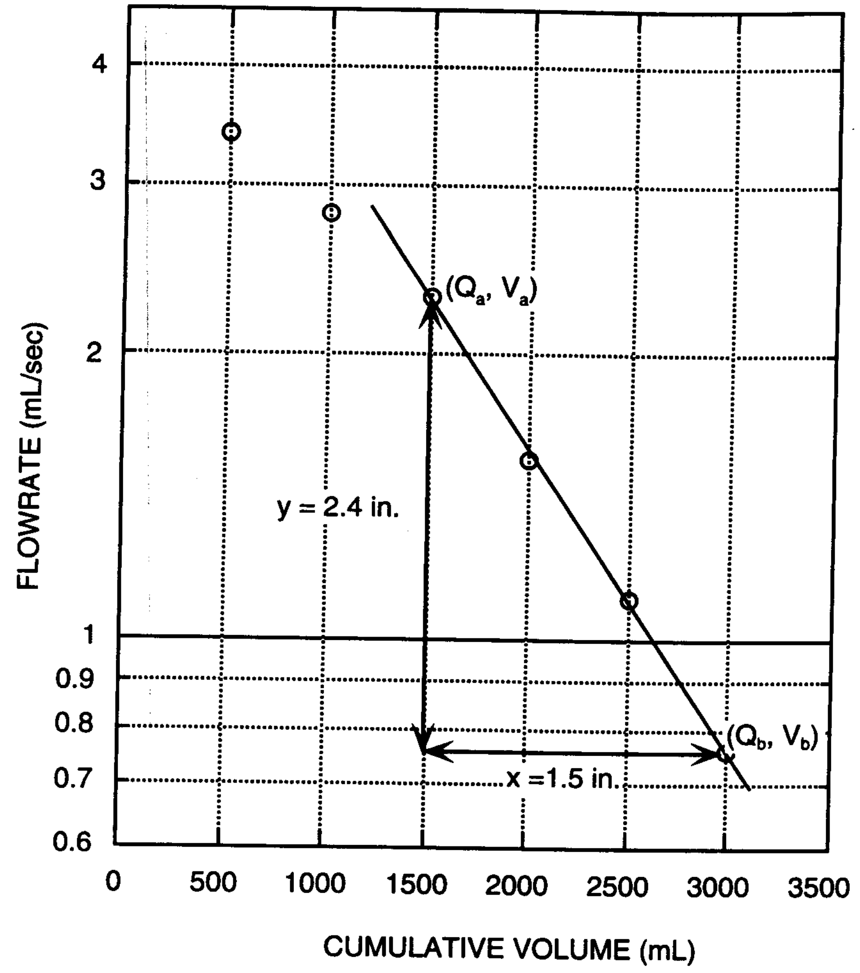


Figure 2.6 Measurement of Cerini Slope

The simplest way to determine the MTSN is to calculate it using the following equation:

$$MTSN = \frac{2500 \log(Q_a/Q_b)}{V_a - V_b} \tag{2.15}$$

Use of this equation permits you to use any ordinate and abscissa scales you choose.

If you wish to determine the MTSN graphically, it is necessary to use graph paper with an ordinate scale of 1 cycle/5 inches, which is usually quite convenient, since that is the normal grid size on 2-cycle semi-log graph paper (8-1/2 × 11 sheet).

There are two options regarding the abscissa scale:

1. Use an abscissa scale of 500 mL/inch.
2. Use an abscissa scale other than 500 mL/inch and calculate the equivalent distance on a 500 mL/inch scale using the following formula:

$$x\,(inches) = \frac{V_a - V_b}{500\,mL/inch} \tag{2.16}$$

MTSN is determined graphically as follows:

1. Measure the vertical distance between Q_a and Q_b, y.
2. Measure the horizontal distance between V_a and V_b, x. If the scale on the horizontal axis is other than 500 mL/in., calculate the difference between the two volumes in milliliters, and divide by 500 to obtain the correct value of x in inches.
3. $MTSN = \frac{-y}{x}$ The MTSN is always negative.

Example 2.1: Given the water quality data in Table 2.11:

The data is plotted in Figure 2.6. The MTSN of the water quality curve is calculated as follows:

$$MTSN = \frac{2500 \times \log(2.3/0.76)}{1500 - 3000} = \frac{2500 \times 0.48}{1500} = -0.8$$

The MTSN can also be determined graphically:

1. y = 2.4 inches
2. $x = \frac{3000 mL - 1500 mL}{500\, mL/inch} = 3.0\ inches$
3. $MTSN = \frac{-y}{x} = \frac{-2.4}{3.0} = -0.8$

TABLE 2.11

Water Quality Data

Flow Rate (mL/sec)	Cumulative Volume (mL)
3.40	500
2.90	1000
2.30	1500
1.55	2000
1.10	2500
0.76	3000

Water Quality Rating Guide

A water quality rating guide proposed by Amoco is given in Table 2.12.$^{(2.9)}$

Well Impairment Prediction

Another approach to the presentation and interpretation of water quality data was developed by Barkman and Davidson.$^{(2.10)}$ They developed methods and theory which can be used to interpret water quality data obtained with membrane filters or cores to predict well impairment from suspended solids.

Although this method can be used to make relative predictions, the calculated half-life values have proven to be unreliable in practice.

TABLE 2.12

Water Quality Rating Guide

RPI	General Quality Rating
< 3	Excellent
3-10	Good to Fair
10-15	Questionable
> 15	Poor

Particle Size Analysis

Solid particles found in injection waters range in diameter from less than one micron up to several hundred microns. Figure 2.7 shows the diameters of some commonly encountered particles for comparison.

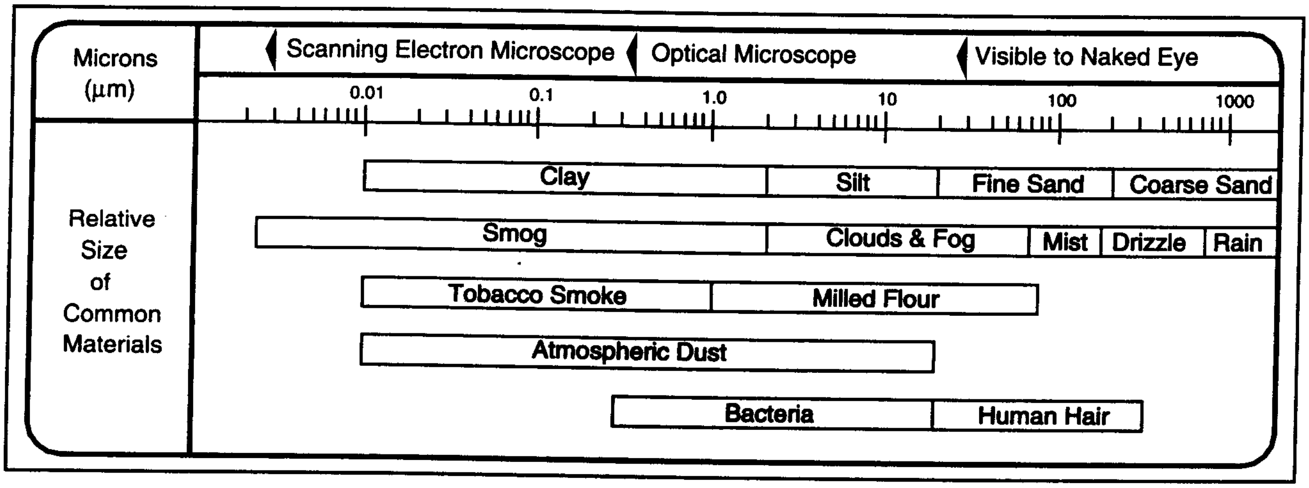


Figure 2.7 Typical Diameter of Common Particles

Although many of the particles found in injection waters are approximately spherical, many are not.

The description of the "size" of a non-spherical particle is one of the fundamental problems of particle technology. The most common approach is to describe the particle by a sphere which will have at least one property in common with it. Thus, a single particle may have several "equivalent sphere sizes" depending on the method used for its measurement, as shown in Table 2.13.

Note that for the particle shown the "diameter" varies by more than a factor of two among the various measurement techniques.

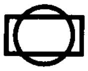
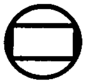
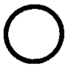
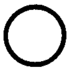
There are a number of techniques which are used to determine the size of particles suspended in water. They are compared in Table 2.14 and discussed in the following paragraphs.

Microscopic Techniques

The use of visual microscopy is probably the oldest technique used to examine particles in oilfield waters. However, it is a rather tedious way to measure particle size distributions, as many particles must be examined if the distribution determined is to be statistically valid. It is more generally used to determine the shape and nature of the particles and to get some idea of their general size range.

TABLE 2.13

Diameters Used for Particle Characterization(2.11)

METHOD OF MEASUREMENT	KIND OF "DIAMETER" MEASURED	EQUIVALENT SPHERES	DIAMETER VALUE ANY UNITS
	True Particle		d x h x w = 1 x 1 x 2
Microscope	Projected-Area Diameter		d_s = 1.58
Microscope	Maximum Feret[a] Dia.		d_f = 2.23
Sedimentation	Stokes Diameter[b]		d_{st} = 1.43
Coulter Counter	Volume Diameter		d_v = 1.55
Sieve	Mesh-Size Diameter		d = 1.00
HIAC Counter	Surface-Area Diameter		d = 1.77

[a] Maximum distance between parallel tangents.

[b] Stokes diameter is included in the expression $3\pi\mu d$, which is the force (resistance to motion) exerted on a particle.

Scanning electron microscopy (SEM) is a popular method of particle examination. Much higher magnifications are possible than with conventional microscopy, and the depth of field is far superior.

Figure 2.8 is an SEM photograph of suspended solids filtered from Aegean seawater, while Figure 2.9 is an SEM photo of solids filtered from North Sea Water.

Both waters contained virtually identical concentrations of suspended solids, but the shapes and types of particles were quite different.

Coulter Counter

Two electrodes are immersed in a beaker of the water of interest, which must contain sufficient dissolved ions to easily conduct electrical current.

The negative electrode is located inside a glass tube which is sealed except for a tiny hole or orifice on the side of the tube. The positive electrode is located in the water sample beaker. (Figure 2.10)

A constant electrical current is passed from the positive electrode to the negative electrode through the orifice. When a non-conductive particle passes through the orifice it causes a change in electrical resistance between the two electrodes which is proportional to the volume of the particle.

TABLE 2.14

Comparison of Commonly Used Particle Analysis Techniques

Technique	Approx Size Range	Sample Requirements	Data Produced	Instrument Portability	Maximum Magnification
Visible Light Microscope		Usually filtered solids on surface of membrane filter although drops of water can be examined.	Particle shape and size.	Easily portable. Requires AC power for illuminating lamp.	800 x (Dry objective) 1500 x (Oil immersion)
Scanning Electron Microscope		Filtered solids on surface of membrane filter. Must be plated with Au or Pd prior to examination. Sample examined under vacuum.	Particle shape and size.	Permanent laboratory installation.	100 000 x
Coulter Counter	0.5 µm to 400 µm	Representative water sample. Counts particles in liquid. Water must have sufficient TDS to be electrically conductive.	Particle size distribution or total number greater than a manually set threshold.	Portable. Requires AC power.	
Spectrex Particle Counter	1 µm to 100 µm	Representative water sample. Counts particles in liquid.	Total number of particles greater than a manually set threshold.	Portable. Requires AC power.	
HIAC and Royco Counters	2 µm to 900 µm	Flowing water sample piped through flow cell or batch sample.	Particle size distribution	Portable. Most require AC power. Some battery powered units available.	

Figure 2.8 Suspended Solids Filtered from Aegean Seawater
Magnification = 1000 x
(Courtesy Brown & Root, Inc.)

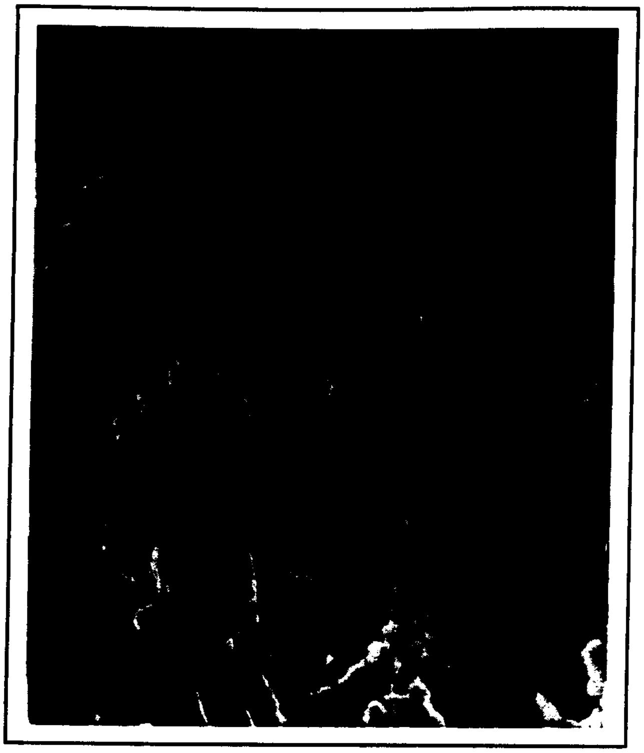


Figure 2.9 Suspended Solids Filtered from North Sea Water
Magnification = 1000x
(Courtesy Nalfloc Ltd.)

A fixed volume of water containing suspended particles is forced through the orifice. As each particle passes through the orifice, the increased resistance results in a voltage pulse which is proportional to particle volume. The series of pulses produced by a series of particles passing through the orifice are electronically scaled and counted, yielding a particle size distribution.

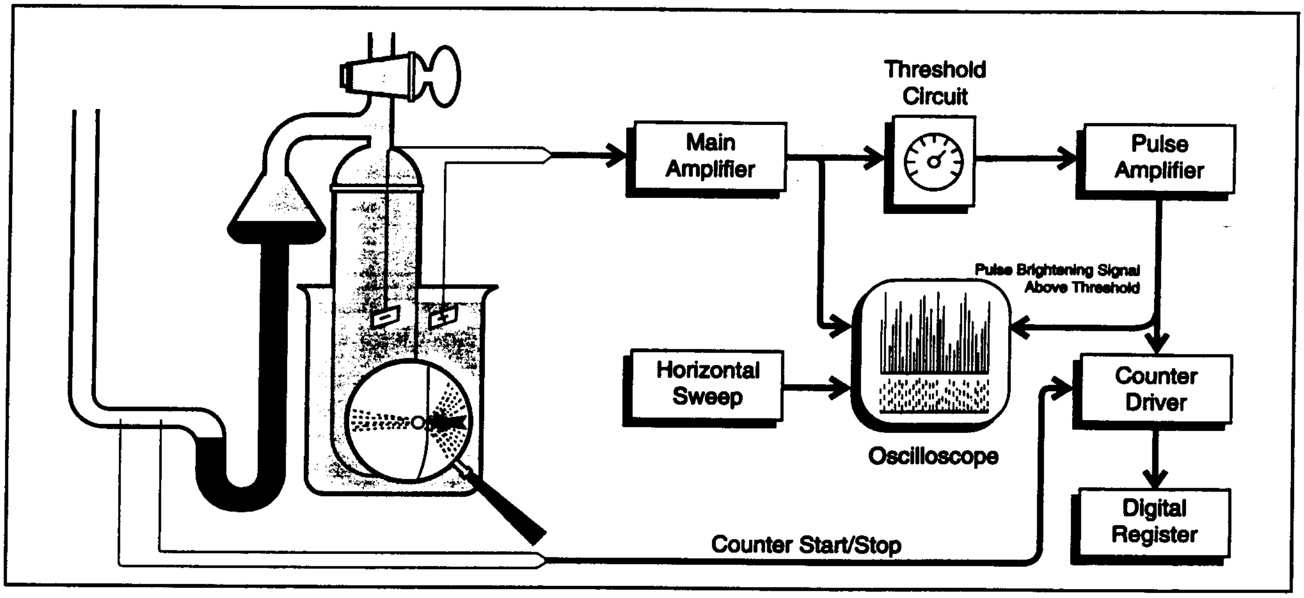


Figure 2.10 Coulter Counter Schematic *(Courtesy Coulter Electronics Ltd.)*

It must be realized that the particle "diameter" given by the counter is the diameter of a fictitious sphere with the same ***volume*** as the real particle. Thus, the more non-spherical the particle, the greater the error.

It should be noted that the Coulter Counter cannot distinguish between solid particles, oil droplets and gas bubbles. Therefore, water must be degassed prior to analysis and accurate particle counts cannot be obtained in waters containing oil droplets.

Light Scattering Counters

Instruments such as those manufactured by HIAC (HIAC Instruments Div., Pacific Scientific Co., Montclair, California) and Royco (Royco Instruments, Inc., Menlo Park, California) use the principle of light absorption/total scatter, or light blockage, to detect particles in a fluid. Water is flowed through a sensor cell and as each particle passes through the intense beam of light in the sensor, it scatters the light. The instrument measures the magnitude of each pulse of scattered light which is proportional to the ***surface area*** of the particle. The particle diameter given by the instrument is the diameter of a sphere with the same surface area as the particle.

The Spectrex Laser Particle Counter (Spectrex Corp., Redwood City, California) operates on the same principle, but uses a laser as a light source. Furthermore, in this instrument, the water sample remains stationary while the laser scans the sample. A sample container of water is placed in the instrument and the laser is activated. The beam revolves rapidly as shown in Figure 2.11, thus scanning a fixed volume of the sample. It gives a count of the total number of particles per milliliter above a certain manually set threshold between 1 μm and 100 μm.

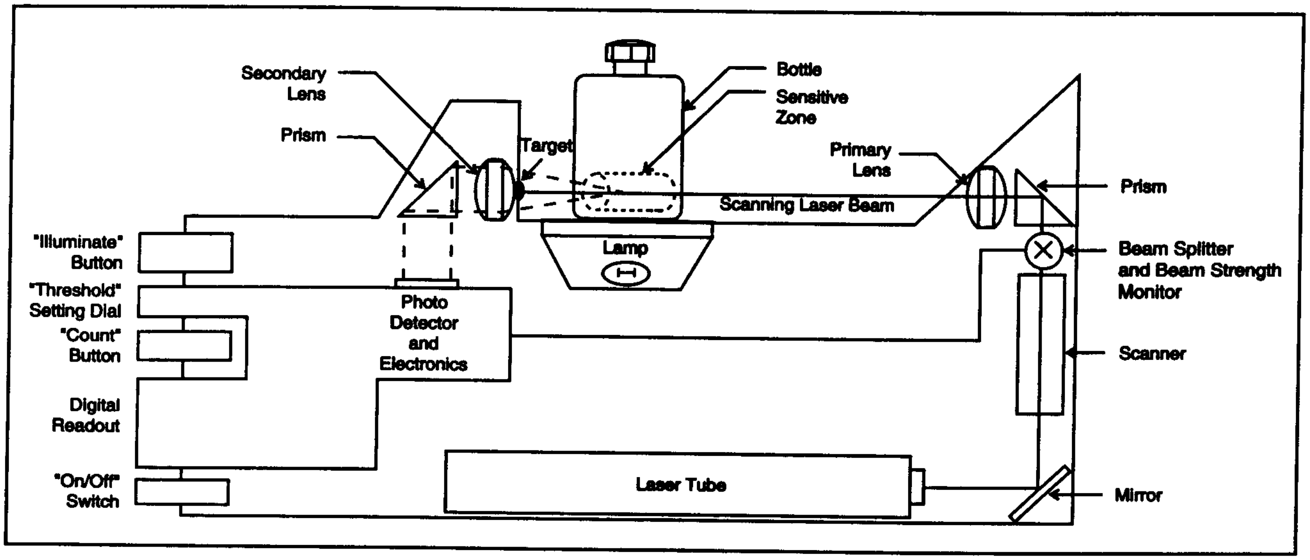


Figure 2.11 Spectrex Particle Counter *(Courtesy Spectrex)*

As in the case of the Coulter Counter, light-scattering particle counters cannot distinguish between solid particles, oil droplets and gas bubbles. Therefore, water must be degassed prior to analysis and accurate particle counts cannot be obtained in waters containing oil droplets.

Membrane Filter Analysis

Membrane filters ***should not be used*** to estimate the size of suspended solid particles in water, as the results have little meaning.

Two techniques are used.

1. Filter a water through two membrane filters in series, the second filter having a smaller pore size than the first, and measure the amount of suspended solids on each filter. The assumption is that the results can be used to estimate the concentration of particles in different size ranges.

   For example, filter one liter of water through a 5 µm pore-size filter followed by a 2 µm pore-size filter as shown in Figure 2.12. Determine the weight of suspended solids on each filter.

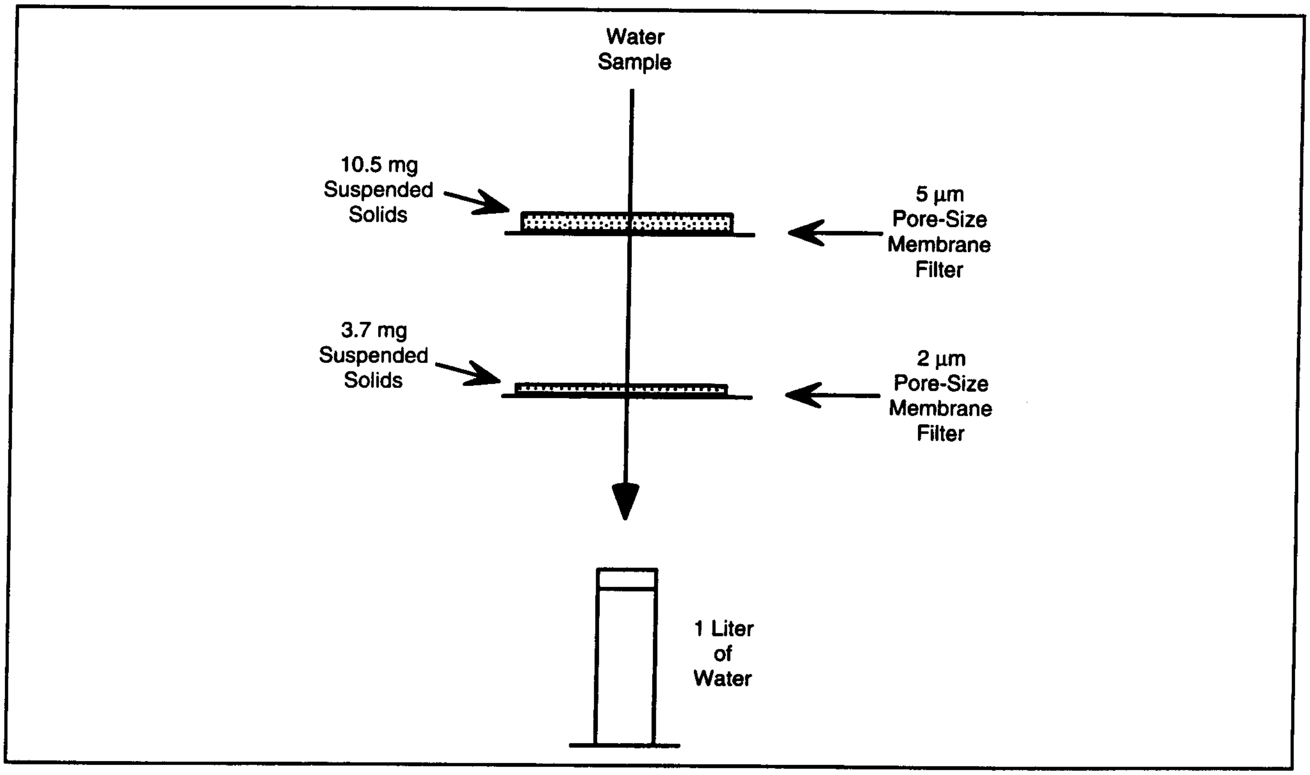


Figure 2.12 Filtration Through Membrane Filters in Series to Determine Particle Sizes

The results are erroneously interpreted as follows:

Particle Diameter	Concentration
$D \geq 5\mu m$	10.5 mg/L
$5\mu m > D > 2\mu m$	3.7 mg/L

This concept is analogous to a sieve analysis for sizing dry particles. However, the set of sieves is shaken vigorously throughout the sieving operation which prevents bridging and gives each particle in the sample the opportunity to pass through a given mesh-size.

Particle bridging occurs when particles are filtered from a liquid slurry which often results in the removal of particles smaller than the membrane pore size. The filter cake formed on the membrane becomes the filter.

2. The second technique employed is to filter a given water through a membrane of a given pore size. Then a second sample is filtered through a different pore size. Consider the example shown in Figure 2.13.

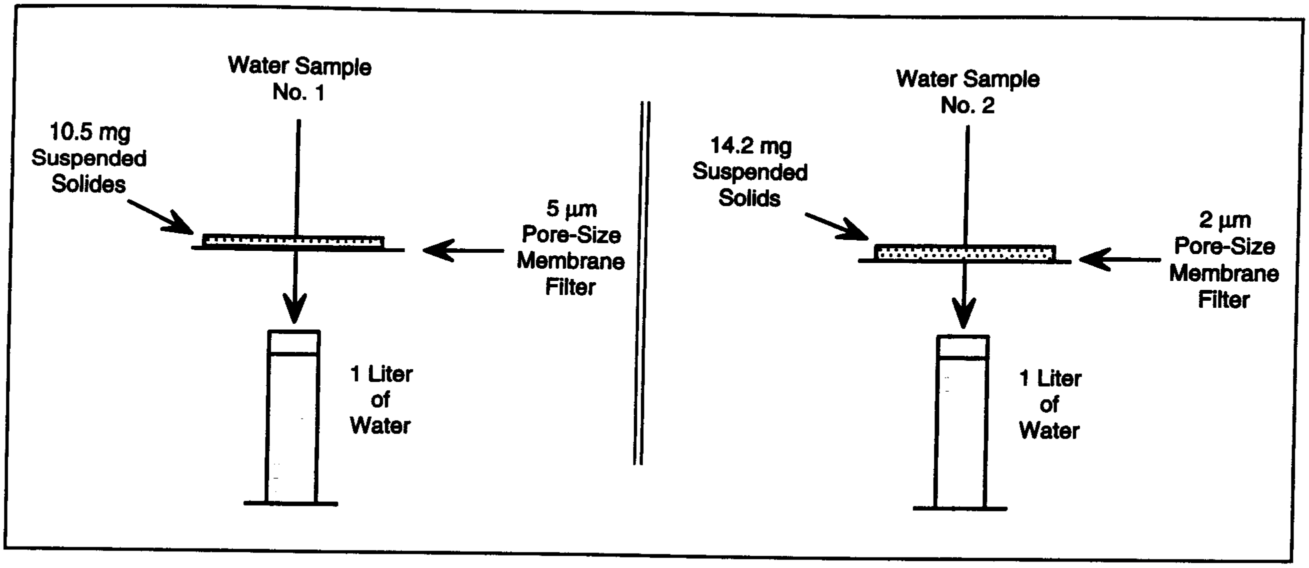


Figure 2.13 Filtration Through Membrane Filters in Parallel to Determine Particle Sizes

The results are erroneously interpreted as follows:

Particle Diameter	Concentration
$D \geq 5\mu m$	10.5 mg/L
$5\mu m > D > 2\mu m$	14.2 – 10.5 = 3.7 mg/L

Once again, the assumption is made that all particles with diameters less than the pore-size of the membrane filter being used will pass through the filter. However, this is not true because of particle bridging.

Filtration of particles from a liquid slurry is a process which is distinctly different from a sieve analysis of dry particles and ***should never be used*** to estimate particle sizes.

Turbidity

Turbidity is an optical property of a liquid which is related to the ability of undissolved particles to scatter light.

In most cases we are interested in a correlation between turbidity and suspended solids content. Unfortunately, ***no general correlation is possible*** because turbidity values are dependent upon the size, color, shape and refractive index of the particles, as well as the refractive index of the carrier medium. It is also dependent upon the wavelength of the incident light and the orientation of the scattered light detector, which means that different types of instruments can give different readings. A correlation between turbidity and suspended solids concentration can be made for a specific water containing a given quantity and size distribution of suspended particles. However, since turbidity values are a function of particle size, a change in particle size distribution will alter the measured turbidity.

Figure 2.14 illustrates the relationship between particle size and the amount of scattered light for a constant weight concentration of suspended particles. The optical response may be divided into three zones:

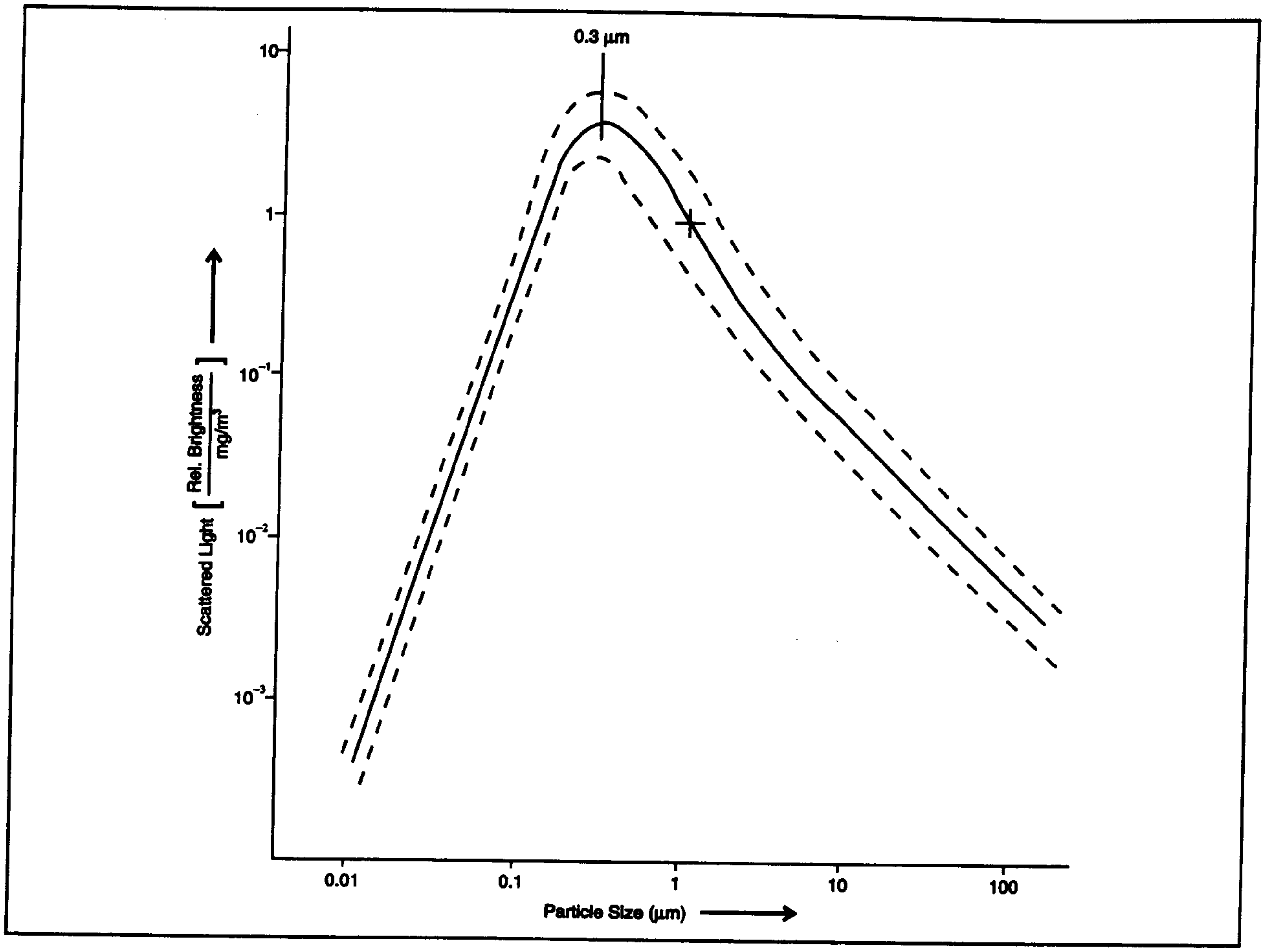


Figure 2.14 Scattered Light as a Function of Particle Size *(Courtesy Sigrist-Photometer AG)*

TABLE 2.15

Scattered Light vs Particle Size

Particle Size	Amount of Scattered Light
<0.1μm	Increases with particle size
0.1μm-1.0μm	Complex transition zone
>1.0μm	Proportional to total surface area. Decreases with particle size

Remember that these relationships apply when the concentration of suspended solids remains constant and only particle size changes. Above 1.0 μm, for example, the amount of light scattered is greater for a larger particle because it is proportional to surface area. However, as particle size increases, it takes fewer particles to give the same weight of suspended solids. The net result is a decrease in the total amount of light scattered.

When a ray of light hits a particle it is scattered in all directions. However, it is not scattered uniformly in all directions, with the result that the scattered light reading obtained for a given particle will be a function of the position of the detector.

For particles less than 0.1 μm diameter, the forward and backscattered intensities are equal, with half that intensity in the perpendicular direction (side scatter) as shown in Figure 2.15.

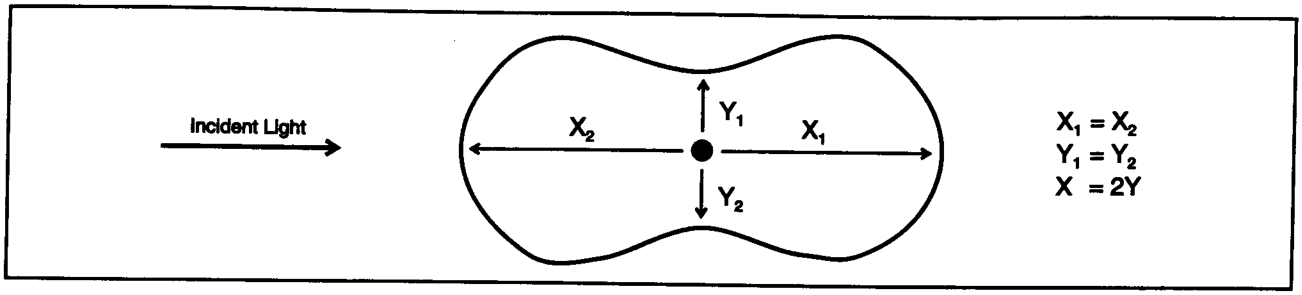


Figure 2.15 Angular Distribution of Scatter Light (Particle Diameter <0.1μm)

The pattern is not affected by particle shape as long as no dimension of the particle is greater than 0.1 μm.

For particles larger than 0.1 μm, the amount of forward scatter increases relative to the amount of back and side-scatter (Figure 2.16).

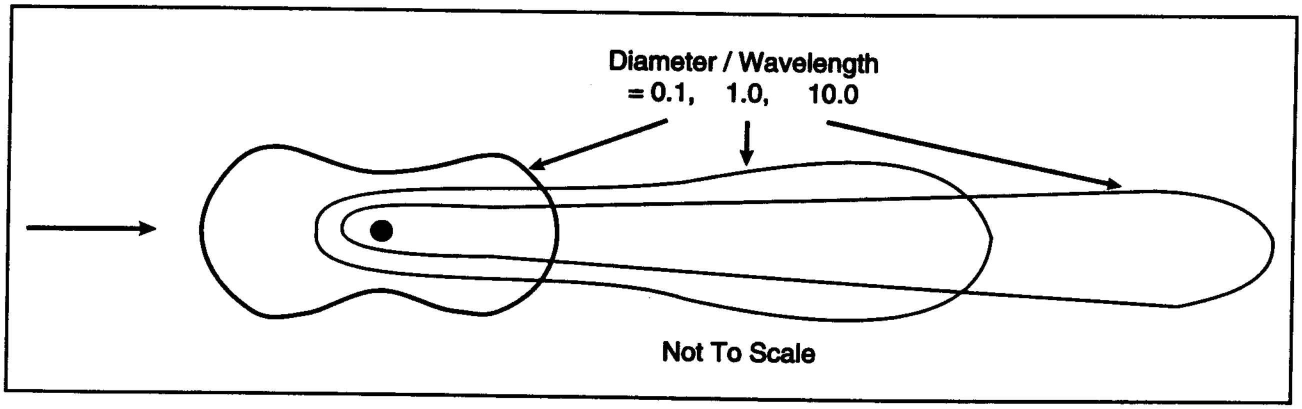


Figure 2.16 Angular Distribution of Scattered Light for Different Particle Diameters
(Courtesy Monitor Technology, Inc.)

The shape and orientation of non-spherical particles will modify the pattern, but in practical situations, the random orientation of the particles will generate essentially the same results as spherical particles of the same average volume.

There are many turbidity instruments on the market. The majority used in water injection systems either measure side scatter or forward scatter. An instrument which measures side scattered light at an angle of 90° to the incident light is called a nephelometer. Forward scatter instruments usually measure the scattered light at an angle of 15-30° to the incident light beam.

Selection of an instrument for a particular water should be based on a knowledge of the nature and size distribution of the suspended particles, and a careful investigation of the response characteristics of each instrument being considered.

The units in which turbidity measurements are reported can be extremely confusing.

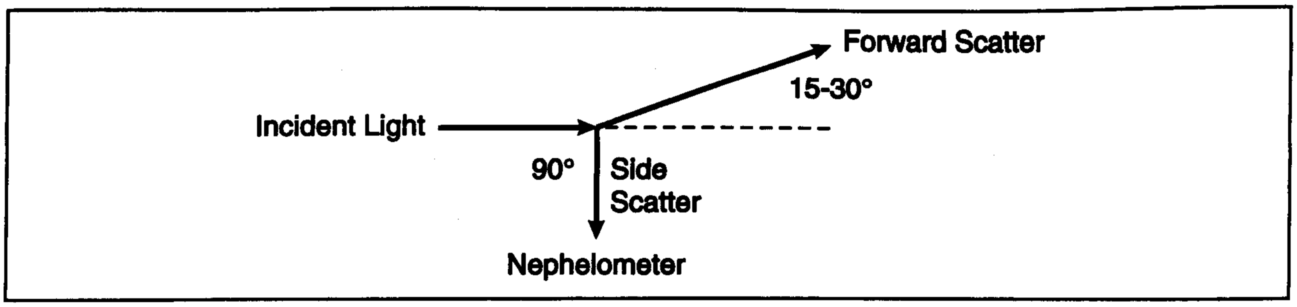


Figure 2.17 Scattered Light Direction

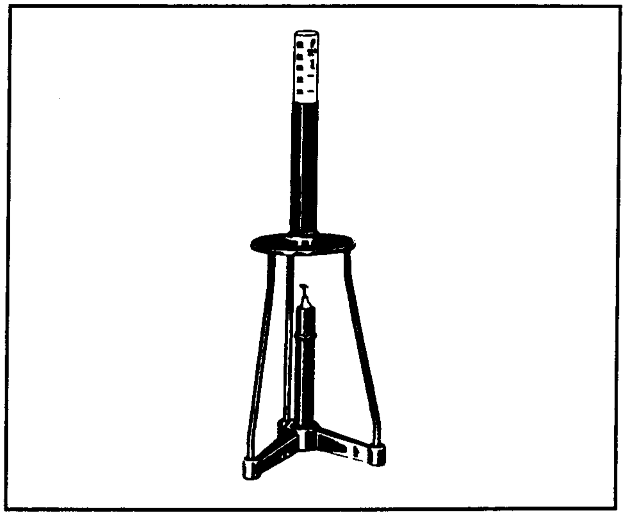


Figure 2.18 Jackson Candle Turbidimeter

The father of modern turbidimeters is the Jackson Candle Turbidimeter. It consists of a vertical glass tube, graduated in units of length, and a candle as shown in Figure 2.18.

A sample of liquid is poured into the tube until the candle can no longer be clearly seen. The height of liquid at which this occurs is dependent upon its turbidity. A standard table is used to convert this height into Jackson Candle Units (JCU's), also called Jackson Turbidity Units (JTU's). With the advent of modern turbidimeters, other units began to appear. These units are based on calibrations made with standard suspensions of materials such as kieselguhr (diatomaceous earth or SiO_2), fullers earth, or formazin (a polymer suspension). Of the many units in use, the following are the most common:

- FTU — Formazin turbidity unit. An instrument is calibrated in FTU's with a standard suspension of formazin. Unfortunately, at least three different "standard" suspensions are used, resulting in three different formazin units.
- NTU — Nephelometer turbidity units are used solely for nephelometers. Nephelometers can be calibrated with kieselguhr, fullers earth or formazin.
- PPM — Parts per million. Actually ppm of the calibration suspension, which usually is diatomaceous earth (SiO_2) or fullers earth. It's use was originally intended to detect breakthrough of DE particles downstream of DE filters. It is not the concentration of the suspended solids in the water.

To make matters more confusing, readings taken with a particular instrument in a given water may not agree with readings taken with another type of instrument in the same water, even when the same turbidity units are being used. This can result from differences in calibration techniques, instrument design or the angle at which the scattered light sensor is located. Conversion among different unit systems must be made with extreme caution.

In summary, turbidimeters are extremely valuable instruments for monitoring suspended solids levels in water systems. However, a separate correlation between suspended solids concentration and turbidity values must be made for each water using a specific turbidity measuring instrument.

Field Water Analyses

As previously stated, certain water properties change very quickly after sampling. The determinations listed in Table 2.16 must be made on-site for maximum accuracy:

- The suspended solids should be collected in the field with a membrane filter by allowing a stream of water to flow through the filter. The filter paper and the collected solids are normally taken to a laboratory for analysis.
- Particle size distribution carried out with either a Coulter Counter or a light scattering device must be performed on a fresh sample to minimize the effect of precipitation of solids after sampling.
- The culture media should be inoculated in the field immediately after sampling, if possible. (See Chapter 5)

TABLE 2.16

On-Site Measurements

Parameters to be Measured On-Site	
pH	Temperature
Carbonate Ion	Suspended Solids Concentration(2.1)
Bicarbonate Ion	Particle Size Distribution(2.2)
Dissolved Oxygen	Turbidity
Dissolved Carbon Dioxide	Water Quality
Total Sulfides as H_2S	Bacteria Counts(2.3)

It is difficult to overemphasize the importance of field analyses. Certain properties may begin to change within minutes; others will be stable for several hours; and some are stable indefinitely.

For example, the pH and dissolved gas content of produced water will usually begin to rise immediately after the sample is taken. This results from the fact that dissolved acid gases begin to escape from solution as soon as the sample is removed from the system due to the reduction in pressure.

The rise in pH along with an increase in temperature may result in the formation of calcium carbonate scale. Bacteria in the sample may begin to multiply within a few hours — or they may begin to die — depending on specific conditions. Little or no H_2S or CO_2 may be found in the sample after a short time period.

If the sample contains dissolved iron, exposure to atmospheric oxygen will result in the precipitation of the iron due to reaction with oxygen.

$$4Fe^{++} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8H^+$$

The generation of hydrogen ions will cause the pH of the sample to drop and lead to an error in the measured value. This is yet another reason why the pH should be measured on-site in a flowing sample.

Thus, if the sample were transported to a laboratory and analyzed after several days, the resulting analyses would give a very distorted picture of the water as it actually existed in the system, because of the changes in water composition which took place after the sample was removed from the system.

Had it been a sample of fresh surface water or a sample of seawater, different changes would be anticipated. However, regardless of the water source, field analyses are absolutely necessary for an accurate and meaningful assessment of oilfield water problems.

Field water analysis kits are available from several manufacturers, as are oxygen analysis equipment, pH meters, and membrane filter equipment. This equipment, and someone skilled in its use, is required during initial sampling, for monitoring of system performance, and for trouble shooting. If you or someone in your organization do not have field analysis skills, then reliable outside personnel should be retained to do the work for you. The important point is that on-site measurement of certain water properties is an integral part of the successful design and operation of a water injection system. Make certain that this point is not overlooked, and that the measurements are carried out by experienced personnel.

General Instructions for Making Analytical Determinations in the Field

Cleanliness

The axiom that "cleanliness is next to Godliness" is the first rule of life to an analytical chemist. Although we may occasionally get a bit sloppy in performing analyses in the field, it is important that we follow this rule as closely as possible in our own analytical work.

The laboratory analyst uses glass beakers, flasks and burettes which he carefully washes and cleans between each usage. This mode of operation is very unhandy in the field. Experience has shown that the use of plastic beakers (disposable), disposable plastic or glass syringes, plastic bottles (disposable) and glass bottles where necessary (disposable) is much easier. Our motto is "Never use anything twice." Throw it away rather than risk contaminating the sample.

The reasoning behind this preoccupation with cleanliness is extremely sound. If you go to a great deal of time and trouble to obtain an uncontaminated, representative water sample and then use a dirty beaker or burette to run your analysis, you have just wasted a lot of time. Your sample is contaminated by any material which may have remained in the analytical ware from the previous analysis. It may or may not have ruined your present analysis, but the chances are good that it has. There are many sources of uncertainty under the best of circumstances. Do not use dirty lab ware and avoid at least one of the known sources of error.

It is permissible to re-use some of the disposable beakers or syringes when analyzing a given water sample. Between determinations they should be carefully rinsed with de-ionized water or preferably with some of the water sample of interest. They must be thrown away after completing the analysis of the sample.

Some discretion is required in the question of cleanliness. If you want to take the time and trouble to clean up your plastic beakers and syringes between determinations, you can do so, just as is done with glassware in a laboratory. However, it is simply often very inconvenient or impossible to do so in the field. The use of inexpensive, disposable materials gives you the alternative of starting with new, clean materials each time. This procedure offers the dual advantage of saving you time and trouble, and of minimizing the possibility of contamination.

Use of Syringes

Syringes are very handy for measuring water sample volumes in the field instead of burettes. A sample volume of 10 mL or 25 mL is most common.

Syringes can also be used for titrating instead of a burette. One-mL and 5-mL syringes are most common for this purpose.

You should always use at least one-half of the volume of any syringe, whether you are measuring a sample or titrating. With less than half of a syringe volume, you lose accuracy. Use a smaller syringe instead.

Normally, when measuring a water sample volume, a needle is not used with the syringe. Titrations are made with syringes equipped with needles so that the titrant may be dispensed drop-by-drop. The use of syringes is detailed in Appendix 10.

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3

WATER FORMED SCALES

Solubility is defined as the limiting amount of a solute which can be dissolved in a solvent under a given set of physical conditions. The chemical species of interest to us are present in an aqueous solution as ions. Certain combinations of these ions are compounds which have very little solubility in water. The water has a limited capacity for maintaining these compounds in solution, and once this capacity, or solubility, is exceeded the compounds precipitate from solution as solids. Therefore, precipitation of solid materials which may form scale can occur if ***both*** of the following conditions are satisfied:

1. The water contains ions which are capable of forming compounds of limited solubility.
2. There is a change in physical conditions or water composition which lowers the solubility below the concentrations present.

Solid precipitates may either stay in suspension in the water, or they may form a coherent scale on a surface such as a pipe wall. Formation plugging may occur by filtration of suspended particles from the water. Or, a solid scale may form on the formation face. Either is undesirable. The difficulty of removal varies with the type of plugging which has occurred.

Scale formation frequently restricts flow through injection and flow lines, and tubing strings. It causes pump wear or plugging and creates additional rod loads when it forms on sucker rods. Fire tubes in all types of heaters fail prematurely when scale formation results in overheating. Corrosion is often more severe under a scale deposit.

Water formed scales are responsible for many production problems and their effective control should be one of the primary objectives of any efficient water handling operation.

COMMON SCALES

Of the many possible water formed scales, only a few are commonly found in oilfield waters. These scales are listed in Table 3.1 along with the primary variables which affect their solubility.

Calcium Carbonate

Calcium carbonate scale can be formed by the combination of calcium ion with either carbonate or bicarbonate ions as follows:

$$Ca^{++} + CO_3^{=} \rightarrow CaCO_3 \downarrow \qquad (3.1)$$

$$Ca^{++} + 2\left(HCO_3^-\right) \rightarrow CaCO_3 \downarrow + CO_2 + H_2O \quad (3.2)$$

TABLE 3.1

Common Oilfield Scales

Name	Chemical Formula	Primary Variables
Calcium Carbonate (Calcite)	$CaCO_3$	Partial pressure of CO_2, pH, temperature, total pressure, total dissolved solids.
Calcium Sulfate Gypsum (Most Common) Hemi-Hydrate Anhydrite	 $CaSO_4 \cdot 2\ H_2O$ $CaSO_4 \cdot 1/2\ H_2O$ $CaSO_4$	Temperature, total dissolved solids, pressure.
Barium Sulfate	$BaSO_4$	Temperature, total dissolved solids, pressure.
Strontium Sulfate	$SrSO_4$	Temperature, total dissolved solids, pressure.
Iron Compounds Ferrous Carbonate Ferrous Sulfide Ferrous Hydroxide Ferric Hydroxide Ferric Oxide	 $FeCO_3$ FeS $Fe(OH)_2$ $Fe(OH)_3$ Fe_2O_3	Dissolved gases, corrosion. Temperature, pressure, pH

Effect of CO_2 Partial Pressure

The presence of CO_2 increases the solubility of $CaCO_3$ in water. When carbon dioxide dissolves in water, it forms carbonic acid, which ionizes according to the following series of equations:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad (3.3)$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad (3.4)$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^= \quad (3.5)$$

Only a small percentage of the bicarbonate ions dissociate at the pH values found in most injection waters to form H^+ and $CO_3^=$, as shown in Figure 3.1. Bicarbonate ions vastly outnumber the number of carbonate ions present under normal circumstances. Therefore, it is thought that Equation 3.2 is the more accurate expression for the precipitation of calcium carbonate.(3.1)

As the concentration of CO_2 in solution is increased, the reaction shifts to the left, resulting in less $CaCO_3$ precipitation. The water also becomes more acidic (the pH decreases) with the addition of CO_2 to the water.

The amount of CO_2 that will dissolve in water is proportional to the partial pressure of CO_2 in the gas in contact with the water:

$$Partial\ Pressure\ of\ CO_2 = \left(Mole\ Fraction\ of\ CO_2\ in\ Gas\right) \times \left(Total\ Pressure\right) \quad (3.6)$$

$$Mole\ Fraction\ of\ CO_2 = \%CO_2\ in\ Gas + 100 \quad (3.7)$$

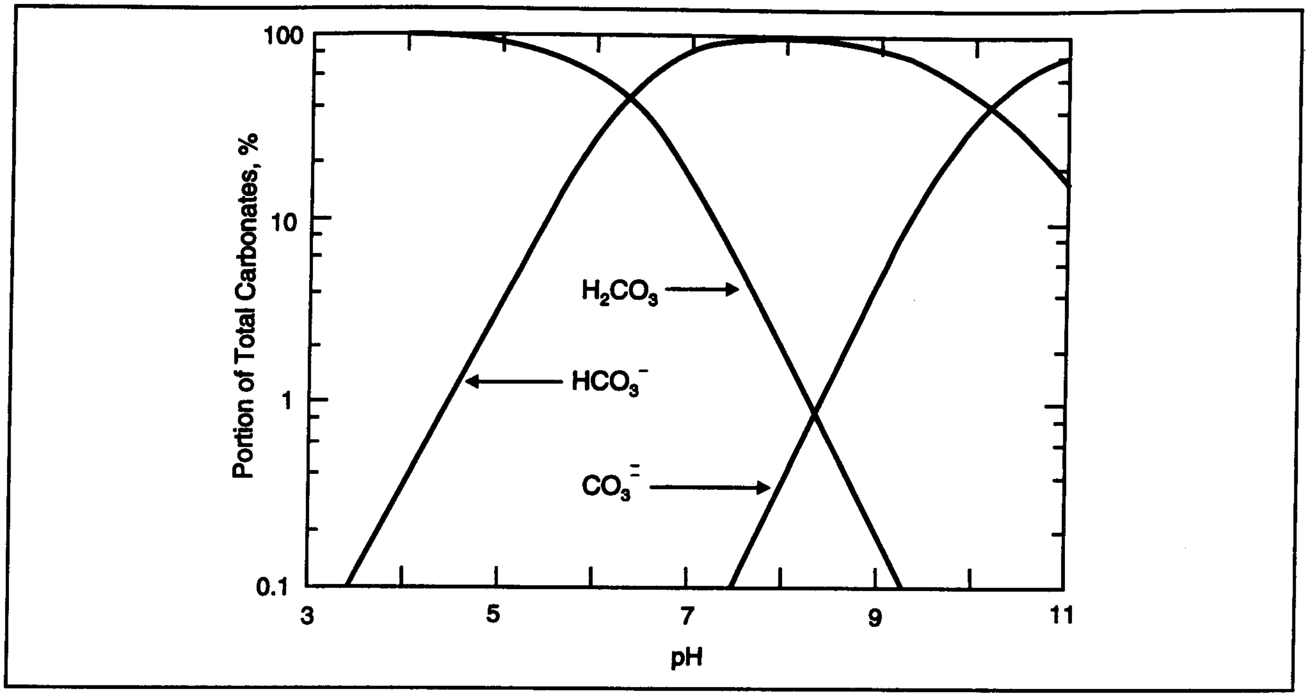

Figure 3.1 Ionization of Carbonic Acid as a Function of pH

Hence, if a two-phase (gas + water) system is operating at 100 psia [690 kPa] and the associated gas contains 10 mol % CO_2 (1 mole of CO_2 per 10 moles of gas), the partial pressure of CO_2 in the gas is:

$$(0.1)(100) = 10 psia\,[69 kPa]$$

So, if either the system pressure or the percentage of CO_2 in the gas were to increase, the amount of CO_2 dissolved in the water also would increase.

Figure 3.2 illustrates the effect of CO_2 partial pressure on the pH of water containing little or no dissolved minerals. This data should not be applied to brines since the presence of dissolved minerals changes the relationship between pH and the amount of dissolved CO_2.

The effect of CO_2 pressure on the solubility of $CaCO_3$ in pure water is shown in Figure 3.3.

This data illustrates that $CaCO_3$ solubility increases with increased CO_2 partial pressures. The effect becomes less pronounced as the temperature increases.

The reverse is also true. It is one of the major causes of $CaCO_3$ scale deposition. At any point in the system where a pressure drop is taken, the partial pressure of CO_2 in the gas phase decreases, CO_2 comes out of solution, and the pH of the water rises. This shifts Reaction 3.2 to the right and may cause $CaCO_3$ precipitation.

Effect of pH

The amount of CO_2 present in the water affects the water pH and the solubility of calcium carbonate. However, it really does not matter what causes the acidity or alkalinity of the water. The higher the pH, the more likely that precipitation will occur.

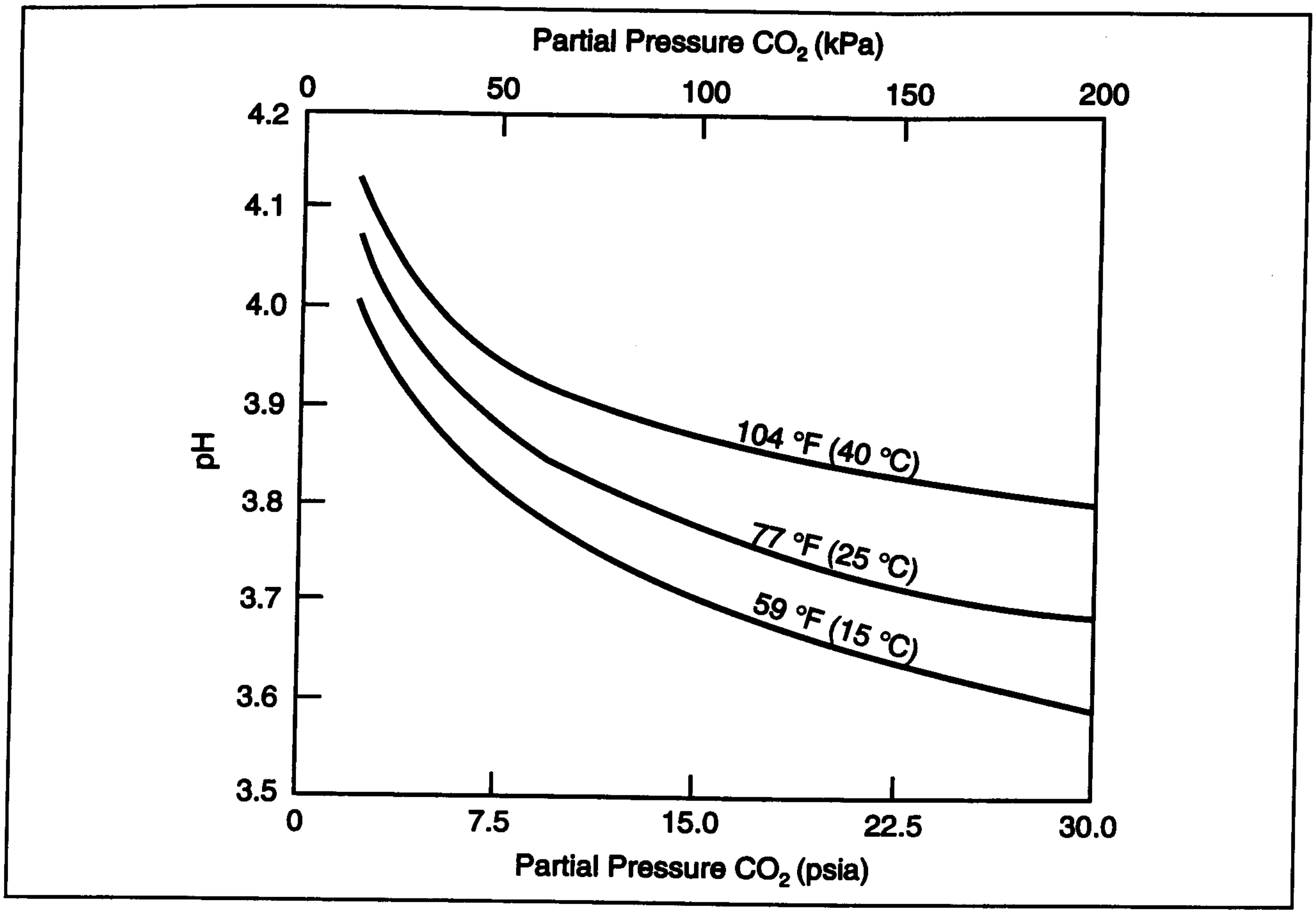

Figure 3.2 Effect of CO_2 Partial Pressure on the pH of Water (3.2)

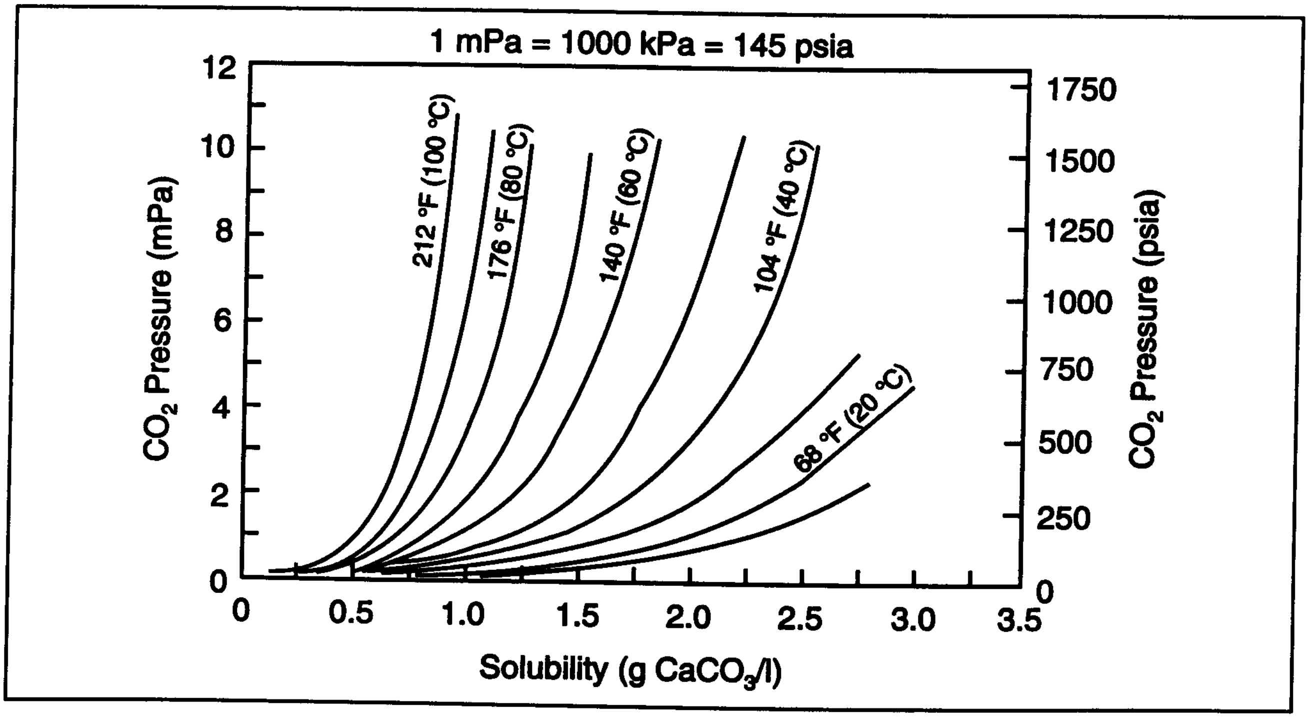

Figure 3.3 Effect of CO_2 Pressure on Calcium Carbonate Solubility (3.3)

Effect of Total Pressure

The solubility of calcium carbonate in a two phase system increases with increased pressure for two reasons:

- Increased pressure increases the partial pressure of CO_2 and increases the solubility of $CaCO_3$ in water as previously explained.
- Increased pressure also increases the solubility due to thermodynamic considerations which will not be discussed here.
- Pressure drops are one of the primary causes of calcium carbonate scale deposition in production systems. In addition to decreasing the solubility of $CaCO_3$ due to the loss of CO_2 and the thermodynamic pressure effect, pressure drops across chokes and valves induce turbulence in the water which helps to overcome supersaturation effects and initiate precipitation.

In single phase (all water) systems, such as a water injection system, increased pressure increases the solubility of calcium carbonate solely due to thermodynamic considerations.

Effect of Temperature

Contrary to the behavior of most materials, calcium carbonate becomes less soluble as temperature increases — the hotter the water gets, the more likely $CaCO_3$ scale will form.

Hence, a water which is non-scaling at the surface may result in scale formation in an injection well if the downhole temperature is sufficiently high. This is also the reason that $CaCO_3$ scale is often found on the fire-tubes of heating equipment.

The solubility of $CaCO_3$ in pure water at 1 atmosphere CO_2 partial pressure as a function of temperature is shown in Figure 3.4.

Methods for calculating the temperature at which $CaCO_3$ scale may be anticipated are given in a later section.

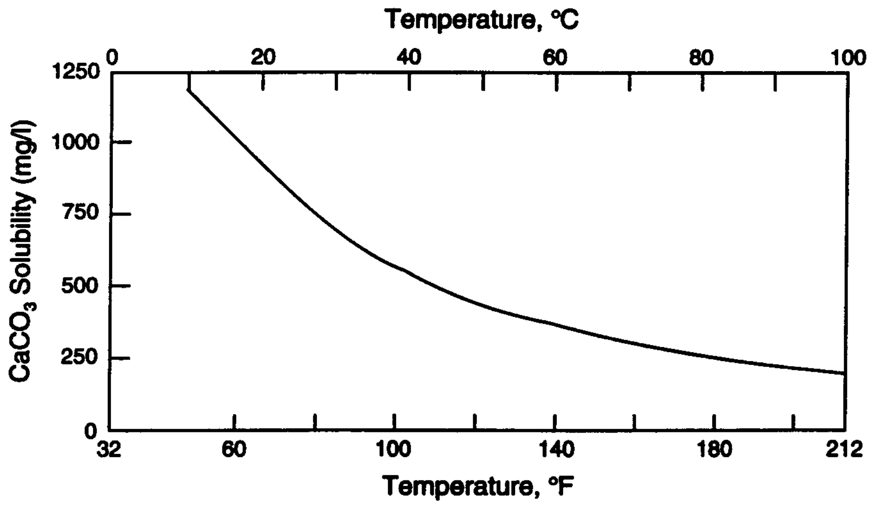

Figure 3.4 Calcium Carbonate Solubility(3.3)

Effect of Dissolved Salts

Calcium carbonate solubility increases as the salt content of the water increases. For instance, adding 200 000 mg/L NaCl to distilled water increases the $CaCO_3$ solubility from 100 mg/L to 250 mg/L.

Actually, the higher the total dissolved solids (not counting calcium or carbonate ions), the greater the solubility of $CaCO_3$ in the water and the lower the scaling tendency up to a maximum of about 200 000 mg/L.

In summary, the likelihood of forming calcium carbonate scale:

- Increases with temperature
- Increases as partial pressure of CO_2 decreases
- Increases as the pH increases
- Increases as total dissolved salts decreases
- Increases as the total pressure decreases

Calcium Sulfate

The precipitation of calcium sulfate from water results from the reaction:

$$Ca^{++} + SO_4^{=} \rightarrow CaSO_4 \downarrow$$

Forms of Calcium Sulfate

Most calcium sulfate deposits found in the oilfield are gypsum. According to Oddo and Tomson, the most likely scale to form from brines will be gypsum at temperatures less than 176°F [80°C].(3.4)

Between 176°F [80°C] and 250 F[121°C], any of the three types of calcium sulfate may form, with gypsum being more likely at the low end of the temperature range and anhydrite more likely at the high end. Hemi-hydrate is commonly found in this temperature range in non-turbulent systems with high ionic strengths.

Above 250°F [121°C], any calcium sulfate scale formed will almost certainly be anhydrite.(3.4)

Effect of Temperature

Gypsum solubility in pure water increases with temperature up to about 100°F [38°C], then decreases with temperature as shown in Figure 3.5.

This is quite different from the temperature-solubility behavior of $CaCO_3$. First, gypsum is considerably more soluble than $CaCO_3$ in the normal temperature range of interest. Second, the maximum in the gypsum curve tells us that an increase in temperature could either increase or decrease the solubility of gypsum depending on which part of the temperature curve we're concerned with. This is decidedly different from $CaCO_3$ where an increase in temperature always decreases the solubility.

Note that above about 100°F [38°C], anhydrite becomes less soluble than gypsum, so it could reasonably be expected that anhydrite might be the preferred form of $CaSO_4$ in deeper, hotter wells. Actually, the temperature at which the scale changes form from gypsum to anhydrite or hemi-hydrate is a function of many factors, including pressure, dissolved salt content, flow conditions, and the speed at which different forms of $CaSO_4$ can precipitate from solution.

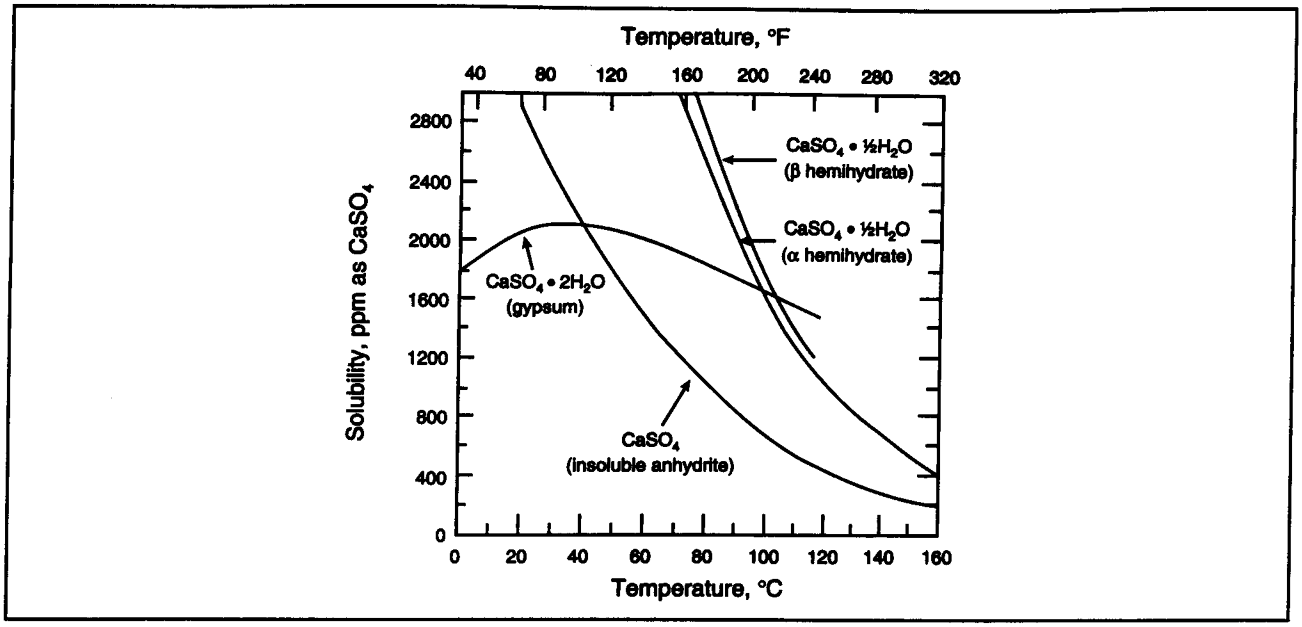

Figure 3.5 Solubility of Calcium Sulfate in Pure Water (3.5)

Predicting which form of calcium sulfate will precipitate under a given set of conditions is very difficult. Even though anhydrite would be expected above 100°F [38°C] in preference to gypsum due to its lower solubility, gypsum may be found at temperatures up to 212°F [100°C].

It is often difficult to precipitate anhydrite directly from solution. However, with the passage of time, gypsum can dehydrate to form anhydrite.

Above 212°F [100°C], anhydrite will precipitate directly in a stirred or flowing system. If the system is quiescent, hemi-hydrate solubility becomes limiting.(3.6) Conversion to anhydrite could be expected with time.

Effect of Dissolved Salts

The presence of NaCl or dissolved salts other than calcium or sulfate ions increases the solubility of gypsum or anhydrite just as it does for $CaCO_3$ up to a salt concentration of about 150 000 mg/L. Further increases in salt content decrease $CaSO_4$ solubility. (Figure 3.6)

Effect of Pressure

Increased pressure increases the solubility of all forms of calcium sulfate due to thermodynamic considerations which will not be discussed here.(3.7,3.8)

Pressure drops are one of the primary causes of calcium sulfate scale deposition in production systems. In addition decreasing the solubility due to thermodynamic considerations, pressure drops across chokes and valves induce turbulence in the water which helps to overcome supersaturation effects and initiate precipitation.

The effect of pressure and temperature on anhydrite solubility is shown in Figure 3.7. Note that the pressure effect decreases as temperature increases.

Effect of pH

pH has little or no effect on the solubility of calcium sulfate.

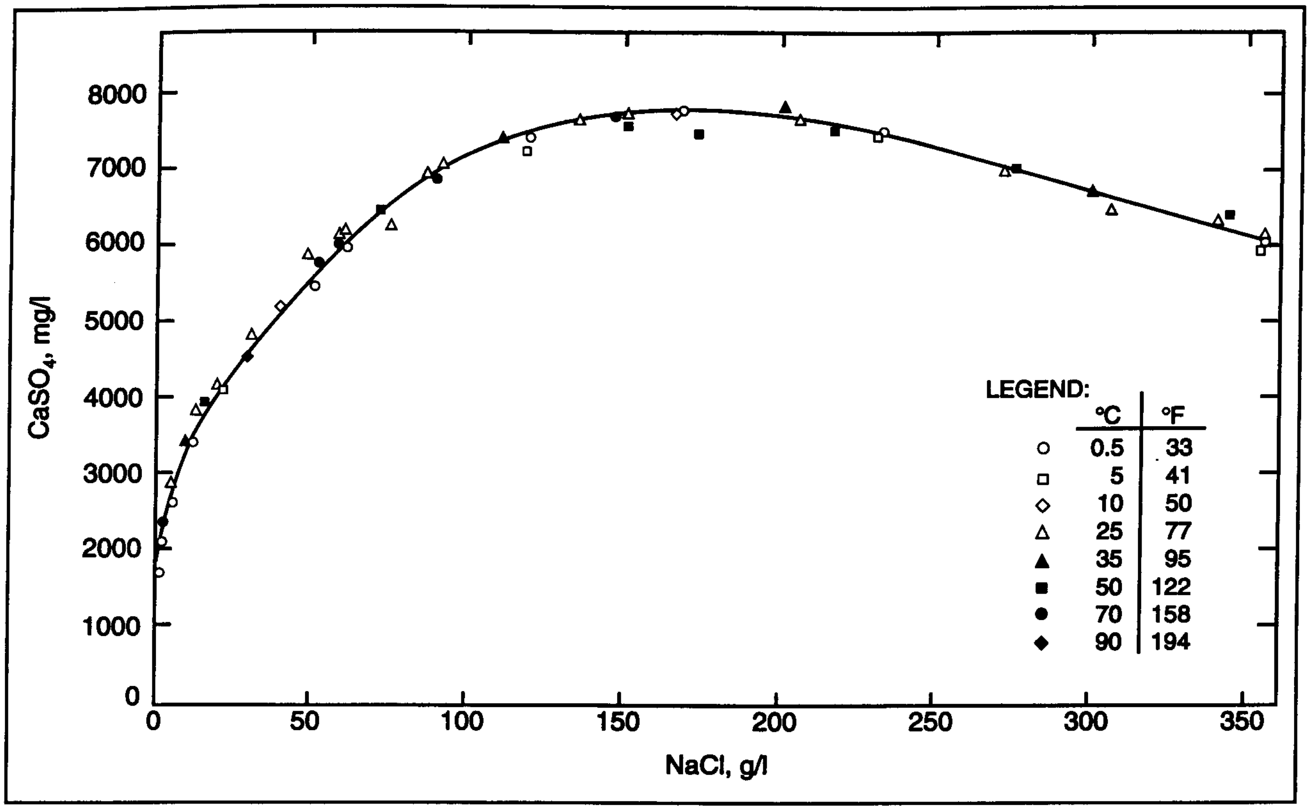

Figure 3.6 Solubility of Gypsum in NaCl Brines[3.6]

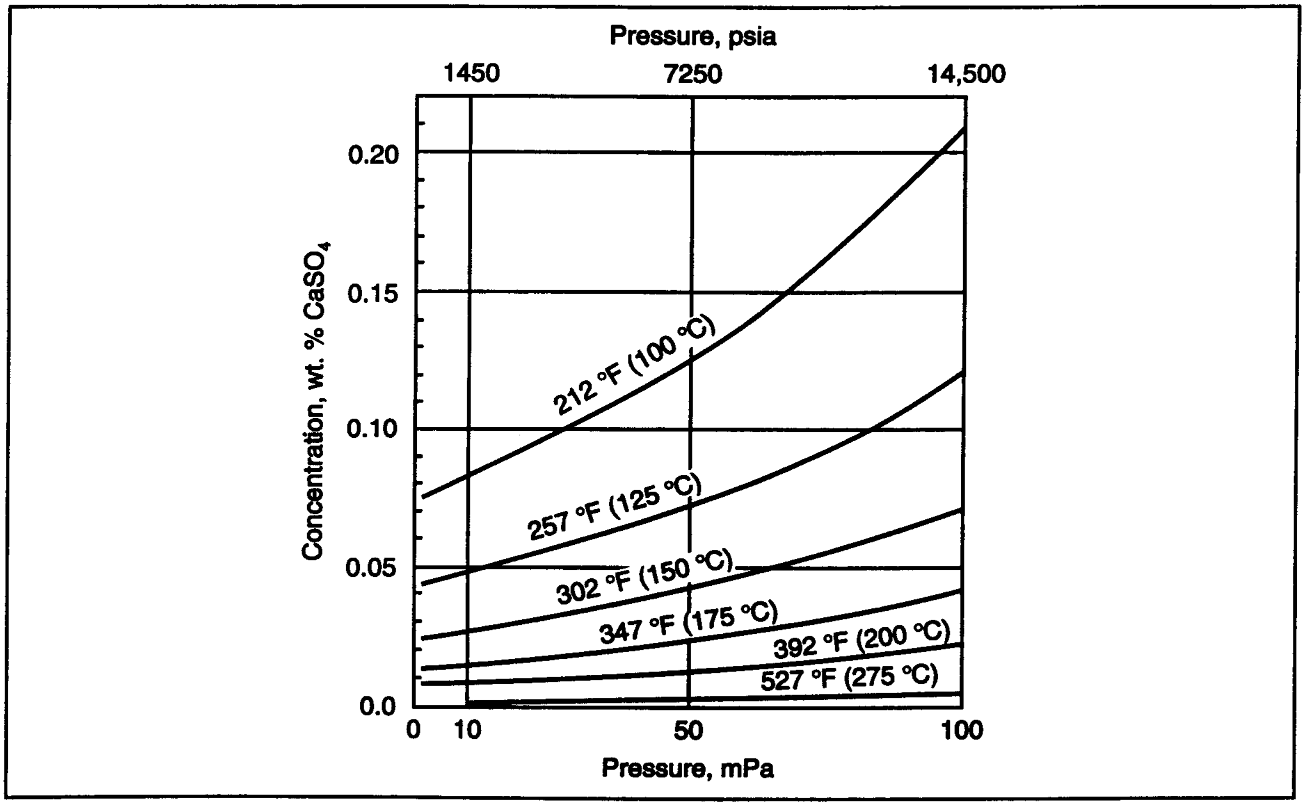

Figure 3.7 Effect of Pressure and Temperature on $CaSO_4$ (Anhydrite) Solubility[3.9]

Barium Sulfate

Barium sulfate is the least soluble of the scales we have discussed thus far.

$$Ba^{++} + SO_4^{=} \rightarrow BaSO_4 \downarrow$$

Table 3.2 compares the solubility of the three scales mentioned thus far, in distilled water at 77°F [25°C]:

TABLE 3.2

Comparative Solubilities at 25°C

Scale	Solubility (mg/L)
Gypsum	2080
Calcium Carbonate	53
Barium Sulfate	2.3

The extreme insolubility of $BaSO_4$ makes it very likely that scaling will occur if both Ba^{++} and $SO_4^{=}$ ions are present in a water.

Most barium sulfate scales also contain some strontium sulfate.

Effect of Temperature

Barium sulfate solubility increases with temperature up to 212°F [100°C]. The solubility in distilled water increases from 2.3 mg/L at 77°F [25°C] to 3.9 mg/L at 203°F [95°C] as shown in Figure 3.8.(3.10) The increase is fairly substantial percentage wise, but barium sulfate is still quite insoluble even at this higher temperature.

Above 212°F [100°C] the solubility decreases with temperature in waters with TDS values less than about 50 000 ppm. The solubility in higher salinity waters shows normal solubility behavior and increases with temperature as shown in Figure 3.9.(3.11)

Because of the increase in solubility over normal temperature ranges, barium sulfate usually presents no downhole scaling problems in an injection well if it is non-scaling at surface conditions. It is more commonly a problem in producing or water-supply wells.

Effect of Dissolved Salts

The solubility of barium sulfate in water is increased by foreign dissolved salts just as in the case of calcium carbonate and calcium sulfate. The addition of 100 000 mg/L of NaCl to distilled water increases the solubility of $BaSO_4$ from 2.3 mg/L to 30 mg/L at 77°F [25°C]. Maintaining 100 000 mg/L NaCl and increasing the temperature to 203°F [95°C].will increase the $BaSO_4$ solubility to about 65 mg/L.(3.1)

Figures 3.8 and 3.9 illustrates the effect of salinity on $BaSO_4$ solubility over a wide range of temperatures. The data in Figure 3.8 is plotted as a function of molar ionic strength rather than sodium chloride concentration. An ionic strength of 1.0 is equivalent to a sodium chloride concentration of approximately 60 000 mg/L. Ionic strength is defined later in this chapter and an example calculation is given in Appendix 14.

As a rule of thumb, you can assume that $BaSO_4$ solubility will double as the temperature is raised from 77°F [25°C] to 203°F [95°C] regardless of the dissolved salt concentration. The effect of dis-

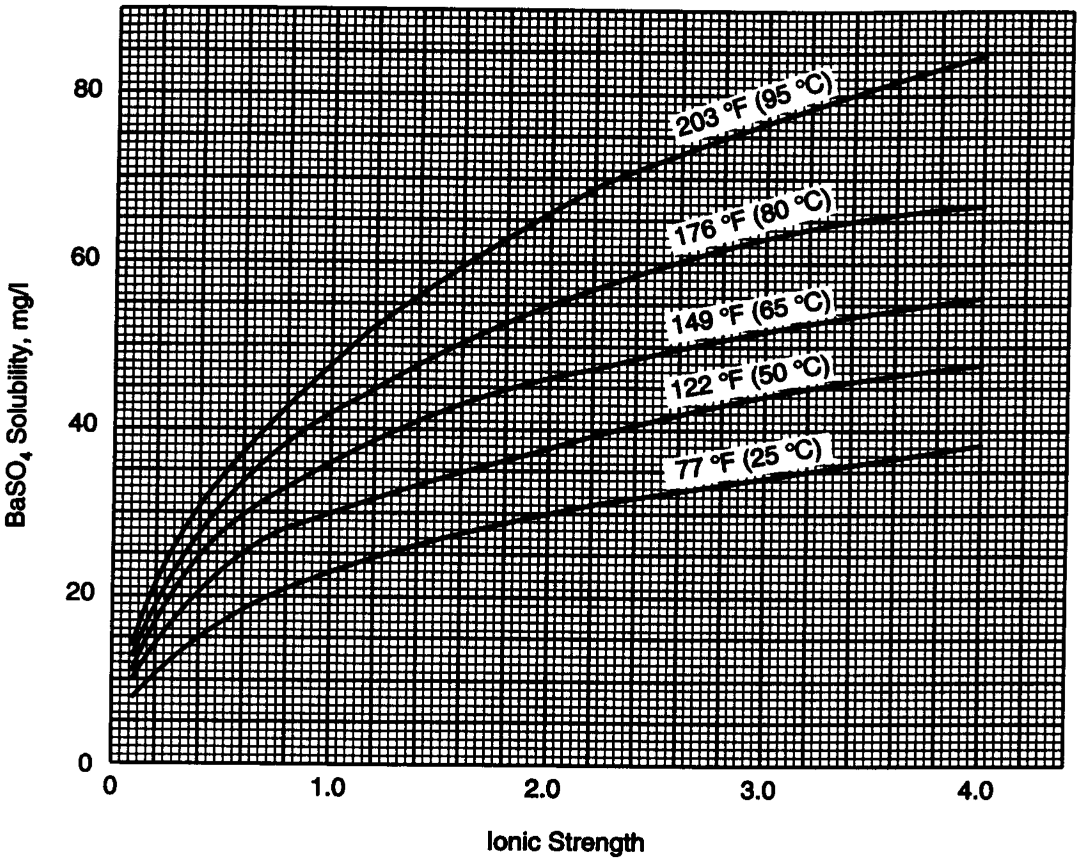

Figure 3.8 Barium Sulfate Solubility in NaCl Solutions Calculated from Templeton's Data(3.10)

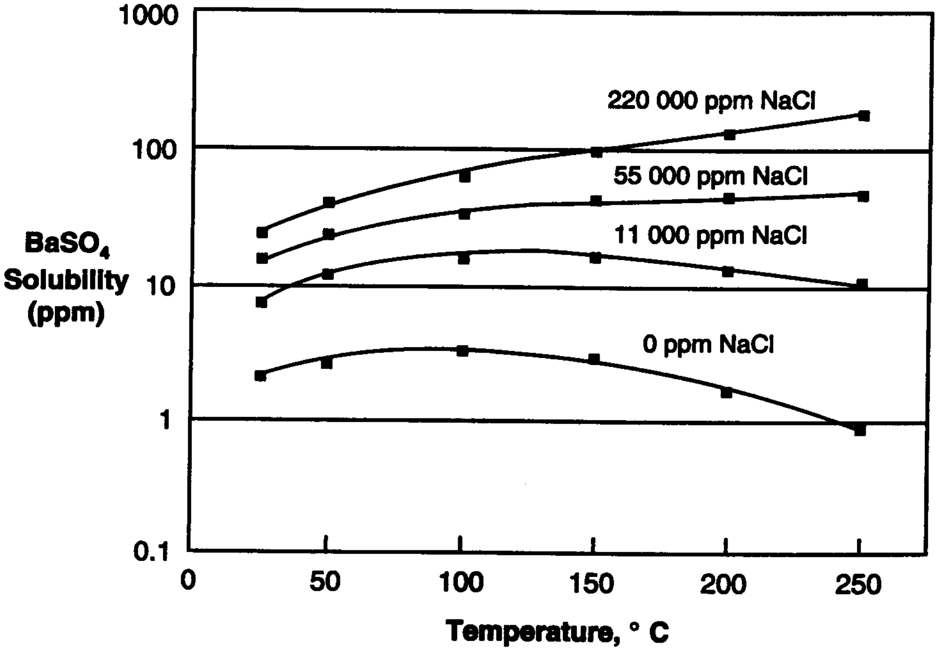

Figure 3.9 Effect of Temperature and Salinity on Barium Sulfate Solubility at Atmospheric Pressure(3.11)

solved salts is much more pronounced, as demonstrated by the 13-fold increase brought about by the addition of 100 000 mg/L NaCl with no change in temperature.

Effect of Pressure

Increased pressure increases the solubility of barium sulfate due to thermodynamic considerations which will not be discussed here.

Pressure drops are one of the primary causes of barium sulfate scale deposition in production systems. In addition decreasing the solubility due to thermodynamic considerations, pressure drops across chokes and valves induce turbulence in the water which helps to overcome supersaturation effects and initiate precipitation.

Increased pressure increases the solubility of $BaSO_4$. Figure 3.10 shows the effect of pressure and temperature on barium sulfate solubility in pure water.

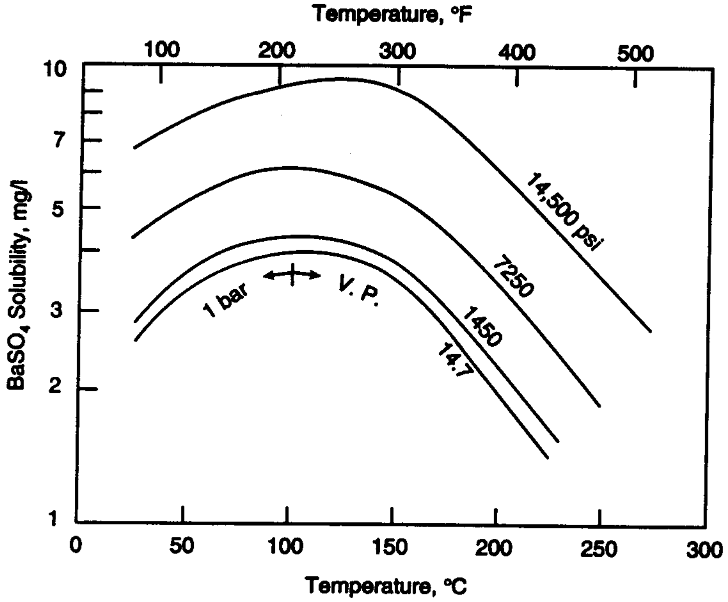

Figure 3.10 Effect of Pressure and Temperature on Barium Sulfate Solubility in Pure Water(3.11)

Effect of pH

pH has little or no effect on the solubility of barium sulfate.

Strontium Sulfate

Strontium sulfate is considerably more soluble than barium sulfate, with a solubility of 129 mg/L in pure water at a temperature of 77°F [25°C].(3.12)

$$Sr^{++} + SO_4^{=} \rightarrow SrSO_4 \downarrow$$

Effect of Temperature

Strontium sulfate solubility decreases with temperature.(3.12-3.14) In pure water the solubility decreases to 68 mg/L at 257°F [125°C].(3.12)

Effect of Dissolved Solids

The solubility of $SrSO_4$ in water increases as the NaCl content of the water increases up to a maximum of approximately 175 000 mg/L. Further increases in salinity result in decreased solubility.(3.12-3.16) In brines containing calcium or magnesium, the apparent solubility of $SrSO_4$ is greater than a NaCl brine of equivalent ionic strength.

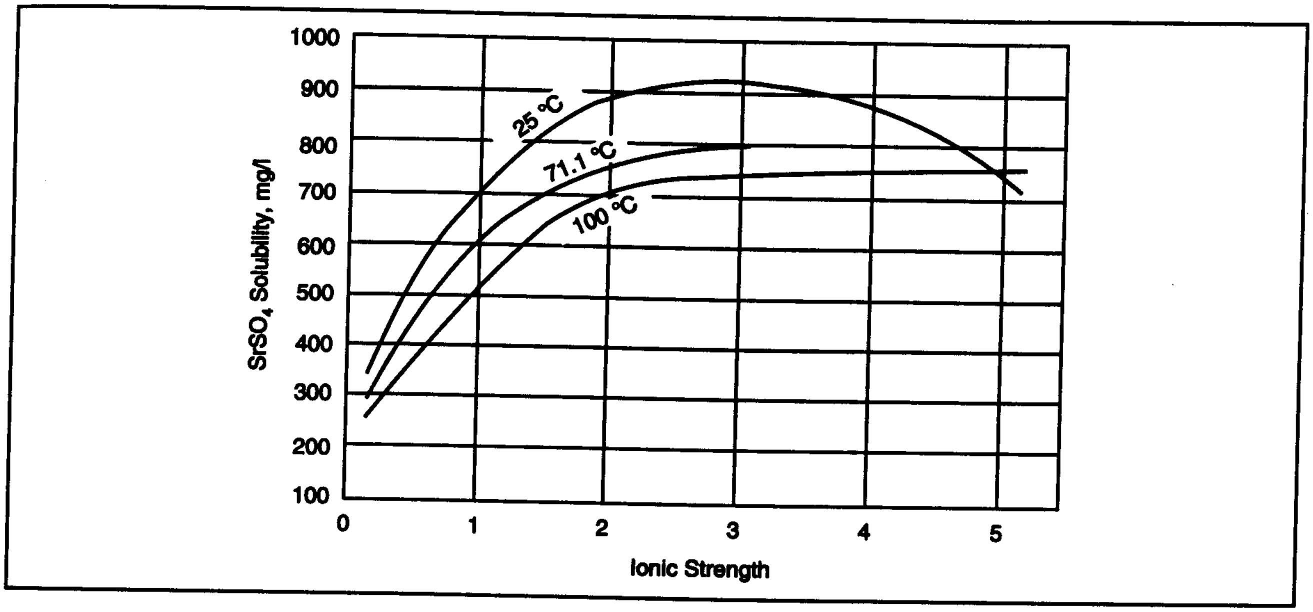

Figure 3.11 Strontium Sulfate Solubility in NaCl Solutions(3.15)

Effect of Pressure

Strontium sulfate solubility in NaCl brines increases with pressure. However, solubility data measured by Jacques and Bourland show that the increase is small up to 3000 psig.(3.13)

Pressure drops are one of the primary causes of strontium sulfate scale deposition in production systems. In addition to decreasing the solubility due to thermodynamic considerations, pressure drops across chokes and valves induce turbulence in the water which helps to overcome supersaturation effects and initiate precipitation.

Until the advent of seawater injection in the Middle East, pure $SrSO_4$ scale was seldom observed and was not considered a major problem in water injection operations. However, serious $SrSO_4$ scale problems have occurred in producing wells in a number of Middle East fields after breakthrough of seawater, due to mixing of the sulfate-bearing seawater and the strontium in the formation waters in the producing wellbores.(3.17-3.19)

In the majority of cases, however, strontium co-precipitates with barium to form (Ba,Sr) SO_4 scale. A study of several barium sulfate scales by Weintritt and Cowan(3.20) showed strontium sulfate contents of 1.2 to 15.9 percent. Barium sulfate concentrations varied from 63.7 to 97.5 percent.

Unfortunately, we have no solubility data on electrolytes containing both barium and strontium.

Effect of pH

pH has little or no effect on the solubility of strontium sulfate.

Iron Compounds

Iron ions present in a water may be either naturally present in the water or the result of corrosion. Formation waters normally contain only a few mg/L of natural iron and values as high as 100 mg/L are rare. Higher iron contents are invariably the result of corrosion. Precipitated iron compounds are a common cause of deposit formation and injection well plugging, as well as being indicative of the equally serious problem of corrosion.

Corrosion is usually the result of CO_2, H_2S or oxygen dissolved in the water. Most of the scales containing iron are corrosion products. However, iron compounds can also form by precipitation of natural formation iron even if corrosion is relatively mild.

Carbon dioxide can react with iron to form iron carbonate scale. Whether or not scale actually forms will depend on the pH of the system. Scale formation is much more likely above pH 7. Figure 3.12 illustrates the solubility of iron carbonate in fresh water.

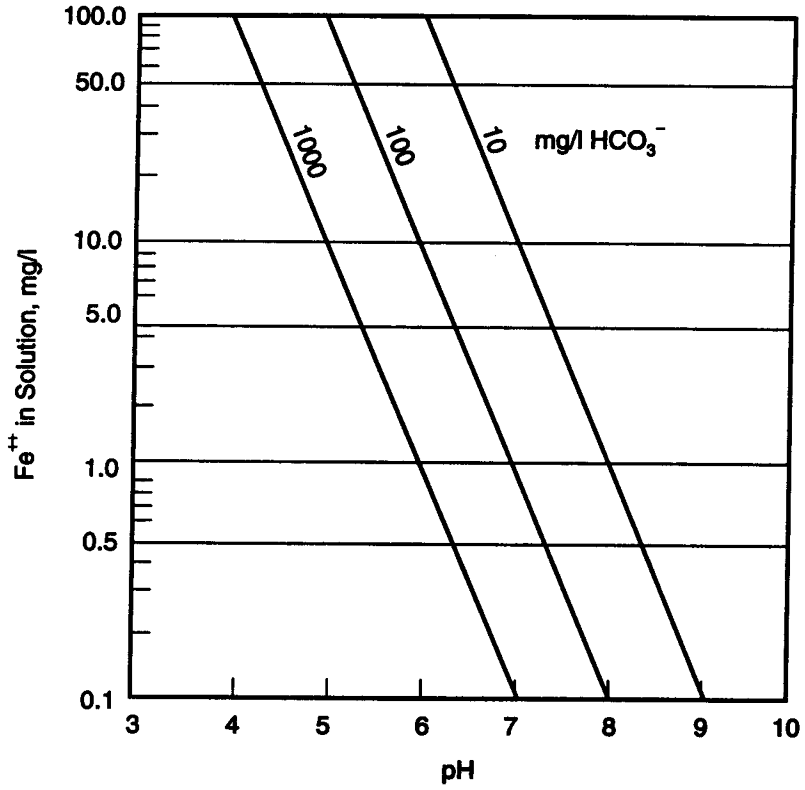

Figure 3.12 Iron Carbonate Stability Diagram

Hydrogen sulfide will form iron sulfide as a corrosion product which is quite insoluble and usually forms a thin, adherent scale. Suspended iron sulfide is the cause of "black water."

The iron sulfide diagram in Figure 3.13 illustrates the concentration of Fe^{++} ferrous ion) which will stay in solution at various pH values and H_2S concentrations in fresh water. Fe^{+++} (ferric ion) is seldom found at pH values above 3.0.

Oxygen combines to form several compounds. Ferrous hydroxide, $Fe(OH)_2$, ferric hydroxide, $Fe(OH_3)$, and ferric oxide, Fe_2O_3, are common scales resulting from contact with air. For example,

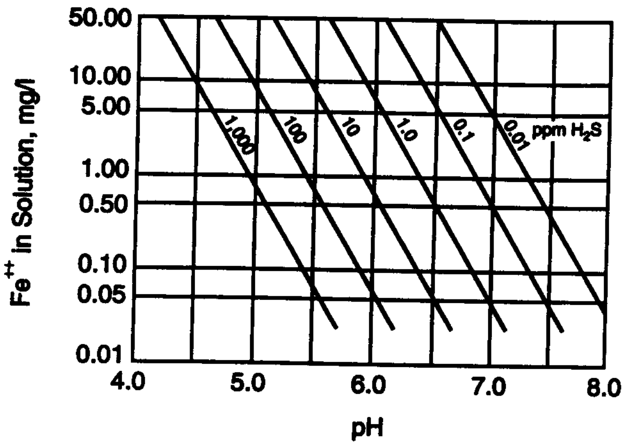

Figure 3.13 Iron Sulfide Stability Diagram

when air-free water containing dissolved ferrous iron ions and bicarbonate ions is contacted by air, ferric hydroxide can be formed.

$$2Fe^{++} + 4HCO_3^- + H_2O + \frac{1}{2}O_2 \rightarrow 2Fe(OH)_3 \downarrow + 4CO_2$$

Ferrous iron (Fe^{++}) is oxidized by the presence of air to give Fe^{+++}, and ferric hydroxide results. This is practically insoluble above pH 4. As shown in Figure 3.14, if oxygen can be excluded, 100 ppm of $Fe(OH)_2$ (ferrous hydroxide) will still be in solution at pH 8.5.

"Red water" is the result of suspended particles of Fe_2O_3, another product of oxygen and iron.

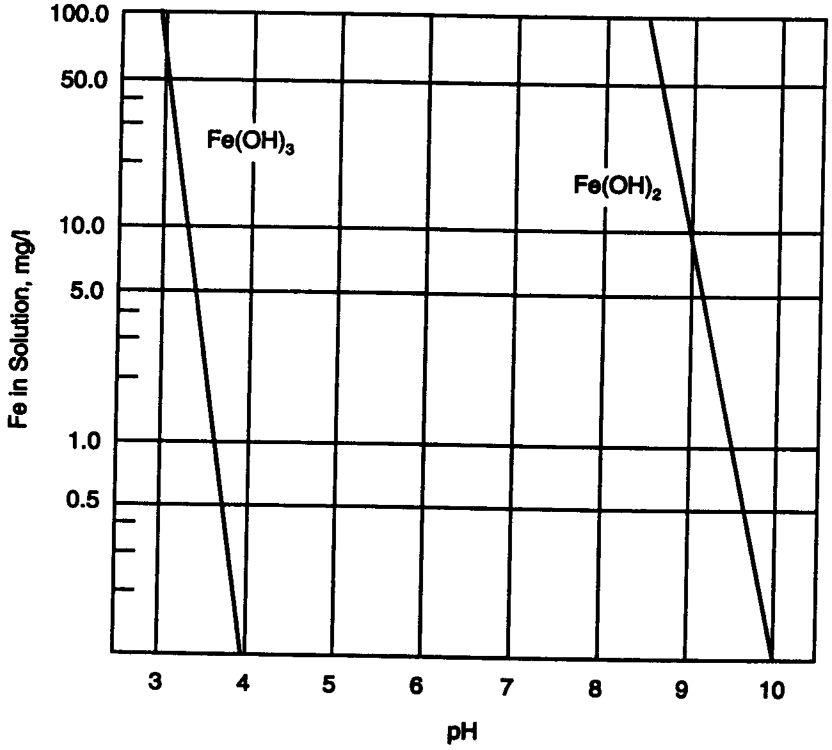

Figure 3.14 Iron Hydroxide Stability Diagram

Iron compounds can also result from the action of certain bacteria (*gallionella ferruginea*) which live in water in the presence of air. These bacteria take Fe^{++} ions from the water and deposit ferric hydroxide.

In summary, the chemistry of iron compounds is much more complex than that of previously discussed compounds. This is due primarily to the fact that iron commonly exists in two oxidation states in water, Fe^{++} (ferrous) and Fe^{+++} (ferric). These two ions form compounds with the same anions that possess very different solubilities. It is difficult to quantitatively predict the behavior of iron compounds. It is far more important to prevent their formation — a topic which will be covered in a later section.

Silica Deposits

Silica deposits are not common in produced waters or in injection projects. However, they can be quite serious in boilers and steam generators, and are sometimes a problem in cooling waters.

Silica is thought to occur in both the colloidal state as SiO_2, or it can combine with magnesium, sodium or aluminum ions to form silicate scales. It can also vaporize in steam boilers and then precipitate on turbine blades. Because of the complexity of this behavior, it is difficult to predict the conditions under which silica can be kept in solution.

NORM

Naturally occurring radioactive materials (NORM) are found in many production and injection systems. Of interest are scales which are radioactive due to the presence of Ra-226 and Ra-228 ions which have co-precipitated from produced water along with scale-forming cations during scale formation. The radium ions are trapped within the crystal lattice of the material.

NORM has been commonly associated with barium sulfate scales. However, in practice, any scale or corrosion product may contain co-precipitated radium ions and be radioactive.

PREDICTING SCALE FORMATION

The Value of Solubility Calculations

Solubility calculations or scaling indexes may be used to predict the formation of certain types of scales. The values obtained from these calculation procedures should be taken merely as guidelines. They indicate the degree of "scaling tendency," or the likelihood of scale formation. Simplifying assumptions have been made in the derivation of each equation; solubility in naturally occurring waters is a complex phenomenon.

It should be emphasized that if scale formation is indicated by calculation, it serves as an alarm. If you are looking at a possible water source, you should avoid those which show scaling tendencies or make provision for treatment in your planning. Similarly, one should avoid mixing waters which would result in a composite analysis which exhibits scaling tendencies under system conditions.

A calculated scaling tendency in an existing system should focus attention on the fact that scale formation is likely and you should begin inspecting the system for signs of scale formation immediately. Solubility calculations are an extremely valuable tool, but like nearly everything else, their absolute value will be greatly influenced by the user's experience and judgment.

The following section is a summary of some of the published scale prediction equations which are commonly used for oilfield waters. No attempt has been made to include all of the published solubility information

The Basis for Solubility Calculations

All scale prediction methods are based on laboratory measurements of the solubility of a specific compound at equilibrium conditions. Normally, solubilities are measured in synthesized waters over a range of temperatures at atmospheric pressure.

Solubility Product Principle

When a sparingly soluble salt is added to water, cations and anions from the crystal lattice of the solid pass into solution until the solution becomes saturated. In the saturated solution an equilibrium exists between the ions in solution and ions present in the solid crystal lattice.

Using barium sulfate ($BaSO_4$) as an example:

$$\underset{\text{Solid}}{BaSO_4} \leftrightarrow \underset{\text{Solution}}{Ba^{++} + SO_4}$$

At a given temperature and pressure the product of the activities of the ions in the saturated solution is constant and is called the ***thermodynamic solubility product constant***, K_{sp}.

$$K_{sp} = a_{Ba^{++}} \times a_{SO_4^=} \tag{3.8}$$

Where:

$a_{Ba^{++}}$ = Barium ion activity

$a_{SO_4^=}$ = Sulfate ion activity

The activity of an ion is defined as the product of the ion concentration and the activity coefficient.

$$a_{Ba^{++}} = C_{Ba^{++}} \times \gamma_{Ba^{++}} \tag{3.9}$$

$$a_{SO_4^=} = C_{SO_4^=} \times \gamma_{SO_4^=} \tag{3.10}$$

Where:

$C_{Ba^{++}}$ = Ba^{++} concentration, moles/L

$C_{SO_4^=}$ = $SO_4^=$ concentration, moles/L

The activity coefficient is a function of temperature, pressure and ionic strength.

It is often convenient to include the activity coefficients in the solubility constant term so that the concentrations of the ions can be used in the equations rather than the activities. The resulting solubility product is then defined as the ***ion product constant*** or ***conditional solubility product constant, K_c***, and is defined in Equation 3.11.

$$K_c = \frac{K_{sp}}{\gamma_{Ba^{++}} \times \gamma_{SO_4^=}} = \left(C_{Ba^{++}}\right)\left(C_{SO_4^=}\right) \textit{ at saturation} \tag{3.11}$$

Where: K_c = Conditional solubility product constant, molar units

Based on this principle, it is possible to evaluate a solution with respect to the possibility of the precipitation of a given salt at a given temperature and pressure by comparing the value of the ion product constant at those conditions with the product of the measured concentrations of the ions in the solution.

If we have a solution which contains a given amount of dissolved $BaSO_4$, and the measured concentrations of Ba^{++} and $SO_4^=$ are $C_{Ba^{++}}$ and $C_{SO_4^=}$ respectively, the possibilities are as follows:

1. The solution is saturated with $BaSO_4$.

$$\left(C_{Ba^{++}}\right)\left(C_{SO_4^=}\right) = K_c \tag{3.12}$$

2. The solution is undersaturated with $BaSO_4$. Precipitation cannot occur.

$$\left(C_{Ba^{++}}\right)\left(C_{SO_4^=}\right) < K_c \tag{3.13}$$

3. The solution is supersaturated with $BaSO_4$. Precipitation can occur.

$$\left(C_{Ba^{++}}\right)\left(C_{SO_4^=}\right) > K_c \tag{3.14}$$

Thus, precipitation can occur only in the last case. However, it may not occur in practice due to the fact that solutions often remain supersaturated until sufficient energy is available to initiate nucleation of the crystalline solid from solution.

Saturation Ratio

Continuing with the example of $BaSO_4$ dissolved in water, the ***saturation ratio*** (sometimes called the supersaturation ratio) is defined as the ratio of the ion product to the ion product constant:

$$SR = \frac{IP}{K_c} = \frac{C_{Ba^{++}} \times C_{SO_4^=}}{K_c} \tag{3.15}$$

Where:
IP = Ion product
SR = Saturation Ratio
$C_{Ba^{++}}$ and $C_{SO_4^=}$ = Measured concentration of Ba^{++} and $SO_4^=$ in solution

Thus, it is also possible to express the conditions necessary for precipitation in terms of the saturation ratio:

1. SR = 1 — The solution is saturated with $BaSO_4$.
2. SR < 1 — The solution is undersaturated with $BaSO_4$. Precipitation cannot occur.
3. SR > 1 — The solution is supersaturated with $BaSO_4$. Precipitation can occur.

Calcium Carbonate Scaling Calculations

Calcium Carbonate Saturation Indexes

It is common to express the degree of supersaturation, and hence the likelihood of precipitation of $CaCO_3$ from a solution in terms of the ***saturation index***, which is defined as follows:

$$\text{Saturation Index} = \log_{10}\left[\frac{IP}{K_c}\right] \qquad (3.16)$$

Although there is agreement as to the definition of the saturation index, different investigators have used different nomenclature to describe the term.

TABLE 3.3

Calcium Carbonate Saturation Indexes

Investigator	Index Name	Abbreviation
Langelier(3.21)	Saturation Index	SI
Ryznar(3.22)	Stability Index	SI
Stiff & Davis(3.23)	Stability Index	SI
Oddo & Tomson(3.24)	Saturation Index	I_s

The saturation index, which we will refer to as SI, is a measure of the degree of supersaturation, and thus the driving force available to cause precipitation. The larger the value of SI, the greater the likelihood that scale will occur. It does not predict the amount of scale which will precipitate.

Figure 3.15 illustrates the relationship between the supersaturation ratio and the saturation index:

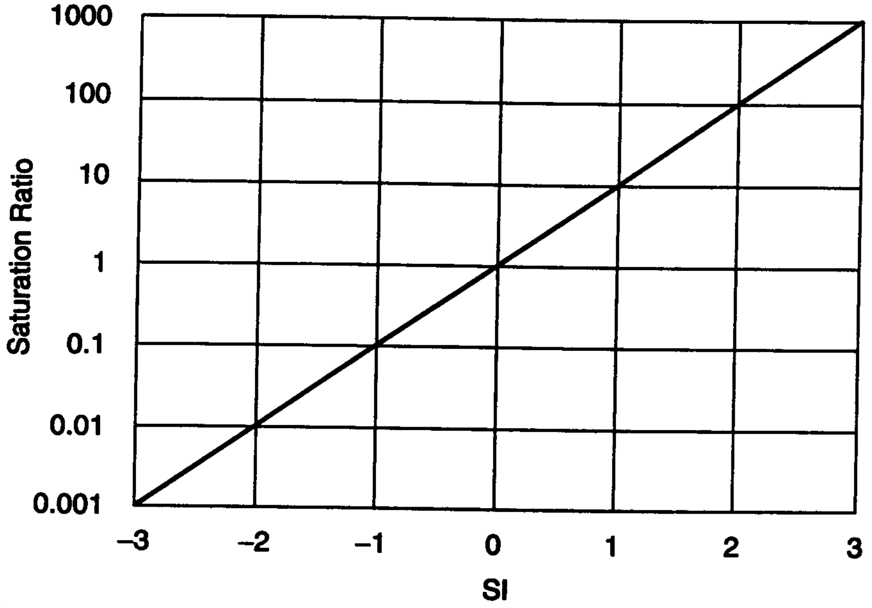

Figure 3.15 Saturation Index (SI) vs Saturation Ratio (SR)

Langelier Saturation Index(3.21)

This well known index was developed to predict whether a fresh water saturated with dissolved oxygen would form calcium carbonate scale or be corrosive.

The Langelier saturation index is calculated from the following empirical equation:

$$\underset{\text{Stability Index}}{SI} = \underset{\text{Actual pH of Water}}{pH} - \underset{\text{pH at which water would be saturated with } CaCO_3}{pH_s} \tag{3.17}$$

$$pH_s = pCa + pAlk\,M + C_t \tag{3.18}$$

$$pCa = \log \frac{1}{Moles\ Ca^{++}/Liter} \tag{3.19}$$

$$pAlk\ M = \log \frac{1}{Equivalents\ M\ Alkalinity\ /\ Liter} \tag{3.20}$$

$$M\ Alkalinity = Total\ Alkalinity = CO_3^{=} + HCO_3^{-}\ ,\ equivalents\ /\ L \tag{3.21}$$

Where: C_t = a constant which is a function of the Total Dissolved Solids and temperature

As previously explained, if SI > 0, precipitation of $CaCO_3$ is indicated. A negative value of SI indicates that the water is corrosive if dissolved oxygen is present. This index indicates the tendency of a water to precipitate calcium carbonate, but it does not indicate the amount of precipitate.

Values of the empirical constants used to solve these equations are given elsewhere for molal ionic strengths of 0-0.02 [0-800 ppm TDS] and temperatures of 32-194°F [0-90°C] at atmospheric pressure.(3.21)

The nomograph developed by Caplan(3.25) is reproduced in Appendix 11 and permits easy determination of the Langelier Index.

Ryznar Stability Index(3.22)

Ryznar developed an empirical equation for calculating the "stability index" of fresh water at atmospheric pressure. This index not only indicates the tendency of a water to precipitate calcium carbonate (or be corrosive if it is saturated with oxygen), it also gives a semi-quantitative estimate of the amount of scale which will form or the seriousness of the corrosion.

$$SI = 2pH_s - pH \tag{3.22}$$

Ryznar's stability index values always are positive. They can be interpreted as follows:

- Stability Index < 6.5 indicates $CaCO_3$ scale formation. The smaller the index, the larger the amount of scale indicated.
- Stability Index > 6.5 indicates corrosion if dissolved oxygen is present. The larger the index, the more severe the anticipated corrosion.

Caplan's nomograph in Appendix 11 can be used to determine the Ryznar Index.

Stiff and Davis Method$^{(3.23)}$

Stiff and Davis empirically extended the Langelier method to apply to oilfield brines. Their equation is as follows:

$$\underset{\text{Stability Index}}{SI} = \underset{\text{Actual pH of Water}}{pH} - \underset{\text{pH at which water would be saturated with } CaCO_3}{pHs} \tag{3.23}$$

$$pHs = K + pCa + pAlk \tag{3.24}$$

Therefore:

$$SI = pH - K - pCa - pAlk \tag{3.25}$$

Where:

SI = Stability Index. If SI is negative, the water is undersaturated with $CaCO_3$ and scale formation is unlikely. If SI is positive, scale is likely to form.
pH = Actual pH of the water
K = A constant which is a function of salinity, composition and water temperature. Values of K are obtained from a graphical correlation with ionic strength and the temperature of the water.

$$pCa = \log\frac{1}{Moles\ Ca^{++}/Liter} \tag{3.26}$$

$$pAlk\ M = \log\frac{1}{Equivalents\ M\ Alkalinity/Liter} \tag{3.27}$$

$$M\ Alkalinity = Total\ Alkalinity = CO_3^{=} + HCO_3^{-},\quad mg/L \tag{3.28}$$

The ionic strength is:

$$\mu = \frac{1}{2}\left(C_1Z_1^2 + C_2Z_2^2 + C_3Z_3^2 + \ldots + C_nZ_n^2\right) \tag{3.29}$$

Where:

C = Concentration of the ion in moles/liter.
Z = Valence of the ion

In order to calculate SI we must know the temperature, pH, and the HCO_3^- and $CO_3^=$ concentrations. In addition, a complete water analysis is necessary to enable calculation of the ionic strength.

It is essential that values of pH, HCO_3^- and $CO_3^=$ be measured in the field immediately after sampling, since these parameters change very quickly once the sample is removed from a pressurized system. Valid calculations cannot be made from laboratory analyses.

Unfortunately, even field measurements of pH values will not suffice when attempting to apply this method to downhole conditions in producing or injection wells. The pH must be calculated.

Equations are given in the following section which enable estimation of pH values at elevated pressures and temperatures.

Values of K as a function of ionic strength are given in Appendix 12. These curves are based on experimental data measured over the following range:

- Molar Ionic Strength: 0-3.6
- Temperature: 32, 86 and 122°F [0, 30 and 50°C]
- Pressure: 1 atmosphere [101.3 kPa]

All curves outside of this data range were extrapolated.

A chart for the determination of pCa and pAlk is given in Appendix 13.

The results of the calculation may be summarized as follows:

TABLE 3.4

Interpretation of Stiff & Davis Index

Case	Conclusion
SI is negative	The water is undersaturated with $CaCO_3$. Scale formation is unlikely.
SI is positive	The water is supersaturated with $CaCO_3$. Scale formation is indicated.
SI = 0	The water is saturated with $CaCO_3$.

An example calculation is given in Appendix 14.

Oddo and Tomson Method(3.4,3.24, 3.26)

The equations developed by Oddo and Tomson enable the calculation of the saturation index, I_s, and considers the effect of total pressure as well as varying CO_2 partial pressures. Its meaning is analogous to that of the Stiff and Davis Index. They also developed equations which permit the calculation of pH.

Their initial work was published in 1982. The method was subsequently modified to include the effects of additional parameters. The equations given here were published in 1994.

Any System (Gas Phase Present or Absent) Where the pH is Known

$$I_s = \log\left[\left(Ca^{++}\right)\left(HCO_3^-\right)\right] + pH - 2.76 + 9.88\times10^{-3}T + 0.61\times10^{-6}T^2 \\ -3.03\times10^{-5}P - 2.348\sqrt{\mu} + 0.77\mu \qquad (3.30)$$

Where:

Ca^{++} = Calcium ion concentration, moles/L

HCO_3^- = Bicarbonate ion concentration, moles/L

T = Temperature, °F

P = Total absolute pressure, psia

μ = Molar ionic strength, moles/L

Gas Phase Absent

These equations are applicable in water injection systems and in production systems where the system pressure is greater than the bubble point pressure of the fluids.

1. Determine C_{aq}, the amount of CO_2 dissolved in the water. This can be determined directly by on-site titration, or it can be calculated using Equation 3.31.

log

$$C_{Aq} = \log P_{CO_2} - 2.212 - 6.51\times10^{-3}T + 10.19\times10^{-6}T^2 - 1.29\times10^{-5}P - 0.77\sqrt{\mu} - 0.059\mu \qquad (3.31)$$

2. Calculate I_s or the pH as desired.

$$I_s = \log\left[\frac{(Ca^{++})(HCO_3^-)^2}{C_{Aq}}\right] + 3.63 + 8.68\times10^{-3}T + 8.55\times10^{-6}T^2 - 6.56\times10^{-5}P - 3.42\sqrt{\mu} + 1.373\mu \qquad (3.32)$$

$$pH = \log\left[\frac{(HCO_3^-)}{C_{aq}}\right] + 6.39 - 1.198\times10^{-3}T + 7.94\times10^{-6}T^2 - 3.53\times10^{-5}P - 1.067\sqrt{\mu} + 0.599\mu \qquad (3.33)$$

3. It is also possible to calculate the change in I_s or pH in a system without a gas phase using the following equations:

$$\Delta I_s = 8.68\times10^{-3}\Delta T + 8.55\times10^{-6}\Delta(T^2) - 6.56\times10^{-5}\Delta P \qquad (3.34)$$

$$\Delta pH = -1.198\times10^{-3}\Delta T + 7.94\times10^{-6}\Delta(T^2) - 3.53\times10^{-5}\Delta P \qquad (3.35)$$

Gas Phase is Present and the pH is Unknown

1. Calculate f_g, the fugacity coefficient of CO_2 gas.

$$f_g = \exp\left[P\times\left(2.84\times10^{-4} - \frac{0.255}{T+460}\right)\right] \qquad (3.36)$$

2. Calculate y_g, the mole or volume fraction of CO_2 in the gas phase at the specified T and P. Given that y_t is the mole fraction CO_2 in the gas at the surface.

$$y_g = \frac{y_t}{\left[1.0 + \frac{Pf_g(5.0BWPD + 10.0BOPD)\times10^{-5}}{MMscf(T+460)}\right]} \qquad (3.37)$$

Where:

BOPD = Barrels of oil per day
BWPD = Barrels of water per day
MMscf = Million standard cubic feet of gas per day

3. Calculate the molar ionic strength.

$$\mu(Moles/L) = 10^{-5}(2.2\times Na^{+} + 5.0\times Ca^{++} + 8.2\times Mg^{++} + 1.5\times Ba^{++} \\ + 2.3\times Sr^{++} + 1.4\times Cl^{-} + 2.1\times SO_4^{=} + 0.8\times HCO_3^{-}) \tag{3.38}$$

Where all ion concentrations are in mg/L and are obtained from a water analysis.

4. Calculate I_s or the pH as desired.

$$I_s = \log\left[\frac{(Ca^{++})(HCO_3^{-})^2}{Py_g f_g}\right] + 5.85 + 15.19\times 10^{-3}T - 1.64\times 10^{-6}T^2 \\ -5.27\times 10^{-5}P - 3.334\sqrt{\mu} + 1.431\mu \tag{3.39}$$

$$pH = \log\left[\frac{(HCO_3^{-})}{Py_g f_g}\right] + 8.60 + 5.31\times 10^{-3}T - 2.253\times 10^{-6}T^2 \\ -2.237\times 10^{-5}P - 0.99\sqrt{\mu} + 0.658\mu \tag{3.40}$$

This method is said to be valid over the following data range:

- Molar Ionic Strength: 0-4.0
- Temperature: 32-392°F [0-200°C]
- Pressure: 0-20 000 psig

Effect of Carboxylic Acids on $CaCO_3$ Saturation Index Calculations

Generally, alkalinity titrated to a pH of approximately 4.5 is assumed to be equal to the bicarbonate ion concentration. In produced waters, a substantial concentration of carboxylic acids (often called volatile fatty acids or "VFA's") is often present. As explained in Chapter 2, the acids are ionized in water and the species which are actually present are the VFA anions, which are typically dominated by the acetate ion. The VFA anions contribute to alkalinity.

The total alkalinity is as follows:

$$Total\ Alkalinity = HCO_3^{-} + \underset{\text{Acetate Ion}}{CH_3COO^{-}} + \underset{\text{Propionate Ion}}{CH_3CH_2COO^{-}} + \underset{\text{Butyrate Ion}}{CH_3CH_2CH_2COO^{-}}$$

In many cases, the acetate ion concentration is far larger than the concentration of the other VFA ions, so their presence can be ignored, and the alkalinity can be assumed to simply be the sum of the bicarbonate and acetate ion concentrations.

The acetate ion concentration can be determined by gas chromatography and the HCO_3^- concentration can then be approximated by the method proposed by Oddo and Tomson.(3,4)

Failure to include the effect of VFA anions will result in a saturation index value more positive than would be calculated if the VFA anions were not subtracted from the total alkalinity.

Effect of H_2S on $CaCO_3$ Saturation Index Calculations

The presence of significant quantities of sulfides in produced water can also significantly effect saturation index values since bisulfide ion concentrations will be included in alkalinity values.

Assuming a sour brine at a pH less than 9 with no VFA anions present:

$$\text{Total Alkalinity} = HCO_3^- + HS^-$$

At a given pH, the HS^-/HCO_3^- ratio in the water is approximately equal to the ratio of the partial pressures in the gas phase:(3.4)

$$\frac{HS^-}{HCO_3^-} = \frac{P_{H_2S}}{P_{CO_2}} \tag{3.41}$$

This equation can be used to calculate the bisulfide ion (HS^-) concentration. It can then be subtracted from the alkalinity to obtain the bicarbonate ion concentration for use in calculating the calcium carbonate saturation index.

Estimation of the Amount of $CaCO_3$ Scale Formed

It is possible to estimate the maximum amount of scale which could form, assuming that the system is at equilibrium.

If a solution is supersaturated with a salt (such as $CaCO_3$, $CaSO_4$, $BaSO_4$ or $SrSO_4$), precipitation can be expected. In this case, let us consider the general case of the formation of a mineral scale, MA. The general reaction is given as:

$$M^{++} + A^{=} \leftrightarrow MA$$

Assume that we have a solution that is supersaturated with respect to MA:

$$m \times a > K_c$$

Where:

m = Initial concentration of M^{++}, moles/liter
a = Initial concentration of A, moles/liter
K_c = Molar ion product constant

If the solution is allowed to reach equilibrium, MA will precipitate until the solution is saturated with MA. Since one mole of M^{++} and one mole of $A^{=}$ is required to make one mole of MA, the concentrations of both ions will be decreased by one mole for each mole of scale which precipitates.

Let P equal the number of moles of MA which precipitate in the act of reaching saturation.

Now:

$$K_c = (m - P)(a - P)$$

Rearranging:

$$P^2 - (m + a)P + ma - K_c = 0$$

Taking the negative root of the resulting quadratic equation:

$$P = \frac{m + a - \sqrt{(m-a)^2 + 4K_c}}{2}$$

Let:

G = m + a, and
X = m − a

Then:

$$P = \frac{G - \sqrt{X^2 + 4K_c}}{2}, \quad moles/L$$

Given the following relationship:

$$mg/L = moles/L \times MW \times 1000$$

Then:

$$P = 500 \times MW \times \left[G - \sqrt{X^2 + 4K_c}\right], \quad mg/L \tag{3.42}$$

Where:

P = Maximum amount of scale which can precipitate, mg/L
MW = Molecular weight of scale compound

This equation can be used to calculate the maximum amount of any scale which might precipitate.

Stiff & Davis

In order to solve this equation for the maximum amount of $CaCO_3$ which could precipitate using data from the Stiff and Davis SI calculation, the following substitution is required for the value of K_c as pointed out by Valone and Skillern:*(3.27)*

$$K_c = 10^{k-pH} \tag{3.43}$$

Where:

k = Stiff & Davis "k"
pH = Actual system pH

Thus, for $CaCO_3$, Equation 3.42 becomes:

$$P = 50000\left[G - \sqrt{X^2 + 4 \times 10^{k-pH}}\right], \quad mg/L \tag{3.44}$$

In certain cases, it may be desirable to express the results in lb/1000 bbl.

$$PTB = \frac{lb}{1000bbl} = 0.35 \times \frac{mg}{L} \tag{3.45}$$

And Equation 3.24 becomes:

$$PTB = 17500\left[G - \sqrt{X^2 + 4 \times 10^{k-pH}}\right] \tag{3.46}$$

Where:

G = $Ca^{++} + HCO_3^-$, moles/L
X = $Ca^{++} - HCO_3^-$, moles/L

Valone and Skillern(3.27) further state that based on Texaco's experience, Table 3.5 can be used to assess the anticipated severity of calcium carbonate scale deposition.

TABLE 3.5

Calcium Carbonate Scaling Severity

PTB Value	Description
PTB < 0	No scale
0 < PTB < 100	Few scaling problems
100 < PTB < 250	Moderate scaling difficulties
PTB > 250	Severe scaling occurs

Oddo & Tomson

In the case of Oddo and Tomson, Equation 3.47 can be utilized to calculate K_c.

$$K_c = \frac{1}{10^{pK_c}} \tag{3.47}$$

Where:

$$pK_c = pH - 2.76 + 9.88 \times 10^{-3} T + 0.61 \times 10^{-6} T^2 - 3.03 \times 10^{-5} P - 2.348\sqrt{\mu} + 0.77\mu \tag{3.48}$$

The pH value in Equation 3.48 can be measured or calculated. Substituting into Equation 3.42 we obtain:

$$P = 50000\left[G - \sqrt{X^2 + \frac{4}{10^{pK_c}}}\right] \tag{3.49}$$

Or when expressed in PTB:

$$PTB = 17500\left[G - \sqrt{X^2 + \frac{4}{10^{pK_c}}}\right] \tag{3.50}$$

Sulfate Scaling Calculations

Traditional Approach to Sulfate Scale Solubilities

Solubility values for $CaSO_4$, $BaSO_4$ or $SrSO_4$, can be calculated using the following equation, providing values of conditional solubility product, K_c, are known for each compound:

$$Solubility\,(meq/L) = 1000\left[\sqrt{X^2 + 4K_c} - X\right] \tag{3.51}$$

The derivation of this equation follows.

The Common Ion Effect

The maximum solubility of a slightly soluble salt is obtained when the concentrations of the cation and anion are equal.

For example: Given a saturated solution of $CaSO_4$ in water, where the Ca^{++} and $SO_4^=$ concentrations are equal:

$$Ca^{++} \; concentration = S \; moles/liter$$

$$SO_4^= \; concentration = S \; moles/liter$$

$$K_c = S \times S = S^2$$

$$S = \sqrt{K_c} \tag{3.52}$$

The solubility of calcium sulfate is equal to S moles/liter, which is simply the square root of the molar ion product constant.

However, in most natural waters, the cation and anion concentrations are not equal. In this case, the difference between the two concentrations is called the ***excess common ion concentration***. The presence of excess common ion reduces the solubility of the salt unless a complex ion or ion pair, such as neutral magnesium sulfate, forms and offsets the effect.(3.6)

For example, consider a saturated solution of $CaSO_4$ in water, where the Ca^{++} and $SO_4^=$ concentrations are unequal:

$$Ca^{++} \; concentration = S \; moles/liter$$

$$SO_4^= \; concentration = S + X \; moles/liter$$

In this case, we have arbitrarily selected the sulfate ion concentration as the larger of the two. The amount by which the sulfate ion concentration exceeds the calcium concentration, X, is the excess common ion concentration.

$$K_c = (S)(S + X) = S^2 + SX$$

The calcium sulfate solubility is equal to S moles/liter, since that is the maximum amount of calcium sulfate which can be formed by combining S moles of Ca^{++} with (S +X) moles of $SO_4^=$.

Rearranging:

$$S^2 + SX - K_c = 0$$

Taking the positive root of the quadratic equation:

$$S = \frac{-X + \sqrt{X^2 + 4K_c}}{2}$$

For a divalent ion such as Ca^{++}, Ba^{++} or Sr^{++}:

$$S(equivalents/L) = \sqrt{X^2 + 4K_c} - X \tag{3.53}$$

Or:

$$S(meq/L) = 1000\left[\sqrt{X^2 + 4K_c} - X\right] \tag{3.54}$$

The "actual concentration" of $CaSO_4$ in solution is equal to the smaller of the Ca^{++} or $SO_4^=$ concentrations (expressed in meq/liter) in the water of interest, since the smaller concentration controls the amount of calcium sulfate which can be formed.

The calculated calcium sulfate solubility, S (meq/liter), is compared with the actual concentration to determine if scale formation is likely.

TABLE 3.6

Interpretation of Sulfate Scale Calculations

Case	Conclusion
S = Actual	The water is saturated with $CaSO_4$.
S > Actual	The water is undersaturated with $CaSO_4$. Scale is unlikely.
S < Actual	The water is supersaturated with $CaSO_4$. Scale is likely.

This formula can be used to calculate the solubility of any divalent salt such as $CaSO_4$, $BaSO_4$, or $SrSO_4$.

Calcium Sulfate (Gypsum) Solubility Calculations

The data measured by Skillman, McDonald and Stiff(3.28) has been widely used to estimate the solubility of gypsum in oilfield brines. They measured ion product constants in simulated oilfield brines over the following range:

- Temperature: 50, 95, 122 and 176°F [10, 35, 50 and 80°C]
- Ionic Strength: 0-6.0 moles/L
- Pressure: 1 atmosphere [101.3 kPa]

Their data are presented in Appendix 15.

The following procedure is recommended to assess the possibility of gypsum precipitation from a given brine:

1. Calculate the molar ionic strength using Equation 3.38.
2. Obtain the appropriate value of K_c for the temperature of interest from Appendix 15.
3. Determine the excess common ion concentration, X, in moles/liter. This is simply the difference between the calcium concentration and the sulfate concentration.
4. Calculate the solubility of gypsum in meq/liter by solving Equation 3.54.
5. Calculate the "actual concentration" of gypsum in the water, which is equal to the smaller of the Ca^{++} or $SO_4^{=}$ concentrations expressed in meq/liter.
6. Compare the calculated solubility with the actual concentration to determine if precipitation of gypsum is likely.

An example calculation is given in Appendix 14.

Other commonly used methods for predicting calcium sulfate solubility which will not be presented here include those of Metler and Ostroff(3.29), and Carlberg and Matthews.(3.6) The latter method can be used for temperatures up to 257°F [125°C]. It assumes hemihydrate solubility to be the limiting solubility above 212°F [100°C].

Barium Solubility Sulfate Calculations

It is possible to estimate the solubility of barium sulfate for waters which contain predominately sodium and chloride ions and very little magnesium or calcium ions using the solubility data measured by Templeton(3.10) for sodium chloride solutions. Molar conditional solubility product constants calculated from his data are presented in Appendix 16 over the following range:

- Temperature: 77, 95, 122, 149, 176 and 203°F [25, 35, 50, 65, 80 and 95°C]
- Ionic Strength: 0-4.15 moles/L
- Pressure: 1 atmosphere [101.3 kPa]

The solubility can be calculated using Equation 3.54, and the probability of $BaSO_4$ precipitation evaluated using the same procedure as previously outlined for gypsum.

Because $BaSO_4$ has such limited solubility, the appearance of Ba^{++} and $SO_4^{=}$ ions in any water indicates a danger of scale formation.

Strontium Sulfate Solubility Calculations

The solubility of strontium sulfate in sodium chloride solutions can be calculated in the same manner as the solubilities of the other sulfate scales.

Values of K_c have been measured by several investigators.(3.12-3.15) However, the values measured by Jacques and Bourland(3.13) cover the widest range of conditions thus published, and include the effect of pressure. The following equation is based on their data and can be used to estimate values of K_c:

$$\log K_c = \frac{X}{R} \tag{3.55}$$

Where:

K_c = Conditional solubility product constant, molar units
X = 1/T

$$R = A + BX + C\sqrt{\mu} + D\mu + EP^2 + FXP + G\sqrt{\mu P} \tag{3.56}$$

The units are:

T = °K = °C + 273
P = Total pressure, psig
μ = Ionic strength, moles/L

The coefficients of the equation are:

$A = 0.266498 \times 10^{-3}$
$B = -244.828 \times 10^{-3}$
$C = -0.191065 \times 10^{-3}$
$D = 53.543 \times 10^{-6}$
$E = -1.383 \times 10^{-12}$
$F = 1.103323 \times 10^{-6}$
$G = -0.509 \times 10^{-9}$

This equation applies over the following range:

- Temperature: 100-300°F [38-149°C]
- Ionic Strength: 0-3.45 moles/L
- Pressure: 100-3000 psig

K_c values measured by Fletcher, French and Collins(3.14) for strontium sulfate in sodium chloride solutions at atmospheric pressure are given in Appendix 17. Their data was measured over the following range:

- Temperature: 50, 75, 122 and 156°F [10, 35, 50 and 69°C]
- Ionic Strength: 0.1-5.25 moles/L
- Pressure: 1 atmosphere [101.3 kPa]

The Effect of Ion Pairing on Sulfate Scale Solubility

The sulfate ion will form neutral ion pairs or complexes with magnesium, calcium, barium and strontium ions. The fraction of these ions which are tied up as ion pairs depends on the temperature, pressure, ionic strength, and total concentrations of the ions in the solution.

The importance of ion pairing in scale prediction centers on the fact that ions occupied in ion pairs are not available to form scale.

For maximum accuracy, the available or "free" sulfate ion concentration should be used in sulfate scaling calculations. It can be calculated using the method of Oddo and Tomson presented in a following section.

Estimation of the Amount of Sulfate Scale Precipitated

When Equation 3.16 is used to calculate the solubility of the sulfate scales, the following equation can be used to calculate the maximum amount of scale which can precipitate:

$$P = (EW)(Actual - S) \tag{3.57}$$

Where:
P = Maximum amount of scale which can precipitate (mg/L)
EW = Gram equivalent weight of compound which precipitates
Actual = Actual concentration of compound in solution, meq/L
S = Calculated solubility of compound, meq/L

Oddo & Tomson Sulfate Scale Calculations — 1994(3.4)

The equations published by Oddo and Tomson in 1994 permit the calculation of the Saturation Index, I_s, for five sulfate scales: Calcium sulfate (gypsum, hemi-hydrate, anhydrite), barium sulfate and strontium sulfate. The equations account for pressure, temperature, ionic strength and ion pairing.

Saturation index calculations have traditionally been reserved for calcium carbonate scale. The saturation index is defined in Equation 3.16.

Although Oddo and Tomson designated the saturation index as "I_s", we have chosen to refer to it as SI in this book and to identify the particular sulfate scale compound with appropriate subscripts.

Mass Action Stability Constant

The degree of ion pairing can be predicted if the mass action stability constant, K_{st}, is known for each ion pair. In the case of the calcium and sulfate ions, the equation is given as:

$$K_{st} = \frac{\left[CaSO_4^o\right]}{\left[Ca^{++}\right]\left[SO_4^{=}\right]} \tag{3.58}$$

Where: $\left[CaSO_4^o\right]$ = concentration of ion pair, moles/L

$\left[Ca^{++}\right]$ = concentration of "free" calcium, moles/L

$\left[SO_4^{=}\right]$ = concentration of "free" sulfate, moles/L

It is assumed that K_{st} values for the four sulfate/metal ion complexes are equal.

Free Ion Concentrations

The total concentration of a given ion in solution is measured in a water analysis. It is the sum of the paired ions and the "free" ions. Only the free ions are available to form scale.

In the case of sulfate, a material balance can be expressed as follows:

$$\underset{\text{Measured Concentration}}{C_{SO_4}} = \underbrace{\left[CaSO_4^o\right]+\left[MgSO_4^o\right]+\left[SrSO_4^o\right]+\left[BaSO_4^o\right]}_{\text{Paired Sulfate}} + \underset{\text{Free Sulfate}}{\left[SO_4^{=}\right]} \tag{3.59}$$

Similar equations can be written for magnesium, calcium, barium and strontium ions.

$$C_{Ca} = \left[Ca^{++}\right]+\left[CaSO_4^o\right] \qquad C_{Mg} = \left[Mg^{++}\right]+\left[MgSO_4^o\right]$$
$$C_{Sr} = \left[Sr^{++}\right]+\left[SrSO_4^o\right] \qquad C_{Ba} = \left[Ba^{++}\right]+\left[BaSO_4^o\right] \tag{3.60}$$

Sulfate Scale Calculations

1. Calculate the molar ionic strength.

$$\mu(moles/L) = 10^{-5}(2.2\times Na^{+} + 5.0\times Ca^{++} + 8.2\times Mg^{++} + 1.5\times Ba^{++} + 2.3\times Sr^{++} + 1.4\times Cl^{-} + 2.1\times SO_4^{=} + 0.8\times HCO_3^{-}) \tag{3.61}$$

Where all ion concentrations are in mg/L and are obtained from a water analysis.

2. Calculate K_{st}

$$K_{st} = 10^{\log K_{st}} \tag{3.62}$$

Where:

$$\log K_{st} = +1.86 + 4.5\times10^{-3}T - 1.2\times10^{-6}T^2 + 10.7\times10^{-5}P \\ -2.38\sqrt{\mu} + 0.58\mu - 1.3\times10^{-3}\sqrt{\mu}T \tag{3.63}$$

and:

T = Temperature (°F)
P = Total Pressure (psia)
μ = Ionic Strength (moles/L)

3. Convert the ion concentrations from mg/L to moles/L by dividing the ion concentrations obtained from the water analysis by the appropriate conversion factor given in Table 3.7.

TABLE 3.7

Conversion Factors: mg/L to moles/L

Ion Concentration (mg/L) From Water Analysis	Divide by	To Obtain Total Concentration (moles/L)
$SO_4^=$	96060	C_{SO4}
Ca^{++}	40080	C_{Ca}
Mg^{++}	24305	C_{Mg}
Sr^{++}	87620	C_{Sr}
Ba^{++}	137330	C_{Ba}

4. Calculate CatSum. This is the sum of the four measured metal cation concentrations (moles/L).

$$CatSum = C_{Ca} + C_{Mg} + C_{Sr} + C_{Ba} \tag{3.64}$$

5. Calculate the free sulfate concentration (moles/L).

$$[SO_4^=] = \frac{-\{1 + K_{st}(CatSum - C_{SO_4})\} + \{[1 + K_{st}(CatSum - C_{SO_4})]^2 + 4K_{st}C_{SO_4}\}^{0.5}}{2K_{st}} \tag{3.65}$$

6. Calculate the free metal-ion concentrations.

$$[Mg^{++}] = \frac{C_{Mg}}{1 + K_{st}[SO_4^=]} \qquad [Ca^{++}] = \frac{C_{Ca}}{1 + K_{st}[SO_4^=]} \\ [Sr^{++}] = \frac{C_{Sr}}{1 + K_{st}[SO_4^=]} \qquad [Ba^{++}] = \frac{C_{Ba}}{1 + K_{st}[SO_4^=]} \tag{3.66}$$

7. Calculate the Saturation Index values for the sulfate scales.

Calcium Sulfate

Equations are given for the calculation of the Saturation Index (SI) for three forms of calcium sulfate scale: gypsum, hemi-hydrate and anhydrite. According to Oddo and Tomson, the most likely scale to form from brines will be gypsum at temperatures less than 176°F [80°C].

Between 176°F [80°C] and 250°F [121°C], any of the three types of calcium sulfate may form, with gypsum being more likely at the low end of the temperature range and anhydrite more likely at the high end. Hemihydrate is commonly found in this temperature range in non-turbulent systems with high ionic strengths.

Above 250°F [121°C], any calcium sulfate scale formed will almost certainly be anhydrite.(3,4)

The saturation index for the three forms of calcium sulfate follow.

- Gypsum

$$\begin{aligned} SI_{Gyp} = {} & \log_{10}\{[Ca^{++}][SO_4^{=}]\} + 3.47 + 1.8\times10^{-3}T + 2.5\times10^{-6}T^2 \\ & -5.9\times10^{-5}P - 1.13\sqrt{\mu} + 0.37\mu - 2.0\times10^{-3}\sqrt{\mu}T \end{aligned} \tag{3.67}$$

- Hemi-hydrate

$$\begin{aligned} SI_{Hemi} = {} & \log_{10}\{[Ca^{++}][SO_4^{=}]\} + 4.04 - 1.9\times10^{-3}T + 11.9\times10^{-6}T^2 \\ & -6.9\times10^{-5}P - 1.66\sqrt{\mu} + 0.49\mu - 0.66\times10^{-3}\sqrt{\mu}T \end{aligned} \tag{3.68}$$

- Anhydrite

$$\begin{aligned} SI_{Anhy} = {} & \log_{10}\{[Ca^{++}][SO_4^{=}]\} + 2.52 + 9.98\times10^{-3}T - 0.97\times10^{-6}T^2 \\ & -3.07\times10^{-5}P - 1.09\sqrt{\mu} + 0.50\mu - 3.3\times10^{-3}\sqrt{\mu}T \end{aligned} \tag{3.69}$$

Barium Sulfate

$$\begin{aligned} SI_{Ba} = {} & \log_{10}\{[Ba^{++}][SO_4^{=}]\} + 10.03 - 4.8\times10^{-3}T + 11.4\times10^{-6}T^2 \\ & -4.8\times10^{-5}P - 2.62\sqrt{\mu} + 0.89\mu - 2.0\times10^{-3}\sqrt{\mu}T \end{aligned} \tag{3.70}$$

Strontium Sulfate

$$\begin{aligned} SI_{Sr} = {} & \log_{10}\{[Sr^{++}][SO_4^{=}]\} + 6.11 + 2.0\times10^{-3}T + 6.4\times10^{-6}T^2 \\ & -4.6\times10^{-5}P - 1.89\sqrt{\mu} + 0.67\mu - 1.9\times10^{-3}\sqrt{\mu}T \end{aligned} \tag{3.71}$$

MIXING WATERS — COMPATIBILITY

One of the primary causes of scale formation and injection well plugging is mixing two or more waters which are incompatible. The individual waters may be quite stable at all system conditions and present no scale problems. However, once they are mixed, reactions between ions dissolved in the individual waters may form insoluble products. When this occurs, the waters are said to be incompatible.

For example, it would be a mistake to mix a water which contained a large quantity of barium (Ba^{++}) with a water containing a large amount of sulfate ($SO_4^{=}$); the formation of $BaSO_4$ would be almost certain.

Two waters might be described qualitatively as shown in Table 3.8:

Table 3.8

Two Qualitative Water Analyses

Component	Water "A"	Water "B"
Ca^{++}	Present	Absent
HCO_3^-	Absent	Present
$SO_4^{=}$	Absent	Present
Ba^{++}	Present	Absent
Fe^{++} or Fe^{+++}	Absent	Present
H_2S	Present	Absent

Depending on the amounts of each constituent present, the pH, temperature and the ratio in which the two waters are mixed, you might expect any or all of the following precipitates to result: calcium carbonate, calcium sulfate, barium sulfate or iron sulfides.

The situation is further complicated if more than two waters are mixed.

Mixing two or more incompatible waters on the surface for subsurface injection is obviously undesirable.

Incompatibility Between Injection and Formation Waters

The second area where problems may arise from incompatibility is when the injection water is not compatible with the natural formation water (connate water) in the zone where the water is being injected. Surprisingly, very few plugging problems due to incompatibility occur in the injection well.

When water is injected into a well, the injection water miscibly displaces the connate water. Mechanical mixing occurs at the boundary between the two liquids. This mixing phenomenon is called ***hydrodynamic dispersion***. Non-homogeneous permeability distribution has been suggested as the primary cause of dispersion. In addition, dissolved ions migrate across the boundary between the two waters as a result of ***diffusion***.

The relative contributions of hydrodynamic dispersion and ionic diffusion to the total mixing process are a function of the velocity with which the boundary between the two waters moves through the reservoir rock. In most injection operations, the injection rates are such that dispersion is the predominate cause of mixing. However, in most laboratory studies, the individual contributions of dispersion and diffusion are not separated, and the amount of mixing is described by an apparent coefficient of dispersion, which includes both effects.

Warner[(3.30)] gives equations for the width and volume of the mixing zone:

$$w = 4.619\sqrt{D' r} \tag{3.72}$$

$$V_m = 5.17h\phi\sqrt{D' r^3} \tag{3.73}$$

Where:
w = Width of mixing zone, ft
V_m = Volume of mixing zone, bbl
D' = D/v = Coefficient of dispersion, ft
D = Coefficient of dispersion, ft^2/sec
v = Average velocity of fluid flow, ft/sec
r = Radial distance from the wellbore to the center of the mixing zone, ft
h = Thickness of injection zone, ft
ϕ = Porosity of reservoir rock, expressed as a fraction

Figure 3.16 illustrates the growth of the mixing zone as it moves away from the injection wellbore.

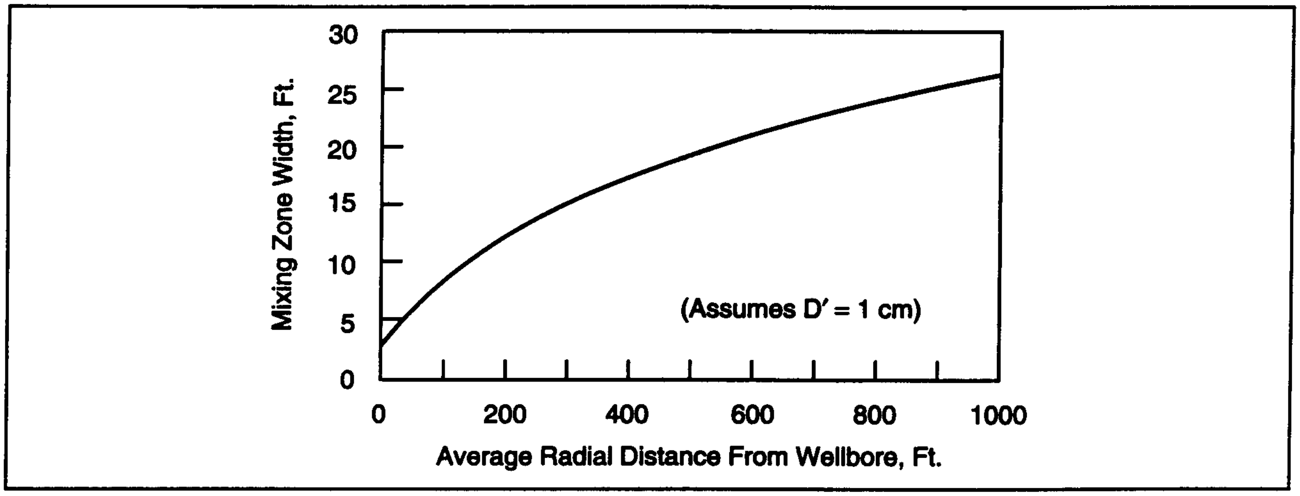

Figure 3.16 Mixing Zone Width as a Function of Distance

The radial distance from the injection wellbore to the center of the mixing zone is given as follows:

$$r = \sqrt{1.79\frac{V_i}{h\phi}} \tag{3.74}$$

Where: V_i = Volume of water injected, bbl

The radial distance to the leading edge of the mixing zone from the wellbore is equal to r + 0.5 w. Therefore, the total cumulative pore volume which is contacted by the mixing zone from the time it leaves the wellbore until it reaches a radius, r, is:

$$V_c = 0.56h\phi(r+0.5w)^2 \tag{3.75}$$

Where: V_c = Volume of pore space contacted by leading edge of mixing zone, bbl

If one assumes the worst case, that two waters are completely mixed within the mixing zone (which they are not), it is possible to calculate the maximum volume of scale which could precipitate for a given set of conditions.

$$V_p = 2.9\times10^{-6}\,\frac{V_m PPT}{SG} \tag{3.76}$$

Where:

V_p = Volume of scale precipitated, bbl
PPT = Weight of scale precipitated, lb/1000 bbl
SG = Specific gravity of the scale formed

Example

Assume the following:

1. The two waters are completely mixed within the mixing zone.
2. Barium sulfate is being formed in the mixing zone. The specific gravity of $BaSO_4$ is 4.2.
3. The maximum amount of scale which can precipitate is 100 mg/L (35 lb/1000 bbl).
4. The injection zone is 10 ft thick.
5. The fractional porosity of the injection zone is 0.20.
6. D' = 1.0 cm = 0.033 ft.

It is now possible to calculate the mixing zone volume, the total volume of reservoir pore space contacted, and the volume of precipitate formed, as a function of the volume of water injected. The results for the conditions stated in the example are presented in the Table 3.9.

The precipitate thus formed is distributed throughout the total volume of pore space contacted by the mixing zone, V_c, and occupies a negligible fraction of that space. In addition, once the mixing zone has passed a given point in the reservoir, any precipitate is exposed solely to the injection water, and will often be at least partially redissolved.(3.30) Therefore, one would not anticipate any significant reduction in injectivity due to incompatibility.

Several investigators have reported laboratory experiments which confirm this conclusion, both in rocks containing 100% water(3.30,3.31) and where an oil saturation is present.(3.31) Injection well plugging due to this phenomena is considered extremely unlikely.

If you wish to avoid completely any possibility of permeability reduction, it is possible to inject a buffer zone of a third water which is mutually compatible with both the injection water and the connate water. The volume required to totally eliminate mixing to any given radius is equal to the volume of the mixing zone, V_m, and can be calculated from Equation 3.73.

It is also possible to treat the injection water with a scale preventive chemical to prevent precipitation in the immediate area of the injection wellbore. However, this approach is unlikely to be effective farther out in the reservoir since most scale inhibitors have a strong tendency to adsorb on solid surfaces. The large amount of surface area presented by the reservoir rock makes it extremely likely that all inhibitor will be adsorbed by the rock within a very short distance from the wellbore.

So the good news is that injection well plugging due to incompatibility between the injection water and the connate water is an extremely unlikely event.

However, there is some accompanying bad news: Severe scale formation can occur in the producing wells after injection-water breakthrough.

TABLE 3.9

Reservoir Mixing Calculations

Volumen inyectado [illegible] [illegible] Producido

V_i (bbl)	r (ft)	W (ft)	V_m (bbl)	V_c (bbl)	V_p (bbl)
1	1	0.8	2	2	4.1×10^{-5}
10	3	1.5	10	15	2.3×10^{-4}
10^2	9	2.6	54	126	1.3×10^{-3}
10^3	30	4.6	306	1151	7.3×10^{-3}
10^4	95	8.1	1733	10833	4.1×10^{-2}
10^5	299	14.5	9675	104736	2.3×10^{-1}
10^6	945	25.7	54364	1027617	1.29

This can occur because there is ample opportunity for mixing of large volumes of injection water and connate water in the producing wells after breakthrough of injection water. When the producing zone is comprised of several layers of different permeability (which is usually the case), the injection water will break through earlier in some layers than in others. The result is the simultaneous production of both injection and connate water. Simultaneous production of both waters can also occur due to differing breakthrough times for water from several injectors into a single producer.

Even in relatively homogeneous reservoirs, simultaneous production of the two waters will occur since the reservoir volume swept by the injection water increases with time. Both injection water from the swept area and connate water from the unswept area will enter the producing wellbore, and the relative amounts will change over the life of the flood.

Evaluation of Incompatibility

Compatibility of water mixtures is assessed either by solubility calculations or by experimental testing.

Solubility Calculations

If solubility calculations are to be performed, the following procedure is recommended:

1. Obtain analyses of the waters to be mixed.
2. Calculate a composite analysis for the waters at various mixing ratios of interest.
3. Calculate the average pH values for the various mixtures
4. Calculate the scaling tendencies of the mixtures.

Calculating the pH of a Mixture

$$pH = -\log\left[H^+\right];\ therefore, \left[H^+\right] = 10^{-pH} \tag{3.77}$$

$$pH_{avg} = -\log\left\{F_1\left[H^+\right]_1 + F_2\left[H^+\right]_2 + F_3\left[H^+\right]_3 + \ldots + F_n\left[H^+\right]_n\right\} \tag{3.78}$$

Where:
$[H^+]$ = Hydrogen ion concentration, moles/liter
$F_1, F_2, F_3, \ldots, F_n$ = Fraction of each water in a given mixture
$[H^+]_1, [H^+]_2, [H^+]_3, \ldots, [H^+]_n$ = Hydrogen ion concentration of each water

Compatibility Testing

Fresh samples of the waters to be mixed are taken, filtered to remove any suspended solids and then mixed in several ratios. The various sample mixtures are set aside and observed to see if any precipitation occurs.

This procedure is quite useful for the detection of potential calcium, barium, or strontium sulfate precipitation problems. However, it cannot be relied upon to give an accurate indication of the precipitation of calcium carbonate or iron compounds because both are quite sensitive to pH changes. The solubility of sulfate compounds is largely insensitive to changes in pH.

PREVENTING SCALE FORMATION

Avoid Mixing Incompatible Waters

The importance of staying away from compatibility problems should be obvious from the preceding discussion. Always be extremely careful when you are considering mixing waters.

If you have two incompatible waters on the surface, and you wish to inject them both, there are two methods of doing so without incompatibility problems.

1. Split System

   Inject the two waters through separate injection systems into two different groups of wells.
2. Sequential Injection

   Store the two waters in two sets of tanks and inject them alternately. The zone of mixing in the injection line is small, and the volume of precipitate generated is insufficient to cause plugging in the injection wells.

Water Dilution

This is just the reverse of the preceding problem. An injection water that normally would be scale forming may be diluted with another water so that the resulting mixture is stable at system conditions.

pH Control

Lowering the pH will increase the solubility of iron compounds and carbonate scales. However, it will also tend to make the water more corrosive, and may create corrosion problems. pH has little, if any, effect on the solubility of sulfate scales.

This is not a widely used method of scale control. It is usually practical only if a small shift in pH is necessary to prevent precipitation of insoluble compounds. Accurate pH control is also necessary and this is often difficult in normal oilfield operations.

Removal of Scale Forming Constituents

Dissolved Gas Removal

Dissolved gases such as H_2S, CO_2, and O_2 can be removed from the water by chemical and/or mechanical means. This can eliminate the formation of insoluble iron compounds.

Simply removing CO_2 from water will actually increase the severity of scale deposition. However, the pH can be lowered sufficiently to convert all carbonates and bicarbonates to CO_2. Then removal of CO_2 will prevent the formation of carbonate scales.

Dissolved gas removal is discussed in Chapter 6.

Water Softening

Processes such as ion-exchange, precipitation softening or distillation are seldom used to prevent scale deposition from injection waters. These processes remove scale forming cations such as Ca^{++} and Mg^{++} and may be used alone or in combination.

The problem with using these processes with oilfield brines centers on the cost involved to remove the inherently large quantities involved. It is nearly always far cheaper to use other methods of scale control.

Of the processes listed, ion-exchange is probably the most generally applied in oilfield-related operations. Ion-exchange units have been widely used to soften water for use as boiler feed water in gas processing plants and for steam generators used in thermal recovery operations. They also are used to soften water in several of the enhanced oil recovery processes.

Ion exchange and other ion removal processes are discussed in Chapter 6.

Nanofiltration

Nanofiltration membranes have been developed which selectively remove divalent ions such as sulfate, magnesium and calcium. Monovalent ions such as sodium and chloride pass through the membrane.

This technology has been applied in the North Sea to reduce the sulfate concentration of the injected seawater as a means of controlling barium sulfate scale formation in the producing wells resulting from incompatibility with the formation water.(3.49) Sulfate removal efficiency is reported to be as high as 98% at a recovery of 75%.

A recovery of 75% means that 75% of the incoming water will be processed for injection. The remaining 25% is the concentrated reject stream which contains the ions removed from the injection water. It is discharged overboard.

Scale Control Chemicals

Scale inhibitors are chemicals which will delay, reduce or prevent scale formation when added in small amounts to a normally scaling water. Most of the scale inhibitors used in the oilfield function by one or both of the following mechanisms:

- When scales first begin to form, very tiny crystals precipitate from the water. At this point, the scale inhibitor ***adsorbs*** onto the surface of the crystals while they are still very tiny and prevents further growth. This is thought to be the primary mechanism by which most oilfield scale inhibitors work.
- In some cases scale inhibitors prevent the precipitated scale crystals from adhering to solid surfaces such as piping or vessels.

The mechanisms by which scale inhibitors accomplish one or both of these objectives are not completely understood.(3.32)

It seems clear that a scale inhibitor which prevents precipitation is required for water injection operations. If precipitation occurs the scale particles can still form deposits and contribute to plugging even if they are prevented from forming adherent scales.

The fact that most commonly used scale inhibitors function by inhibiting the growth of the scale crystals means that the inhibitor must be present in the water at the point where the crystals begin to form. Providing an effective chemical has been chosen, two rules must be observed if scale inhibition is to be successful.

- The inhibitor must be present in the water at the point where scale crystals begin to form in order to have maximum effectiveness in inhibiting further growth. This means that the inhibitor must be applied upstream of the problem area.
- The inhibitor must be present in the water on a continuous basis so that it is available to inhibit the growth of each scale crystal as it precipitates from the water. Therefore, continuous injection of scale inhibitor is required.

All commonly used scale inhibitors are organic compounds. The most common types are:

- Phosphate Esters

  Phosphate esters are not recommended for application above approximately 175°F [79°C] as there is a danger of hydrolysis (reaction with H_2O) resulting in a loss of effectiveness.
- Phosphonates

  Phosphonates are more temperature stable than the esters and should provide some protection up to 350°F [175°C].
- Polymers

  Polymers such as the acrylics are primarily used for high temperature applications. They can be used up to 350°F [175°C].

Selection and Evaluation of Scale Inhibitors

Like any other operation in the oilfield, scale inhibitors should be selected on a cost/effectiveness basis. It is very tempting to choose the cheapest chemical available. This is very often a tragic error. Sometime the most expensive material on a ***cost per unit volume of chemical*** basis will be the cheapest to use based on ***cost per volume of water treated.***

1. Chemical Composition of the Scale

   Certain compounds are more effective for specific scales.
2. Severity of Scaling

   The efficiency of scale inhibitors is primarily dictated by the level of supersaturation. The higher the saturation index, the more difficult it is to inhibit scale formation.
3. System Temperature

   Scale inhibitors generally become less effective as the temperature increases. Each inhibitor has an upper temperature limit above which they become progressively less effective.
4. Laboratory Scale Inhibitor Performance Tests

   Laboratory scale inhibitor performance tests are comparative tests which determine percent inhibition as a function of scale inhibitor concentration. The data from this type of testing is intended to measure relative inhibitor effectiveness. It does not provide a recommended scale inhibitor treatment concentration for field use.

5. Effect of Suspended Solids

   If substantial amounts of suspended solids are present, higher inhibitor concentrations will be necessary. The reason is that scale inhibitors will adsorb onto the surface of solids in the water, thereby reducing the amount available to inhibit scale formation.

6. Compatibility with Other Chemicals

   The scale inhibitor should be compatible with any other chemicals being added to the system, such as oxygen scavengers, corrosion inhibitors, or biocides. It is important that there is no reaction or interference among the different chemicals being used in a system.

7. Compatibility with the Water

   Some scale inhibitors will react with calcium, magnesium or barium ions to form rather insoluble compounds. Precipitation of these compounds can result in the formation of a scale, thus creating a new problem. Generally, phosphonates and polymers are more prone to give this problem than the esters.(3.32)

   If high concentrations of these ions are present in the water the scale inhibitor must be selected with care to avoid this problem.

8. Effect of Dissolved Iron on Calcium Sulfate Inhibition

   Most scale inhibitors are less effective in inhibiting calcium sulfate scale formation when dissolved iron is present in the water. The effect is severe in the case of phosphate esters and phosphonates, while most polymers show only slight decreases in performance.

   While it is possible to compensate for this effect by increasing the scale inhibitor concentration, the additional cost can be substantial.

   Soluble iron concentrations are typically quite low in sour waters and in waters containing dissolved oxygen, since most of the iron will precipitate as iron sulfide or ferric hydroxide. However, concentrations can be substantial in sweet, air-free systems.

   Since corrosion is the most common source of soluble iron in oilfield waters, an effective corrosion control program is essential for cost-effective scale inhibition. If the source of iron is the producing formation, the use of polymer-type scale inhibitors should be considered.

9. Effect of pH

   Some scale inhibitors become less effective against $BaSO_4$ and $CaSO_4$ scales at pH values below 6. Since values less than 6 are quite common in oilfield waters, this can be an extremely important consideration in chemical selection.

10. Weather

    Is it a cold weather operation? Be sure to determine the pour point of any scale inhibitors and design the chemical injection system to avoid freezing problems.

Inhibitor Application

Organic scale inhibitors are supplied as liquids with the exception of certain polymers which can be obtained in powder form. The powder is dissolved in water prior to application.

Organic inhibitors are applied to surface facilities and injection wells by continuous injection using standard chemical pumps. it is essential that pumps be maintained and checked frequently to ensure that the proper amount of chemical is being injected. This is especially important for scale inhibitors since they must be injected on a continuous basis to be effective. Therefore, the success of any scale inhibition program will depend on the percentage of time which the pump is operating properly. If the chemical pump is down half of the time, the most effective scale inhibitor cannot be expected to give good results.

Scale problems in water-supply wells are treated by continuous injection from the surface or by squeezing the inhibitor into the water producing formation. The choice of methods usually depends on the well completion and the nature of the problem.

Monitoring

The minimum effective scale inhibitor concentration is often difficult to determine with precision. Some commonly used monitoring methods are:

- Pipe Spools or Nipples

  Often used for corrosion monitoring, spools are simply short sections of pipe installed at various locations which may be removed and inspected for scale buildup. If scale is present, the thickness can be measured or the scale can be scraped off and weighed. In order to be useful, the spool must be easily removable from the system. In some cases it is relatively simple to depressure the system and remove the spool. In other cases the system cannot be easily depressured and a bypass around the spool should be installed so that operation can continue while the spool is being removed.

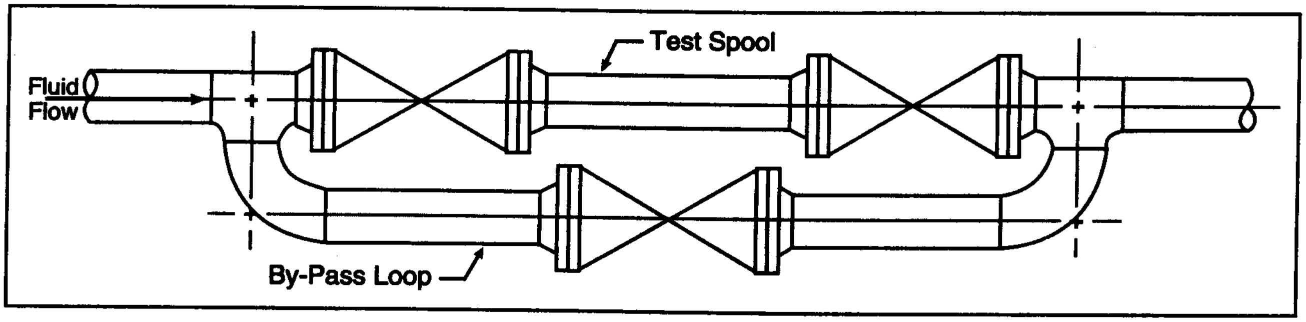

Figure 3.17 Pipe Spool Installed in Bypass Loop

- Scale Coupons

  Scale coupons may be used to detect scale buildup. They are similar to corrosion coupons except that they are perforated with a minimum of 6 to 8 holes. The coupon is placed in the system with the flat side facing the direction of flow. This induces turbulence which accentuates any scaling tendencies. The coupon is weighed before and after exposure to the fluid and the amount of scale determined by the difference in the two weights.

- Visual Inspection

  Although not too quantitative, this method is quite reliable. Look inside tanks, break open lines, look inside valves, look for spots where you might expect scale and inspect them ***regularly***.

- Infrared Thermography

  Infrared thermography has been used to detect and monitor internal scale accumulations in North Sea production facilities. This technique is used to measure the surface temperature of piping and vessels which handle hot produced fluids. Internal scale accumulations will cause the external temperature to be cooler than normal due to the fact that scales have a lower thermal conductivity than steel.

- Increased Pressure Drops in the System

  The flow rate must also be measured.

- Decreased Injectivity

  Injectivity decline is evidenced by increasing injection pressures to maintain injection rate. This indicates formation plugging which may be due to scale particles. It also may be due to other causes.

Non-Chemical Scale Control Devices

Various devices are available which are claimed to prevent scale deposition. Water is passed through the device, and scale is prevented by rather vaguely described mechanisms. There are three major categories of devices:

Magnetic Treatment Devices

A magnetic field (imposed by either a permanent magnet or an electromagnet) is claimed to cause alterations in the structure of water or dissolved ions, which prevents scale formation.(3.33-3.36)

Electrostatic Devices

They typically contain an electrically insulated, electrostatically charged electrode which is claimed to neutralize or alter the ionic charges, thus preventing scale.(3.33)

Catalytic Devices

Pressure fluctuations within the device are said to cause precipitation on a special alloy metallic core which is washed away as a suspension of scale crystals.(3.33)

Theories proposed to explain the operation of these devices are typically unsubstantiated and could charitably be described as pseudoscientific.(3.35) Both positive and negative results have been reported for both laboratory and field application of the devices. However, the conditions under which the devices are evaluated are often poorly controlled and documented, leaving ample room for skepticism.

Based on presently available information, the use of any of these devices to prevent scale formation in oilfield systems cannot be recommended.

SCALE REMOVAL

Scale Identification

The success in removing scale accumulations will be determined to a great extent by your knowledge of the scale composition. Identify the problem correctly and you have a much greater probability of solving it.

We have already covered methods of predicting which types of scales might be expected for a particular water under certain conditions. However, the only reliable method of assessing the problem is to obtain a sample of the scale or plugging solids and analyze it.

If scale is occurring in surface facilities, a sample can be obtained by opening the system and scraping out some of the scale. Samples can be obtained from an injection well by backflowing the well or by running a bailer.

The general scheme for identifying the components of a scale sample is much the same whether performed in a commercial laboratory or in the field. The primary difference is that a laboratory analysis will usually give the amount of each component present, where a field analysis is very qualitative. A quantitative scale analysis procedure is given by Ostroff(3.1).

Field Scale Analysis

In a field scale analysis we attempt to guess the composition of the solid by doing the following:

- Soak the sample in a solvent to dissolve any hydrocarbons. Watch to see if the solvent gets darker in color.
- Check to see if the sample is magnetic. If it is strongly magnetic, it probably contains a major amount of Fe_3O_4 (magnetic iron oxide). If it is weakly magnetic, it may contain a small amount of Fe_3O_4, or it may be iron sulfide.
- Place the sample in 15% HCl. Note whether or not a violent reaction occurs. Note any smell. (H_2S indicates FeS.) Note the color of the acid. If it turns yellow, an iron compound is indicated.

  It should be noted that when iron sulfide is placed in contact with air, it will oxidize and convert to an iron oxide. This means that the composition of scales or deposits originally containing iron sulfide is a function of the length of time the deposit has been exposed to air. Analyses performed several days or weeks after the sample has been removed from the system will frequently find predominantly iron oxide and little or no iron sulfide.
- Check the solubility in water. NaCl is water soluble.

Qualitative identification of the components present can be summarized in terms of the preceding properties in Table 3.10.

TABLE 3.10

Qualitative Analysis of Scales

Component	Soluble in Solvent	Soluble in HCl				Soluble in Water
		Magnetic	Reaction	Acid Color	Smell	
Hydrocarbon	Yes					
$CaCO_3$			Violent			
$CaSO_4$						
$BaSO_4$						
$SrSO_4$						
FeS		Weak	Strong	Yellow	Stinks!(H_2S)	
Fe_2O_3			Weak	Yellow		
Fe_3O_4		Strong	Weak	Yellow		
$FeCO_3$			Very strong	Yellow		
NaCl						Yes
Sand, Silt, Clay						

Note: Neither sulfates nor sand, silt or clay reacts with anything. A magnifying glass may help to recognize sand grains or spot sulfate crystals. However, if nothing happens to the sample when you run a field analysis, send a fresh sample (not the one you worked on) to a commercial laboratory.

After the sample has been identified a scheme to dissolve or remove the scale or deposit can be formulated. Chemical removal of scale follows the same principles as scale analysis. Basically, the problem is to find something that will dissolve the various components of the deposit. If it consists primarily of a single component, such as calcium carbonate, then a single solvent (hydrochloric acid in this case) is sufficient. If it contains more than one component, a series or combination of treating chemicals may be dictated. In addition, mechanical removal methods may be used, either alone or in conjunction with chemicals.

Scale Removal Chemicals

Hydrocarbons

Although hardly a scale, hydrocarbons are often present and can greatly interfere with the action of acid or other scale removal chemicals. Acid will not react with oil-coated scale! A hydrocarbon solvent is needed to remove any oil, paraffin or asphaltic materials on the scale so that the chemical of your choice can get at the solid scale.

Selection of a solvent for hydrocarbons is usually based on trial and error. However, we do know that the more asphaltic the oil or deposit, the more aromatic the solvent should be. The best approach is to consult your chemical supplier.

Hydrocarbon solvents can be applied as a pre-wash. They have also been emulsified in hydrochloric acid to improve its effectiveness.(3.37)

In addition to simple organic and inorganic solvents, various complex proprietary solvents are available which can be used alone to remove oil(3.38,3.39) or can be miscibly mixed with hydrochloric acid to improve its effectiveness in penetrating hydrocarbons.(3.40) These materials range from mixtures of alcohols to micellar solutions.

Calcium Carbonate

Hydrochloric Acid

is recommended as the cheapest and easiest way to dissolve $CaCO_3$ scale under most conditions. Concentrations of 5, 10, or 15% HCl are normally used.

$$CaCO_3 + 2HCl \rightarrow H_2O + CO_2 \uparrow + CaCl_2$$

A corrosion inhibitor must be added to the acid to keep it from dissolving the pipe. You should think of the useful lifetime of an acid inhibitor in terms of hours rather than days or weeks. Once the inhibitor ceases to be effective, the pipe will be subject to extremely severe pitting which often results in perforation of the pipe wall. Therefore, it is essential that all acid be immediately flushed from the system once the cleanout is completed.

A surfactant is often added to help remove any oil film from the scale, but a pre-wash with a solvent or addition of one of the previously mentioned proprietary solvents is preferred unless the amount of oil is extremely small. Acid will either not react at all or it will react very slowly if the scale is oily.

Figure 3.18 shows the effect of a coating of light oil on the reaction rate of 10% HCl with $CaCO_3$ scale. The scale was 1/8" thick on the internal surface of a 1/4" x 1" nipple.

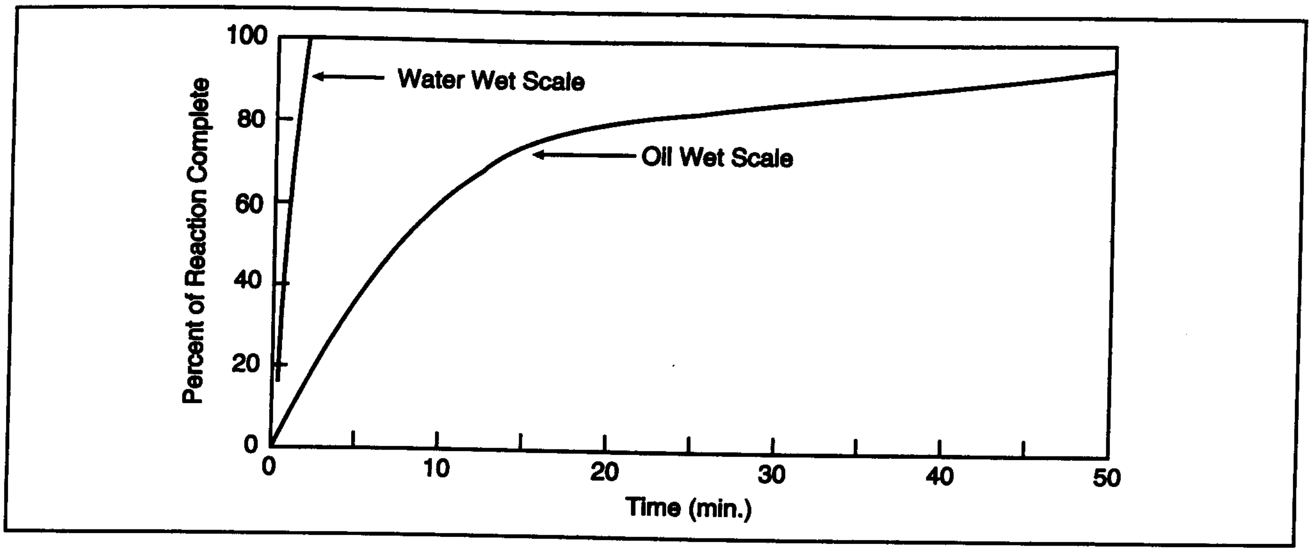

Figure 3.18 Reaction Rate of HCl with $CaCO_3$ Scale(3.5)

Table 3.11 gives the amount of $CaCO_3$ which will be dissolved by different concentrations of HCl.

TABLE 3.11
Reaction of HCl with Calcium Carbonate

% HCl	$CaCO_3$ Dissolved (lbs/gal of acid)
5	0.6
7.5	0.9
10	1.2
15	1.8
28	3.7

Figure 3.19 is helpful in calculating the amount of 15% HCl required to dissolve various acid soluble scales.

Chelating Agents

It is possible to dissolve calcium carbonate scale with chelating agents, such as EDTA (ethylenediaminetetraacetic acid). They function by reacting with the calcium ion to form a water soluble complex, thereby effectively removing the ion from solution.

When calcium carbonate scale is in equilibrium with a water which contains calcium ions and carbonate ions, then the equilibrium can be described as:

$$CaCO_3 \leftrightarrow Ca^{++} + CO_3^{=}$$

If a chelating agent is added to the water, some of the calcium ions will be chelated, resulting in a decrease in the Ca^{++} ion concentration. When this occurs, some of the $CaCO_3$ scale will dissolve and replace the Ca^{++} ions lost to the chelating agent in order to maintain the equilibrium of the reaction.

$$\text{For} \begin{bmatrix} CaCO_3 \\ Fe_2O_3 \\ FeS \end{bmatrix} \text{use} \begin{bmatrix} 95 \\ 318 \\ 180 \end{bmatrix} \text{gal 15\% HCl/ft}^3 \text{ of scale}$$

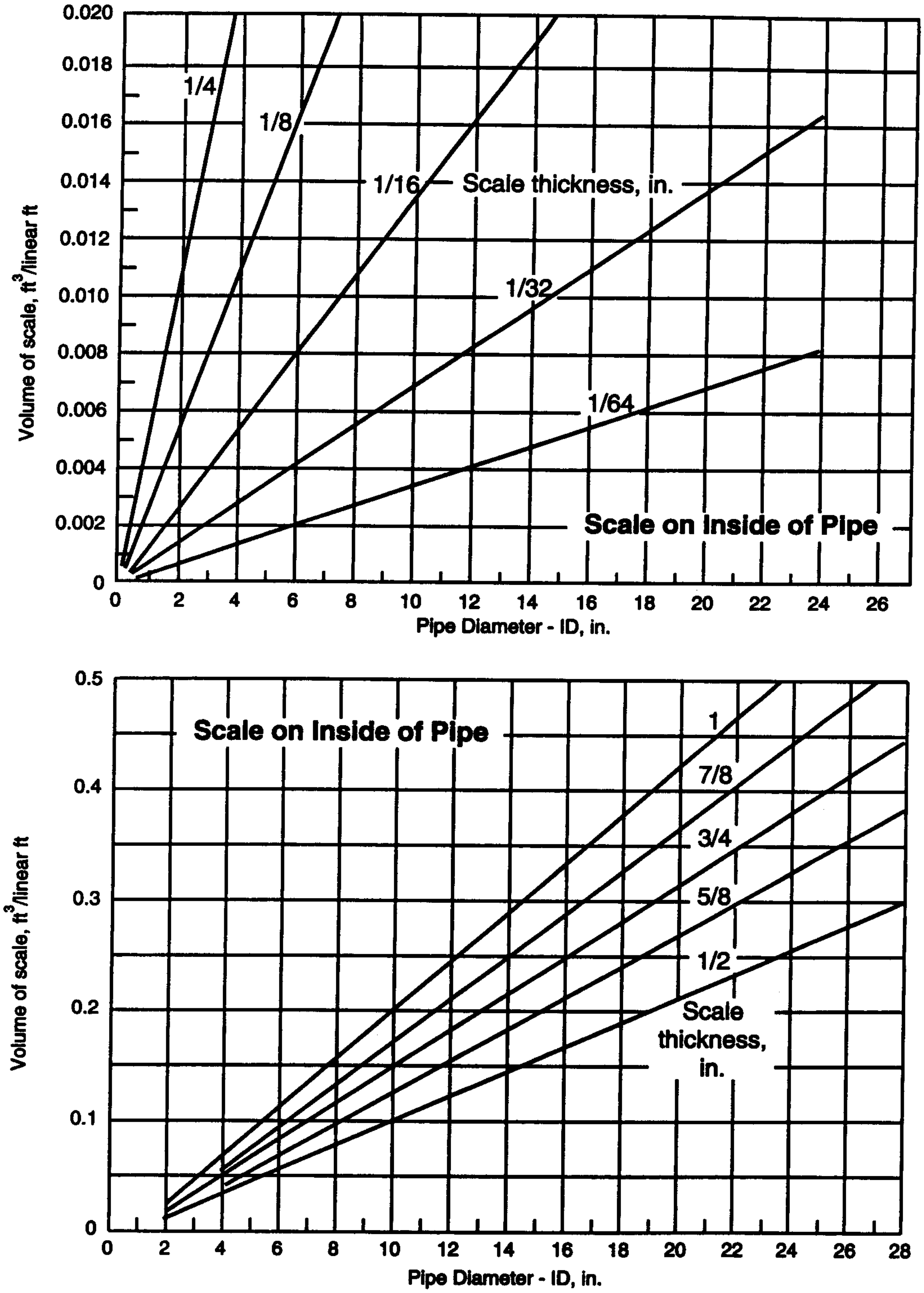

Figure 3.19 Determination of Scale Volume Inside Pipe(3.41)

Chelation can also occur at the solid surface of the calcium carbonate scale, taking calcium ions directly from the crystal lattice.

The basic disadvantages to the use of chelants to dissolve calcium carbonate scale are:

- Chelating agents are not efficient "solvents." For example, it takes 7.4 ppm EDTA to chelate 1.0 ppm Ca^{++}.
- The chemicals are relatively expensive.

Chelating agents are seldom used to remove calcium carbonate scale in normal oilfield operations. However, their use has been reported in Prudhoe Bay.(3.42)

Calcium Sulfate (Gypsum)

Hydrochloric acid is not a good solvent for $CaSO_4$. The maximum solubility of $CaSO_4$ in HCl is only 1.8 wt % at 25°C and atmospheric pressure.(3.43)

Converters

Inorganic Converters

Inorganic converters are usually carbonates or hydroxides which react with calcium sulfate and "convert" it to acid soluble calcium carbonate or calcium hydroxide. The conversion treatment is then followed by a hydrochloric acid treatment to dissolve the resulting calcium carbonate or calcium hydroxide.(3.44)

A good example of this type of chemical is ammonium carbonate which has been marketed under several trade names. The reaction is:

$$CaSO_4 + (NH_4)_2CO_3 \rightarrow \underset{\text{Soluble}}{(NH_4)_2SO_4} + CaCO_3$$

The calcium carbonate is then dissolved with HCl:

$$CaCO_3 + 2HCl \rightarrow H_2O + CO_2 \uparrow + CaCl_2$$

The CO_2 liberated by the acid reaction helps to mechanically dislodge any remaining deposit. Inorganic converters are not recommended for dense deposits and are seldom used.

Organic Converters

Organic converters such as sodium citrate, potassium glycollate, and potassium acetate are also used.(3.44) These materials react with calcium sulfate deposits causing them to swell and become soft so they may be removed easily by flushing with water. These chemicals are expensive, require several hours contact time to work on thick deposits, and should be checked on an actual sample of the scale before application, if possible.

Chelating Agents

The same comments apply here as for use to remove calcium carbonate.

Sodium Hydroxide (Caustic)

A 10% solution of NaOH will dissolve up to 12.5% of its weight of gypsum scale. ***Be careful — caustic burns skin!***

Salt Water

Water containing 55 000 mg/L of NaCl will dissolve three times as much gypsum at 104°F [40°C] as will fresh water at the same temperature.

Barium Sulfate

Dense barium sulfate is almost impossible to chemically remove. However, several proprietary "scale dissolvers" are available which have been used to dissolve thin layers of barium sulfate scale.

These materials are chelating agents rather than true solvents. Barium sulfate has a "solubility" of approximately 0.5 lb per gallon of chemical [120 g/L] in most of the commonly used scale dissolvers. This is rather low for a "solvent" by most standards. In addition, their reaction rates are often slow and their cost is relatively high.

However, they are the only chemicals which have been used successfully for the removal of downhole barium sulfate. Their disadvantages limit their application to the removal of thin layers of scale in systems where extremely large amounts of revenue are at risk, such as the North Sea.

Iron Compounds

Hydrochloric acid is normally used to dissolve iron compounds. Once again, it must contain a corrosion inhibitor to prevent pipe corrosion. In addition, it should contain an iron-stabilizing agent to prevent precipitation of iron compounds once the acid spends.

Iron dissolved during acidizing can exist as either ferric (Fe^{+++}) or ferrous (Fe^{++}) ions. As the acid spends, the pH will rise, and ferric ions will begin to precipitate as $Fe(OH)_3$ (ferric hydroxide) at a pH of about 2.2.(3.45) Once the pH reaches a pH of 3.2, essentially all of the ferric iron will have precipitated. Iron stabilizing agents are employed to prevent precipitation of ferric hydroxide.

There are two primary types of iron stabilizers:

- Chelating or Sequestering Agents

  These materials react with ferric ions to form a water soluble complex, thus preventing precipitation. Commonly used chelants are citric acid, acetic acid, mixtures of citric and acetic acids, ethylenediaminetetraacetic acid (EDTA), and nitrilotriacetic acid (NTA).

- Reducing Agents

  Reducing agents convert ferric ions to the more soluble ferrous ions. Erythorbic acid has been used for this purpose, and is capable of solubilizing up to nine times as much ferric iron as citric acid.(3.46)

In contrast, ferrous ions are quite soluble at pH values up to 7 and above. Since spent acid usually reaches a maximum pH of about 5.3, precipitation of ferrous iron is seldom a problem.

If iron sulfide is to be dissolved, care is suggested. The reaction between FeS and HCl is:

$$FeS + HCl \rightarrow FeCl_3 + H_2S \uparrow$$

H_2S is ***extremely poisonous*** and a few ppm in the air can ***kill*** you. A toxicity guide is given in Appendix 18. Fresh air masks should be on location and in use if there is any possibility that personnel may breathe any H_2S.

Salt (NaCl)

A fresh water wash is the best medicine for salt deposits.

Sand, Silt, Clay

These are usually present as occluded particles in scale deposits. Once the bulk scale material is dissolved, these materials may be washed out.

Scale Removal from Surface Lines

The Use of Line Scrapers

Scale removal from surface lines is usually accomplished by the combined use of chemicals and line scrapers, or "pigs." The basic types of pigs available are shown in Figure 3.20.(3.47)

Foam Pigs

Foam pigs are normally used for cleanout of lines which are not routinely pigged. They are made of an open-cell foam with a hard rubber or plastic wrapper. They are also made in brush form.

These pigs can be pumped through a series of lines of different diameters, and the body will deform sufficiently (within limits) to permit the pig to continue to do an effective scraping job.

Foam pigs are available in various lengths and styles. However, the length is usually twice the diameter. Foam pigs form a seal against the inside of the pipe by compressing the foam and do not seal from pressure differential as do the other types of pigs.

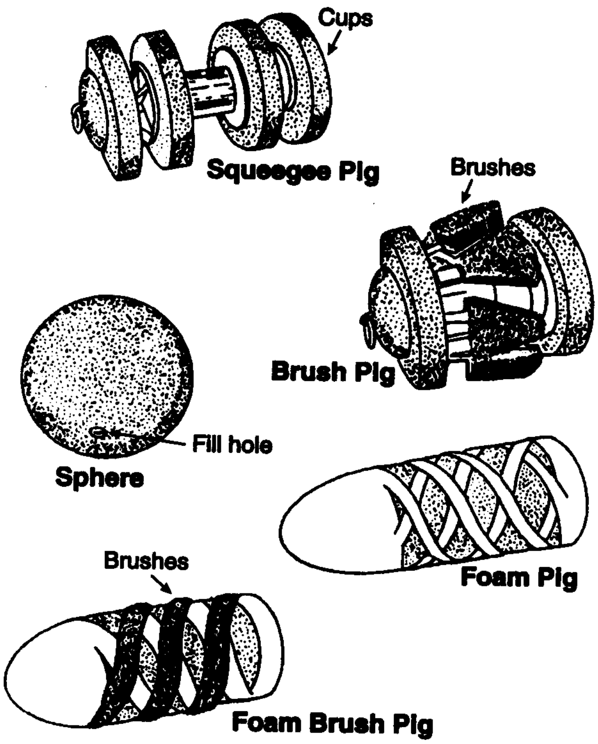

Figure 3.20 Types of Pigs

Brush or scraper pigs have holes in the pig to allow for bypass. Fluid passing through the holes in the pig will disperse the scraped solids in front of the pig. This will prevent a build-up of material in front of the pig which could create a plug and cause the pig to become stuck in the line.

Foam pigs with brushes have a built-in bypass. The brushes are short and fixed to the pig body. The blow-by occurs through the brush and helps to keep the brushes clean. If additional bypass area is necessary, the rubber or plastic covering on the nose of the pig can be cut out allowing passage of liquid through the open-cell foam body.(Figure 3.21)(3.47)

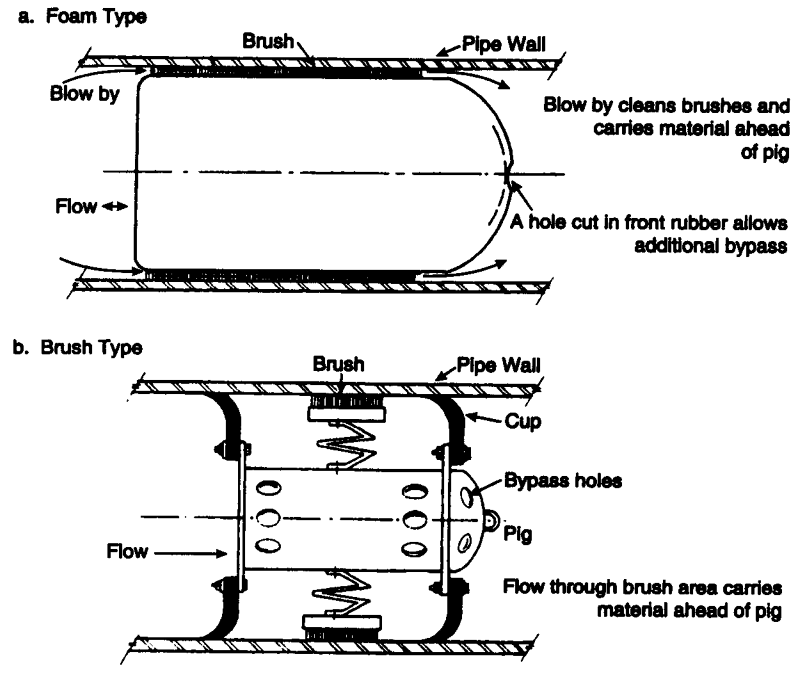

Figure 3.21 Cleaning Pigs

A typical flowline cleanout to remove oil coated calcium carbonate from a line might consist of the following steps:

1. Slug of solvent followed by a pig.
2. Slug of inhibited HCl followed by a pig.
3. Either a neutralizing solution (high pH water) or a thorough water wash to remove all acid. Acid inhibitors break down with time and all acid, spent or otherwise, must be flushed from the line or severe pitting corrosion may result.

Gelled Plugs

Gelled fluids can be injected into a line ahead of a conventional line scraper to aid in the transport of large volumes of solids. For example, a gelled-water and scraper system was used to remove approximately 350 tons of mill scale and other debris from a 280 mile-long, 36-in. OD gas line in the North Sea.(3.48)

Batches of gelled fluids (Kelzan XC polymer in water) and pipeline scrapers were used to remove loose and loosely adherent rust, silt, welding rods, weld slag, and other debris from the pipeline.

A wide variety of water-base gels, including hydrochloric acid, as well as hydrocarbon-base gels can be formulated to satisfy the specific requirements of a cleaning operation.

When a gelled fluid is in laminar flow in a pipeline, the central portion of the fluid flows as a plug with little exchange between the plug and the annular fluid. The velocity of the central plug can be significantly higher than the mean flow velocity.

A scraper behind a gel forces the fluid in the vicinity of the pipe wall, which contains entrained solids, to move into the central plug-flow region where it is carried forward through the length of the gel batch.

The debris that would remain in front of a mechanical pig in a conventional operation is picked up, carried forward, and eventually circulated and evenly distributed over a relatively long distance. This greatly reduces or eliminates the possibility of sticking the mechanical pig by debris build-up in front.

Downhole Cleanout

Downhole cleanout usually consists of removing scale from the tubing, the perforations, or formation face (open-hole completions) and sometimes from the pore spaces or fractures in the formation matrix.

Removing scale from tubing is basically the same as removal from surface lines, although pigs cannot be used. Except for special boring tools which normally are not used, tubing cleanout must be accomplished by chemical means alone. Obviously, if the tubing is badly scaled or plugged it may be necessary to pull the tubing and clean it on the surface.

Removal of scale from the formation face or perforations usually involves a simple soaking operation with one or more solvents. However, if scale has formed in the perforation tunnels and pore spaces back into the formation for several inches, chemical soaking may not be successful. Here special downhole tools such as casing brushes, surge/swab tools, suction washers, circulation washers or retrievable bridge plugs and squeeze packers may be required in conjunction with a solvent to achieve removal of the scale.

In extreme cases, hydraulic fracturing may be the only way to penetrate the scaled interval.

Downhole scale problems are more prevalent in producing wells than in injection wells. Hence, most of the complex scale cleanout procedures are aimed at producers. It is possible to prevent scaling problems in injection wells. Downhole cleanout should not be a frequent problem in injection systems if they are being monitored properly. It is much easier and cheaper to prevent or treat the problem on the surface than to try to remove downhole deposits after they have formed.

If injection pressures begin to rise and injection well plugging or scaling is indicated, the following is suggested:

1. Try to backflow the well. If suspended particles have simply filtered out the formation face, this alone may solve the problem. If you can backflow the well, be sure and try to catch samples of any solids which come to the surface. If gas is available, a gas-lift valve can be installed in the injection tubing to assist in the periodic backflow of an injection or disposal well.
2. If backflowing is not successful, go to a chemical cleanout procedure.

Technically, it is advisable to swab the solvents back to the surface or backflow the well after treatment. Solvents may become supersaturated and re-precipitate the material just dissolved. If re-precipitation occurs in the wellbore area, serious plugging can result. Thus, cleaning solutions should be brought back to the surface rather than displaced into the formation whenever possible.

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NOTES:

9

WATER TREATMENT FOR ENHANCED OIL RECOVERY

Oil recovery mechanisms for petroleum reservoirs can be categorized as shown in Figure 9.1.

Those mechanisms listed under "Secondary Recovery" are usually referred to as "Enhanced Oil Recovery" techniques, or simply EOR.

The EOR processes which use water are listed in Table 9.1 along with an estimate of the required water volumes.

Note that the volume of water required for the EOR techniques listed is typically far greater than the volume of oil recovered. Proper treatment of the water for each process is of extreme importance.

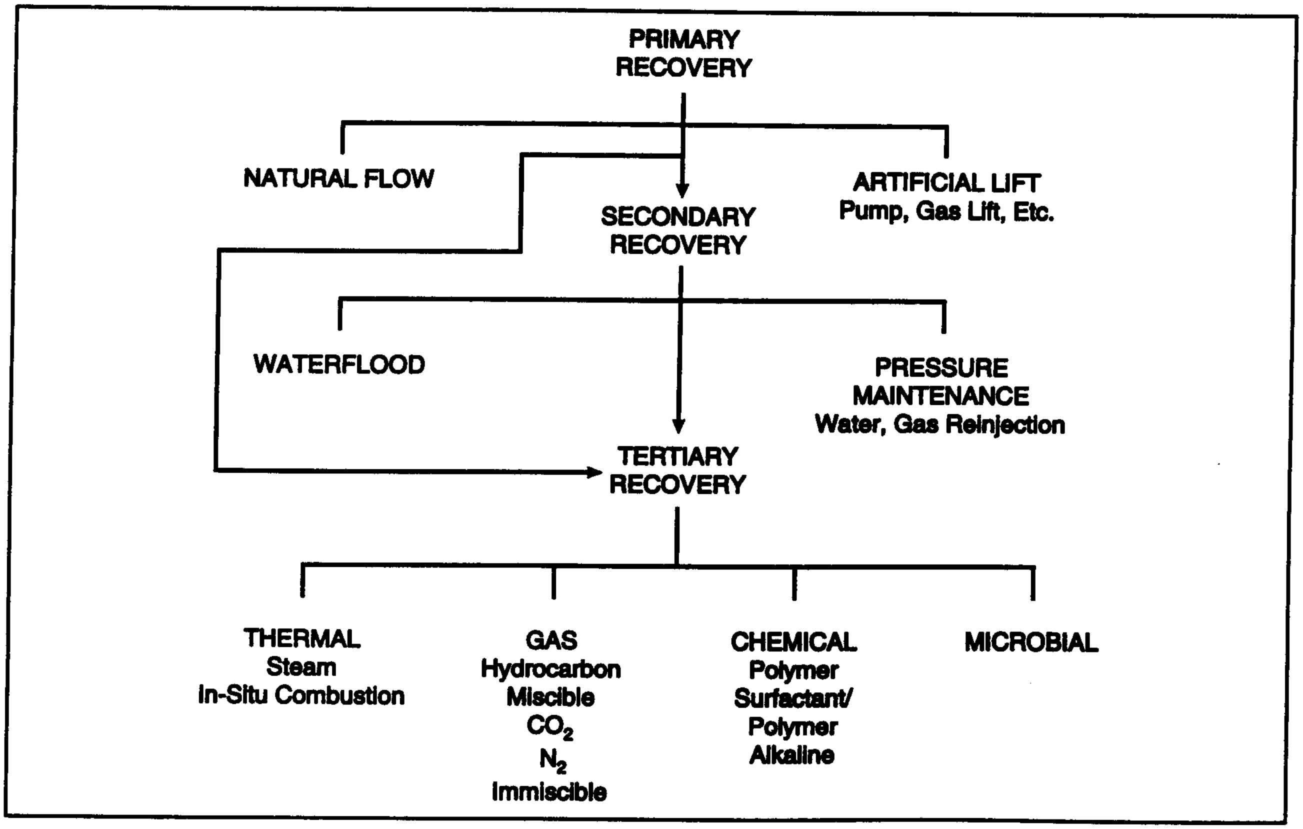

Figure 9.1 Oil Recovery Mechanisms(9.1)

TABLE 9.1

Estimated Water Usage for EOR Processes(9.2)

Process	Water Usage (bbl water/bbl oil)
Polymer	16-50
Surfactant — Polymer	10-15
Alkaline (Caustic)	22-33
Carbon Dioxide	1-3
In-situ Combustion (Wet)	0.5-1
Steam	2-5

POLYMER FLOODING

A polymer flood is carried out by injecting an aqueous polymer solution into the reservoir to displace the oil from the rock into producing wells. The polymer increases the viscosity of the solution which increases its ability to displace viscous crude oils. Other mechanisms are also involved, but they will not be discussed.

The composition and properties of the water which is used to make up the polymer solution are quite important, as they affect the viscosity of the solution. Also important are the agents which cause polymer degradation and decreases in solution viscosity, which can cause a reduction in displacement efficiency.

Two basic types of polymers are currently the most widely used: polysaccharides and polyacrylamides.

Polysaccharides

The polysaccharide typically used in enhanced oil recovery processes is xanthan gum and is often referred to as a "biopolymer." It has a molecular weight of about 5 million.

Xanthan gum is produced by the microbial action of *xanthomonas campestris* on a carbohydrate substrate. The biopolymer is an extracellular slime which forms on the surface of the bacterial cell. The fermentation broth is pasteurized to kill the *xanthomonas campestris*, and the polymer is precipitated from the broth by a suitable alcohol.(9.3)

Xanthan gum solutions exhibit relatively stable viscosity properties as a function of salt concentration, pH, and temperature.(9.4)

Microbiological Problems

Once a biopolymer is dissolved in water, it is highly susceptible to bacterial attack by both aerobic and anaerobic microorganisms, resulting in a significant reduction in solution viscosity.(9.3,9.5) In addition, some aerobic slime forming bacteria produce biological masses which contribute significantly to formation plugging.(9.3)

Water Salinity Effects

The viscosity of xanthan solutions increases with increasing brine salinity. The presence of multivalent cations has no additional effect on viscosity beyond their contribution to total salinity.(9.6)

Dissolved Oxygen

At room temperature, dissolved oxygen has no apparent effect on the viscosity of biopolymer solutions. However, at higher temperatures, enormous losses in viscosity are observed. (9.7)

pH Effects

The maximum fresh water solution viscosity has been observed at a pH of 5.5. Polymer viscosity is highest in high or low pH solutions.(9.8)

Polyacrylamide

The polyacrylamide molecule is a long chain made up of acrylamide monomer molecules. It has a basic structure as follows:

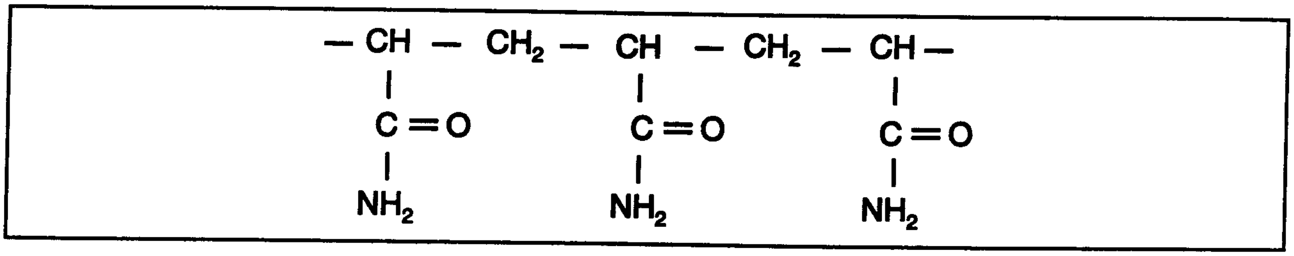

Figure 9.2 Basic Structure of Polyacrylamide

There are several mechanisms involved in the formation of the polymer molecule, which results in a wide range of chain lengths. The average molecular weight of commercial polyacrylamides typically ranges from 1 to 10 million.

Polyacrylamide is usually modified by chemically replacing some of the amide groups with carboxyl groups. This process is called hydrolysis, and the percentage of amide groups which have been replaced by carboxyl groups is referred to as the percent hydrolysis. The percent hydrolysis typically ranges from 0 to 30%. The primary reason for carrying out partial hydrolysis is to increase the viscosity of the polymer solution. The apparent solution viscosity of a partially hydrolyzed polyacrylamide dissolved in fresh water is much greater than that of a corresponding unhydrolyzed polyacrylamide.(9.3)

The carboxyl group ionizes in water, leaving a negative charge. The net result is a series of negative charges along the polymer chain, creating a negatively charged polymer.(9.9) This type of polymer is often referred to as an anionic polyelectrolite.

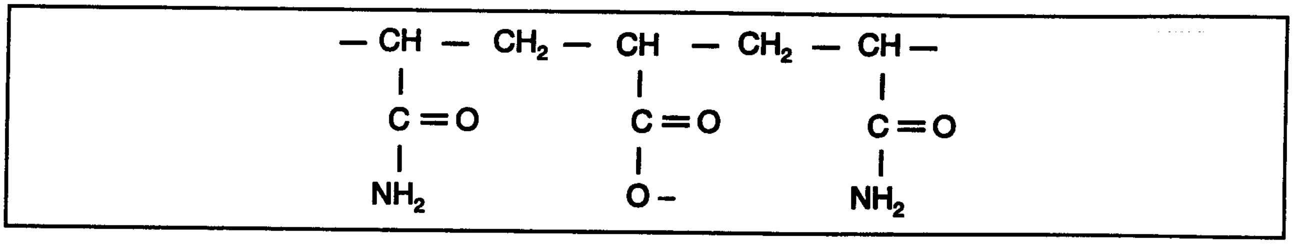

Figure 9.3 Partially Hydrolyzed Polyacrylamide

Polyacrylamides can be manufactured in the field using small portable plants.

Effect of Sodium, Calcium and Magnesium Ions

Increasing concentrations of sodium ions result in decreased viscosity of partially hydrolyzed polyacrylamide solutions. This is illustrated for a 0.25% solution of partially hydrolized polyacrylamide in Figure 9.4.

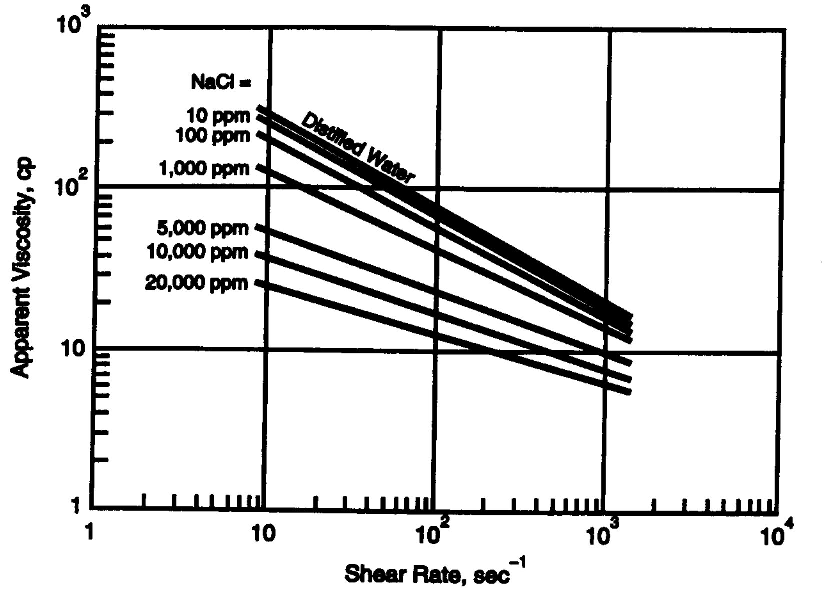

Figure 9.4 Effect of NaCl Concentration on Polymer Solution Viscosity(9.9)

This occurs because of neutralization of the electrical charges within the polymer molecules by the oppositely charged sodium ion. As the net charge on the polymer molecules decreases, the repellent force between molecules diminishes. The polymer chains coil up into a ball, thus causing a decrease in solution viscosity.(9.9,9.10,9.11)

Both calcium and magnesium ions cause larger decreases in viscosity than sodium ions.(9.9) Calcium ions cause a greater reduction in viscosity than an equivalent amount of magnesium ions, and mixtures of calcium and magnesium ions cause even greater reductions than either ion alone. The effect of salts on the viscosity of a 2500 ppm solution of partially hydrolyzed polyacrylamide is shown in Figure 9.5.

Effect of Oxygen

The presence of dissolved oxygen has a number of negative effects. It can cause:

- Dramatic increases in the corrosion rate of any carbon steel in the system.
- Precipitation of dissolved iron.
- Support the growth of aerobic microorganisms.
- Significant polymer degradation. Partially hydrolyzed polyacrylamides are very sensitive to oxidation, especially in higher temperature reservoirs.(9.9,9.12)

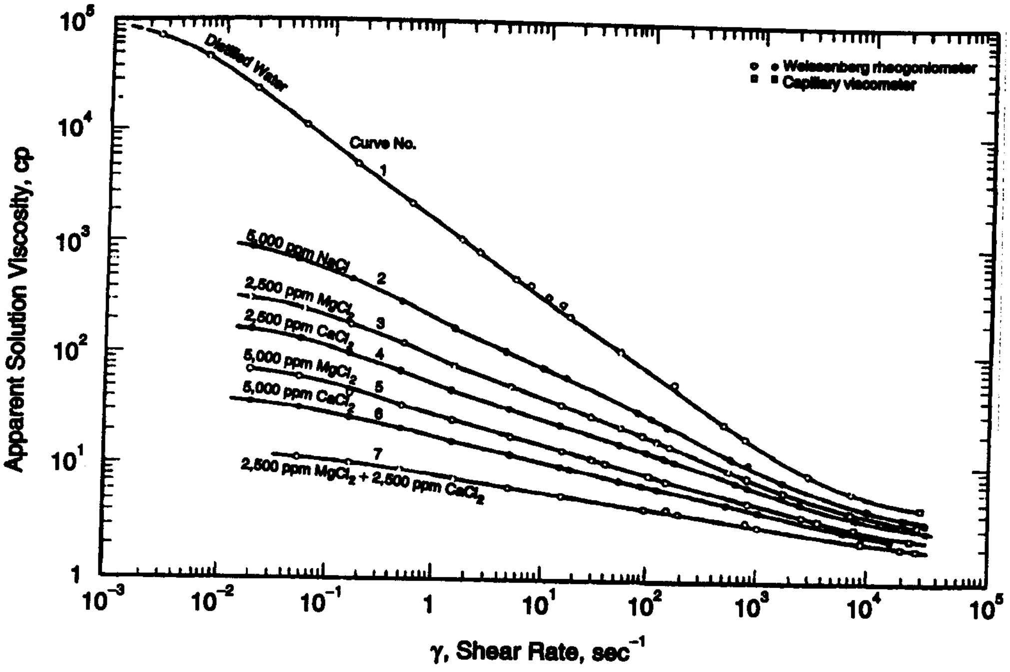

Figure 9.5 Effect of Salts of the Viscosity of a Polymer Solution

Microbiological Problems

Polyacrylamides are relatively immune to bacterial attack.(9.3) However, the presence of aerobic microorganisms can contribute significantly to corrosion and plugging problems, and sulfate reducing bacteria have been observed as a contributor to corrosion problems in polymer injection systems.(9.13)

pH Effects

Lowering the pH of the polymer solution by adding a small amount of acid lowers the viscosity of the solution. Acid exerts a greater influence on the shape of the molecules than an equivalent amount of a neutral salt. The hydrogen ions convert the ionic carboxylate groups in the molecules to uncharged carboxylic acid groups.(9.10)

Effect of Oxygen Entry

If oxygen is excluded, the presence of dissolved iron ions appears to have only a slight effect on solution viscosity. However, if oxygen entry is permitted, a rapid decline in viscosity occurs.(9.14)

Oxygen entry also results in the precipitation of iron ions from solution as insoluble ferric hydroxide. It is an excellent plugging agent by itself, but in the presence of high molecular weight polymers, the problem is considerably more severe.

Water Treatment for Polymer Flooding

The water used to make up polymer solutions should be as clean as possible.

Polymers tend to adhere to solids and agglomerate. When produced water is used, oil carryover is not generally considered an acute problem, but should be minimized because of relative permeability considerations and the fact that oil also helps to agglomerate solids and aggravate plugging.

Filtration and Oil Removal

Filtration is frequently necessary, and dispersed oil removal is nearly always necessary when produced waters are used.

Permissible levels of suspended solids and oil are subject to discussion. One prominent chemical supplier advocates 1 ppm suspended solids and 1 ppm oil.(9.15) A major oil producer in West Texas quotes polymer supplier recommendations that the water should have less than 20 ppm of hydrocarbons, and no solid particles over 2 microns.(9.16)

It may also be necessary to filter the polymer solution to remove any gelled agglomeration of high concentration polymer that might result in injection well plugging.

Corrosion

Plastic piping and plastic or coated steel vessels and equipment should be used to prevent corrosion and the generation of iron compounds.

Bacterial Control

The water should normally be treated with a biocide prior to mixing with the polymer.(9.13) Laboratory testing should be conducted to ensure that the biocide will not degrade the polymer.(9.17)

The use of an effective biocide is absolutely essential for polysaccharide polymer solutions and is strongly recommended for polyacrylamide solutions.

Dissolved oxygen should be excluded to prevent the growth of aerobic bacteria.

Dissolved Oxygen Removal

Oxygen must be excluded or removed from polyacrylamide solutions to prevent degradation. It is best to eliminate all oxygen before the polymer is added, and then add the polymer in such a way that oxygen is not introduced. This minimizes the need for oxygen scavengers in the polymer solution.

Oxygen exclusion is also recommended for polysaccharide polymer solutions, although degradation only occurs in high temperature applications.

Oxygen also accelerates the corrosion of carbon steel, causes the precipitation of soluble iron from solution, and facilitates the growth of aerobic bacteria.

The use of ***oxygen scavengers*** in polymer solutions presents a number of unusual problems, and they must be used with care. It is usually best to remove dissolved oxygen from the water before the polymer is added, and then try to prevent air entry during polymer mixing.

One of the problems with the use of conventional sulfite oxygen scavengers is that, given a choice between reacting with sulfite and ferrous ions, oxygen will first oxidize the ferrous iron to insoluble ferric iron. However, oxygen reacts with sodium hydrosulfite in preference to the ferrous ion.

In addition, it is such a powerful reducing agent that it is able to re-solubilize ferric hydroxide which has already formed in the system.

For this reason, many early polyacrylamide polymer floods used sodium hydrosulfite (sodium dithionate) as an oxygen scavenger.(9.13) The problem with this material is that while stable in powder form, it deteriorates within a few hours when dissolved in water.(9.17)

Because of the difficulties in applying a powdered product in the field, it is more common to control the ferrous iron content of the water and use sodium or ammonium bisulfite oxygen scavengers. The problem in their use arises from the fact that they usually must be catalyzed with divalent metal ions, which can contribute to polymer degradation.(9.17)

Although dissolved oxygen does not cause degradation of polysaccharides at normal ambient temperatures, it does result in serious degradation at elevated temperatures. Unfortunately, neither sulfite or sodium hydrosulfite oxygen scavengers can be used to remove dissolved oxygen from polysaccharide polymer solutions, because they produce free radicals as intermediate products that can initiate biopolymer degradation. Thus oxygen removal prior to mixing is necessary. The use of antioxidants may also be required.(9.7)

All vessels should be blanketed with nitrogen.

Iron

Many waters contain very small amounts of natural iron. When this is the case, oxygen exclusion and the use of plastic piping, and plastic or coated steel vessels and equipment to prevent the generation of iron due to corrosion, will minimize any problems due to iron.

If high iron levels are naturally present, dissolved iron removal and oxygen exclusion will be necessary.

Scale Control

The scaling tendencies of all waters should be evaluated. Because the pH of polymer solutions is frequently basic, calcium carbonate scale may be a problem. Scale inhibitors must be selected which are compatible with the polymer.

Sodium, Calcium and Magnesium Ions

Since the viscosity of polysaccharide polymer solutions increases with increasing salinity, it may be desirable to increase the salinity of the water when using biopolymers.

The presence of sodium, calcium and magnesium ions has the opposite effect on partially hydrolyzed polyacrylamide solutions, and their concentrations must be limited for maximum viscosity increase. For that reason fresh waters are normally used where available. Softening may be employed to remove calcium and magnesium ions if desired.

In many cases, however, brines are used with polyacrylamides and the negative effects of these ions are ignored if a sufficient increase in viscosity can be achieved to materially increase oil recovery.

SURFACTANT-POLYMER FLOODING

In this process, oil is displaced from the reservoir rock as shown in Figure 9.6.

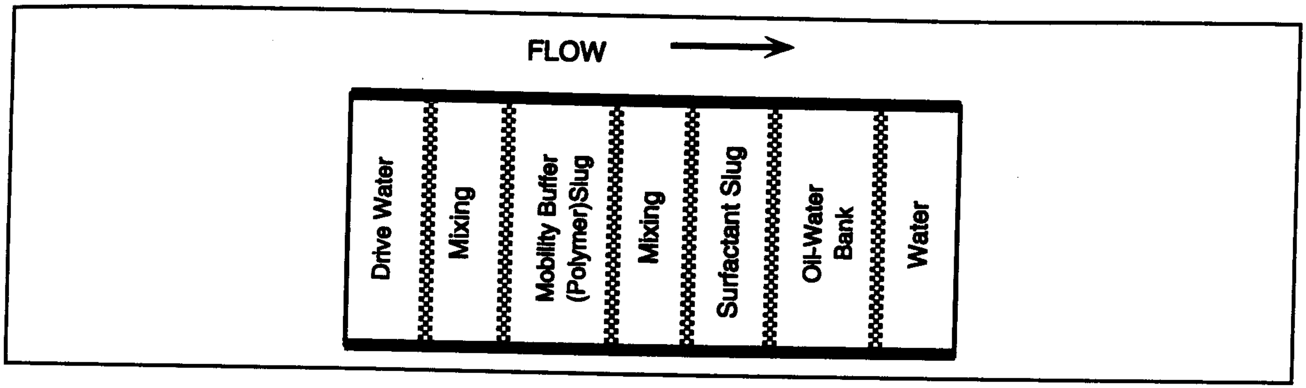

Figure 9.6 Schematic Diagram of the Surfactant-Polymer Process

In most cases, the surfactant slug ahead of the polymer is a micellar solution, sometimes referred to in the literature as a microemulsion, soluble oils, or swollen micelles.(9.1) Its primary purpose is to lower the interfacial tension and miscibly displace oil that cannot be displaced by water.

Micellar solutions contain at least three components: hydrocarbon, surfactant, and water. The hydrocarbon can have a broad range of compositions, and the surfactant is usually a petroleum sulfonate. The water must be fresh.

Alcohol can be added as a fourth component. It serves as a co-surfactant and increases the latitude in the composition of micellar solutions.

If distilled or deionized water is used, salts may be added. They tend to lower the viscosity of the micellar solution and increase phase stability.(9.18)

Additives such as biocides may be incorporated into the micellar solution.

Surfactant slugs with compositions other than micellar solutions are also used.(9.13)

Water Treatment

Exceptionally clean water of carefully controlled composition is used to make up the surfactant slug. Requirements vary with the specific surfactants used.

CAUSTIC OR ALKALINE FLOODING

When crude oil is displaced by water, the displacement efficiency can be improved by lowering the interfacial tension between the two fluids. In many cases this can be accomplished by the addition of a strong base to water. Sodium hydroxide (caustic) and sodium orthosilicate have been widely used due to cost considerations.

At typical use concentrations, the pH of the alkaline solution is in the range of 12 to 13.

Effect of Divalent Ions

At these very high pH values, the precipitation of divalent ions such as calcium, magnesium and iron as hydroxides can be anticipated. Hence, these ions must not be present, and softening is normally required to reduce the total hardness of the water used to make up the alkaline solution to less than 1 mg/L as $CaCO_3$.(9.19)

Effect of Salinity

It usually requires a lower concentration of caustic or sodium orthosilicate to achieve the required interfacial tension when some NaCl is present.(9.19) The required level is established experimentally for the specific crude oil in question.

Water Treatment

Suspended solids and dispersed oil must be removed. Additional water treatment usually consists of adjustment of salinity to the desired value by the addition of NaCl, or by blending with another water, followed by softening to remove the divalent metal ions.

CARBON DIOXIDE INJECTION

When carbon dioxide mixes with crude oil, under certain conditions a single-phase fluid is formed which is miscible with the reservoir oil. The objective of CO_2 injection is to form a miscible bank to displace the oil, and then to displace the miscible bank with gas or water.

Of the several methods of CO_2 injection, three also utilize water injection:(9.20)

- Injection of a slug of CO_2 followed by water.
- Alternate injection of slugs of CO_2 and water. Also known as the WAG process.
- Simultaneous injection of CO_2 and water.

Water Treatment

The water which is injected is usually produced water, and it should be processed in exactly the same way it would be for normal water injection.

Corrosion Control

The only additional problem is the increased corrosiveness when the water and carbon dioxide mix. Mixing occurs only once in the first process: at the interface between the CO_2 and water. The effect of the increased corrosion rates during this period on the overall life of the system should be minimal.

In the WAG process water and CO_2 are transported to the injection wells through separate lines. Mixing of the two fluids occurs in the injection wells at the end of each cycle, and can result in severe corrosion.(9.20)

Simultaneous injection of the two fluids presents the largest amount of mixing of the two fluids, as well as the most severe corrosion problems.

The primary methods of corrosion control in the areas where mixing occurs are corrosion resistant materials (both metallic and non-metallic), coatings and linings.(9.20)

IN-SITU COMBUSTION

In-situ combustion involves the injection of air or oxygen into the reservoir. Spontaneous ignition occurs in the vast majority of reservoirs, and the combustion zone moves away from the injection well consuming part of the reservoir oil as fuel. The result is an extremely complex displacement process, as shown in Figure 9.7.

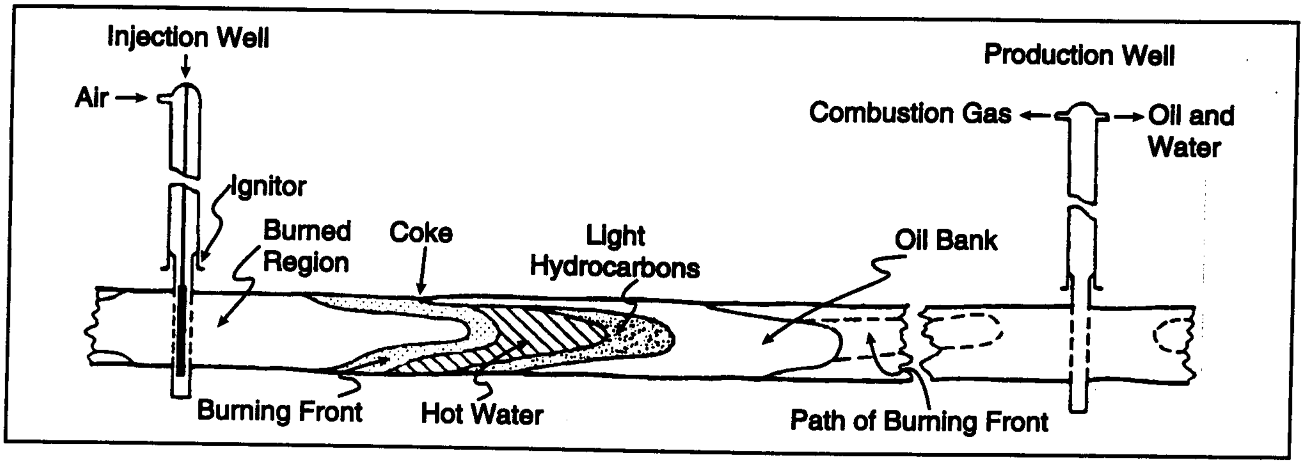

Figure 9.7 Forward In-Situ Combustion Process(9.3)

Water may also be injected along with the air. This process is referred to as a Combination of Forward Combustion and Waterflooding (COFCAW). The water is heated by the residual heat in the rock behind the combustion zone, flashes into superheated steam and enhances the oil displacement process. However, the major benefit of simultaneous water injection is a reduction in the amount of air required to recover a barrel of oil by a factor of three or more.(9.21)

The water and air are normally kept separate by injecting one fluid down the tubing and the other down the annulus in order to minimize oxygen corrosion. A joint of Inconel tubing on the bottom of the tubing string will effectively control corrosion in the area of mixing.(9.22)

There seems to be no special requirement for water used in the COFCAW process other than it should be of good quality to avoid downhole plugging problems.(9.22) Hence, normal treatment procedures should be adequate.

STEAM INJECTION

Although listed last, steamflooding is by far the major enhanced recovery process at present. An Oil and Gas Journal survey of enhanced recovery projects published in April, 1984, concluded that over 75% of all enhanced production came from steam projects.(9.1)

The purpose of injecting steam into a reservoir is to heat the crude oil and reduce its viscosity. Since the flow rate of oil through a reservoir rock is inversely proportional to its viscosity, considerable increases in production rates can be achieved.

There are two steam recovery techniques:(9.3)

- Steam Stimulation

  Sometimes known as cyclic steam injection, steam soak, or huff and puff. Steam is into a producing well for a period of several weeks. Steam injection is halted, the well is shut-in for a few days, and then placed on production. This cycle is then repeated as many times as desired.

- Steamflooding

  Steamflooding is similar to waterflooding in that steam is injected into a number of injection wells and oil is produced from adjacent producing wells in a pattern. It is the principal steam injection method.

In either case, the injected steam is produced by a boiler which is usually referred to as a steam generator in oilfield operations. It is a once-through system which converts water to a mixture of approximately 80 percent steam and 20 percent water, normally referred to as 80% quality steam.

The steam generator feedwater must be treated to prevent corrosion and/or scale formation on the boiler tubes, as well as to prevent corrosion and the formation of scales or precipitates in the water phase. It should be noted that all of the dissolved solids in the feedwater will be concentrated in the water phase, which is injected along with the steam.

Corrosion Control

If the feedwater contains dissolved oxygen, it must be removed. This prevents boiler tube corrosion as well as the precipitation of soluble iron ions as iron hydroxide. Otherwise, no treatment is required.

The feedwater supply system should be constructed from non-metallic materials, or coated or lined steel. This prevents corrosion and the generation of iron.

Scale Control

All steam generator feedwaters must be softened to remove calcium and magnesium ions and prevent scale. The softened water should contain zero hardness (Total Hardness < 1 mg/L as $CaCO_3$).

Waters with less than 5000 mg/L TDS are softened using sodium ion exchangers. This process uses a strong-acid resin which is regenerated with a NaCl solution.

In order to achieve zero hardness with waters containing more than 5000 mg/L TDS, it is necessary to use weak-acid resins. Regeneration requires an acid followed by a base (usually HCl and NaOH).(9.23)

Resin Fouling

Steam generator feedwater entering the ion exchange units must be quite clean. Dispersed oil, suspended solids, and precipitated iron compounds must be eliminated. Otherwise the resin will become fouled and its capacity for ion exchange will be reduced.

Other Precipitates

There is always a possibility of the formation of silica or sodium salt deposits when high TDS waters are used. However, this is usually controlled by limiting steam quality.(9.23)

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NOTES:

11

BOILER WATER TREATMENT

Although there are many different types of boilers, they are all essentially devices for transforming liquid water to steam by heating the water. When the water evaporates, the dissolved solids are left behind and frequently form scales and deposits. Deposition on heat transfer surfaces can cause the metal to overheat, leading to premature failure.

Corrosion can also be a serious problem in boilers. Dissolved gases such as oxygen, carbon dioxide or hydrogen sulfide pass with the steam, causing corrosion of steam and condensate lines. Low pH values also contribute to corrosion.

Boilers are usually classified in terms of their operating pressure, but it is the corresponding operating temperature which dictates the degree of treatment required for boiler feedwaters. The higher the operating pressure (and temperature), the more stringent the treatment requirements.

An arbitrary classification of boilers is given in Table 11.1.

TABLE 11.1

Boiler Classification

Operating Pressure	Classification
Less than 200 psi	Low Pressure
200-500 psi	Intermediate Pressure
500-2000 psi	High Pressure

Most boilers used in the oifield are of the low or intermediate class. The purpose of boiler feedwater treatment is threefold:(11.1)

1. Prevent the formation of scales and deposits.
2. Minimize or prevent corrosion in the boiler and steam systems.
3. Maintain steam purity. The primary causes of decreased purity are carryover of water droplets, and silica dissolved in the steam.

Boiler feedwater treatment is classified as external or internal treatment. External treatment means that the water composition is altered before it enters the boiler. Typical external treatment processes include softening, demineralization, deaeration, iron and manganese removal, filtration, or some combination.

Internal treatment refers to chemicals added to the water which react inside the boiler to prevent scale, corrosion, or foaming.

EXTERNAL TREATMENT

Boiler feedwater should have the lowest hardness, alkalinity, sulfates, silica, and suspended solids levels that can be economically afforded.

Maximum permissible concentrations for each constituent in the feedwater cannot be set. However, a preliminary estimate can be made from the recommended boiler water composition limits published by the American Boiler Manufacturers Association (ABMA) as shown in Table 11.0.

TABLE 11.2

Recommended Maximum Limits in the Boiler

Boiler Pressure (psig)	Total Dissolved Solids (ppm)	Total Alkalinity ppm)	Suspended Solids (ppm)	Silica (ppm)
0-300	3500	700	300	125
301-450	3000	600	250	90
451-600	2500	500	150	50
601-750	2000	400	100	35
751-900	1500	300	60	20
901-1000	1250	250	40	8
1001-1500	1000	200	20	2.5
1501-2000	750	150	10	1.0
Over 2000	500	100	5	0.5

*Silica limits based on limiting silica in steam to 0.02-0.03 ppm

Iron and oxygen in the feedwater should be near zero.

Continuous blowdown can be employed to limit the concentration of the various constituents in the boiler shell. However, if the feedwater composition is such that very high blowdown rates are required, then it is generally more economical to remove offending constituents by external treatment of the feedwater.

Three basic types of processes may be carried out in the external treatment of boiler feedwater:

1. Suspended solids removal
2. Dissolved gas removal
3. Water softening

These processes are discussed under the heading of Water Processing Technology.

INTERNAL CHEMICAL TREATMENT

Internal chemical treatment is usually necessary to provide insurance against scale and corrosion even if the water has been externally treated. When boilers are operated at low to moderate pressures, and the raw feedwater is of good quality (low hardness, silica, and turbidity), internal treatment alone will often be adequate.

Scale Control

Scale formation within a boiler is controlled by precipitation of calcium and magnesium as a non-adherent sludge, or by chelation of the calcium and magnesium ions.

Phosphate Treatment

A soluble sodium phosphate is added which reacts with calcium to form an insoluble precipitate, calcium phosphate. Magnesium and silica are precipitated as magnesium hydroxide, magnesium silicate, or calcium silicate. The alkalinity of the makeup is usually adequate to produce the necessary OH^- for the magnesium precipitation, although in some cases caustic must be added. The pH should be maintained above 9.5 both for magnesium precipitation and to ensure the formation of less adherent precipitates. A reserve or excess of 40 ppm $PO_4^=$ should be maintained.

Sludge dispersants may be used in conjunction with phosphates to prevent adherence of the precipitated particles and to maintain the resulting "sludge" as a non-adherent slurry. Sludge dispersants coat the finely divided particles as they are formed so that they will not form large crystalline precipitates. Smaller particles will remain dispersed at the velocities encountered in most boilers, enabling efficient removal during blowdown.

Typical examples of sludge dispersants are tannins, lignins, starches and certain synthetic polymers, such as the polyacrylates.

Soda Ash or Caustic Treatment

In this process, sodium carbonate, sodium hydroxide, or both are added to the boiler water to supplement the alkalinity supplied by the makeup water, which is not softened. The sodium carbonate results in the precipitation of calcium ions as calcium carbonate. The addition of caustic elevates the pH, causing the precipitation of magnesium and silica as magnesium hydroxide and magnesium silicate.

Sludge dispersants are often used in this process to prevent deposit formation.

This method of treatment is only used with boilers operating below 250 psi which utilize high hardness feedwaters.

Chelating Agents

Chelating agents are materials such as EDTA which form soluble, complex ions with calcium and magnesium. Thus, precipitation is prevented and the calcium and magnesium ions are effectively maintained in solution.

The cost of chelating agents limits their use to very low hardness feedwaters (usually 5 ppm).

Over treatment by even 1-2 ppm in the feedwater can result in a buildup of chelant concentration to very high levels in the boiler. Over a period of several months the chelant will attack metal resulting in general thinning corrosion, especially in stressed areas. Therefore, addition of chelating agents must be very carefully controlled.

Corrosion Control

Pitting corrosion in boilers is usually caused by dissolved oxygen. Caustic embrittlement can also occur which can result in catastrophic failure.

Oxygen Corrosion

Oxygen scavengers are used to remove dissolved oxygen and prevent corrosion due to its presence. Catalyzed sodium sulfite or hydrazine are commonly used. Scavengers are discussed under Water Processing Technologies.

Unreacted hydrazine can decompose at elevated temperatures yielding ammonia and nitrogen. Ammonia in the presence of small amounts of oxygen will result in the corrosion of copper alloys. For this reason, it is important not to maintain excessive hydrazine residuals.

Caustic Embrittlement

When ordinary carbon steels or austenitic stainless steels are stressed and placed in contact with hot water containing a high concentration of hydroxyl ions, intergranular cracking can occur, resulting in failure. This type of failure is referred to as caustic embrittlement and is a form of stress corrosion cracking.

In order for caustic embrittlement to occur, four conditions are necessary:

1. Hydroxides must be present in the boiler water. The use of caustic or sodium carbonate (which can decompose at elevated temperatures to yield hydroxyl ions) is a major contributor.
2. A joint or seam into which the water can leak must be present.
3. Concentration of the boiler water must occur within this seam.
4. The steel exposed to this concentrated solution must be stressed.

The presence of cracks or seams and large residual stresses can be reduced by proper design. However, it can still be a problem, especially at tube ends.

All boilers should be tested using an Embrittlement Detector such as the one designed by U. S. Bureau of Mines. If cracking tendencies are detected, treatment utilizing phosphates or sodium nitrite should be initiated.

Foaming

Foaming results in water being carried from the boiler with the steam. It is influenced by several factors, including:

1. Water level in the boiler
2. Dissolved solids concentration
3. Suspended solids in the water

Foaming can be prevented or reduced by boiler blowdown, a complete change of boiler water, or by the addition of antifoamers.

Use of antifoamers as a routine part of internal treatment is good practice. However, the use of excessive amounts can actually cause foaming and should be avoided.

BOILER BLOWDOWN

When steam is generated, essentially pure water vapor is discharged from the boiler, leaving all dissolved and suspended solids behind in the boiler. Therefore, the solids concentration in the liquid water in the boiler continuously increases as the water evaporates. In order to maintain the dissolved solids content below the allowable maximum, some of the concentrated water must be removed from the boiler and replaced with water containing a lower amount of dissolved solids. The water removed from the boiler is called blowdown.

In order to hold the dissolved solids content at an acceptable level the amount of solids removed by blowdown must equal the amount entering the boiler with the feedwater. This is illustrated in Figure 11.1.

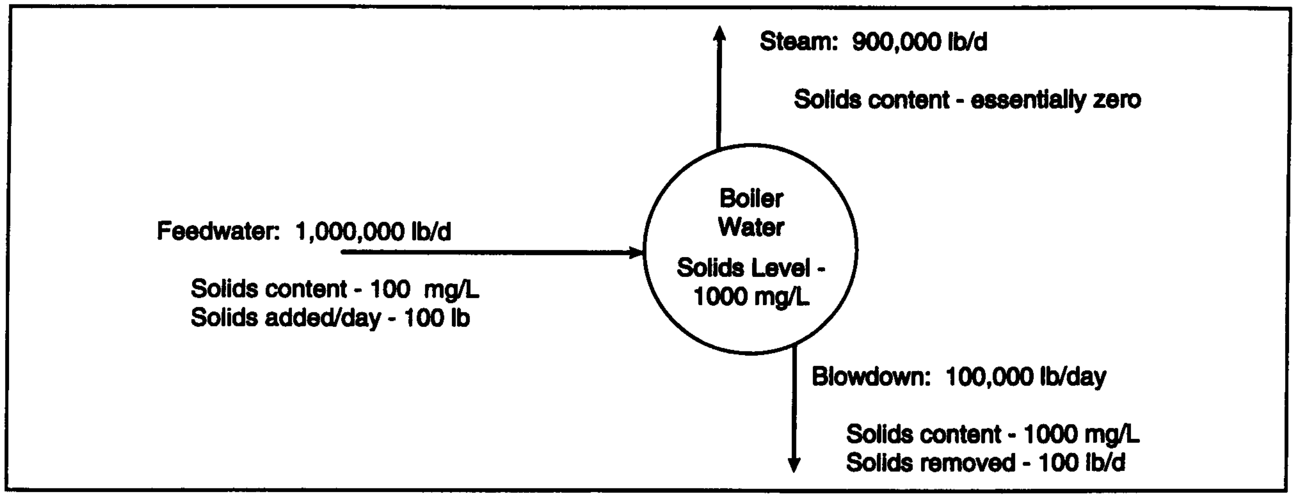

Figure 11.1 Control of Boiler Water Solids by Blowdown *(Courtesy Nalco Chemical Co.)*

Guidelines for maximum levels of key constituents in boiler waters recommended by the ABMA were given in Table 11.0. The desired maximum levels can be maintained by continuous blowdown.

The required amount can be calculated from the following formula:

$$B = \frac{TDS_f}{TDS_{\max}} \times 100 \qquad (11.1)$$

Where:
B = Blowdown, % of feedwater
TDS_f = Total dissolved solids in feedwater, ppm
TDS_{max} = Maximum allowable dissolved solids in boiler water, ppm

The total dissolved solids can be estimated from conductivity measurements. Chloride concentrations are often used in place of TDS values when the feedwater composition is relatively constant. Silica content can also be used if it is the limiting factor.

CONDENSATE RETURN SYSTEMS

Once steam leaves the boiler and is used for its intended purpose, heat will be lost and the steam will condense and form hot water. This condensed water is called condensate, and all or a portion of it is usually returned to the boiler as feedwater.

Corrosion

Although condensate is essentially distilled water, it is usually quite corrosive due to the presence of carbon dioxide. Oxygen may also be present due to leaks in the condensate lines, poor oxygen removal from the original feedwater, or exposure to the atmosphere in open condensate receiving tanks.

The primary source of carbon dioxide in steam systems is the thermal decomposition of carbonate and bicarbonate ions in the feedwater.

Carbonate ions: $CO_3^= + H_2O + Heat \rightarrow 2\,OH^- + CO_2$

Bicarbonate ions: $2\,HCO_3^- + Heat \rightarrow CO_3^= + H_2O + CO_2$

$$CO_3^= + H_2O + Heat \rightarrow 2\,OH^- + CO_2$$

Only about 80% of the carbonate ions convert to hydroxyl ions and carbon dioxide. Therefore, 1 ppm of $CO_3^=$ will produce 0.58 ppm of CO_2.

The bicarbonate decomposition to form carbonate ions, water and carbon dioxide is 100% complete. This means that 1 ppm of bicarbonate ion will produce 0.36 ppm of CO_2 plus 0.49 ppm carbonate ion. When the carbonate ion decomposes (assuming 80% completion), an additional 0.29 ppm CO_2 is created, giving a total of 0.65 ppm CO_2 for every ppm of bicarbonate ion which decomposes.

When alkalinities are expressed as equivalent $CaCO_3$, the following factors apply:

1. One ppm of $CO_3^=$ (as $CaCO_3$) will form 0.35 ppm CO_2.
2. One ppm of HCO_3^- (as $CaCO_3$) will form a total of 0.79 ppm CO_2.

This assumes that the carbonate decomposition is 80% complete.

When the steam condenses, the carbon dioxide dissolves in the condensed water, increasing its corrosivity.

Condensate return systems can be chemically treated to prevent corrosion by dissolved carbon dioxide by using neutralizing or filming amines. Ammonia can also be used, but it has the disadvantage of attacking copper or brass.

When a large portion of the steam condensate is returned to the boiler feedwater, the condensate must be deaerated (degassed) to remove the carbon dioxide and keep it from accumulating in the system.

Oil Contamination

Oil is hazardous in boilers because it forms a heat insulating film. There are normally two major sources of oil contamination in plants and facilities:

1. Reciprocating pump discharge.
2. Condensation and recovery of the still stripping steam.

Emulsified oil can be removed with DE filters and a variety of other methods. Free oil can be removed in a skimming tank.

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APPENDIX 1

Selected Elements, Symbols and Atomic Weights

Element	Symbol	Atomic Weight*
Aluminum	Al	27.0
Barium	Ba	137.3
Calcium	Ca	40.1
Carbon	C	12.0
Chlorine	Cl	35.5
Chromium	Cr	52.0
Cobalt	Co	58.9
Copper	Cu	63.5
Flourine	F	19.0
Gold	Au	197.0
Hydrogen	H	1.0
Iron	Fe	55.8
Magnesium	Mg	24.3
Manganese	Mn	54.9
Mercury	Hg	200.6
Nickel	Ni	58.7
Nitrogen	N	14.0
Oxygen	O	16.0
Phosphorus	P	30.0
Potassium	K	39.1
Sodium	Na	23.0
Strontium	Sr	87.6
Sulfur	S	32.1
Zinc	Zn	65.4

* Rounded off to one decimal

APPENDIX 2

Selected Ions, Compounds and Equivalent Weights

Cations	Symbol	Equivalent Weight	Anions	Symbol	Equivalent Weight
Barium	Ba^{++}	68.7	Bicarbonate	HCO_3^-	61.0
Calcium	Ca^{++}	20.0	Carbonate	$CO_3^=$	30.0
Hydrogen	H^+	1.0	Chloride	Cl^-	35.5
Iron			Hydroxyl	OH^-	17.0
– Ferrous	Fe^{++}	27.9	Oxide	$O^=$	8.0
– Ferric	Fe^{+++}	18.6	Phosphate	$PO_4^=$	31.6
Magnesium	Mg^{++}	12.2	Sulfate	$SO_4^=$	48.0
Sodium	Na^+	23.0	Sulfide	$S^=$	16.0
Strontium	Sr^{++}	43.8	Sulfite	$SO_3^=$	40.0

Compounds & Gases	Symbol	Valence	Equivalent Weight
Barium Sulfate	$BaSO_4$	2	117.0
Calcium Carbonate	$CaCO_3$	2	50.0
Calcium Sulfate	$CaSO_4$	2	68.0
Chlorine	Cl_2	2	35.5
Ferrous Carbonate	$FeCO_3$	2	58.0
Ferric Oxide	Fe_2O_3	6	26.6
Oxygen	O_2	4	8.0
Carbon Dioxide	CO_2	4	11.0
Sodium Bicarbonate	$NaHCO_3$	1	84.0
Sodium Chloride	$NaCl$	1	58.5

APPENDIX 3

Selected Conversion Factors

SI	English	English	SI
1 µm	0.039 mil	1 mil	25.4 µm
1 m	39.37 in	1 in	0.0254 m
1 m	3.28 ft	1 ft	0.3048 m
1 km	3280 ft	1 ft	0.0003 km
1 km	0.62 mile	1 mile	1.61 km
1 mm/y	39.37 mpy	1 mpy	0.0254 mm/y
1 µm/y	0.039 mpy	1 mpy	25.4 µm/y
1 m/s	3.28 ft/s	1 ft/s	0.305 m/s
1 m^2	10.76 ft^2	1 ft^2	0.093 m^2
1 m^3	35.3 ft^3	1 ft^3	0.0283 m^3
1 m^3	6.29 API bbl	1 API bbl	0.159 m^3
1 L	0.0353 ft^3	1 ft^3	28.3 L
1 L	0.264 US gal	1 US gal	3.785 L
1 L	0.629 API bbl	1 API bbl	1.59 L
1 m^3/m^3	5.61 ft^3/API bbl	1 ft^3/API bbl	0.178 m^3/m^3
1 $m^3/hr/m^2$	0.41 USgpm/ft^2	1 USgpm/ft^2	2.44 $m^3/hr/m^2$
1 bar = 100 kPa	14.5 psi	1 psi	6.897 kPa

English Unit Conversions	
1 API bbl	42 gal US
1 API bbl	35 gal Imperial
1 API bbl	5.6 ft^3
1000 bbl/day	29.2 USgpm
1 US gal	0.134 ft^3
1 USgpm	34.3 bbl/day
1 mil	0.001 in

APPENDIX 4

Temperature Conversion Chart

NOTE: The numbers in boldface refer to the temperature in degrees, either Centigrade or Fahrenheit, which it is desired to convert into the other scale. If converting from Fahrenheit to Centigrade degrees, the equivalent temperature will be found in the left column; while if converting from degrees Centigrade to degrees Fahrenheit, the answer will be found in the column on the right.

°C		°F	°C		°F	°C		°F	°C		°F
–73.3	**–100**	–148.0	2.8	**37**	98.6	33.3	**92**	197.6	293	**560**	1040
–67.8	**–90**	130.0	3.3	**38**	100.4	33.9	**93**	199.4	299	**570**	1058
–62.2	**–80**	–112.0	3.9	**39**	102.2	34.4	**94**	201.2	304	**580**	1076
–59.4	**–75**	–103.0	4.4	**40**	104.0	35.0	**95**	203.0	310	**590**	1094
–56.7	**–70**	–94.0	5.0	**41**	105.8	35.6	**96**	204.8	316	**600**	1112
–53.9	**–65**	–85.0	5.6	**42**	107.6	36.1	**97**	206.6	321	**610**	1130
–51.1	**–60**	–76.0	6.1	**43**	109.4	36.7	**98**	208.4	327	**620**	1148
–48.3	**–55**	–67.0	6.7	**44**	111.2	37.2	**99**	210.2	332	**630**	1166
–45.6	**–50**	–58.0	7.2	**45**	113.0	37.8	**100**	212.0	33	**640**	1184
–42.8	**–45**	–49.0	7.8	**46**	114.8	43	**110**	230	343	**650**	1202
–40.0	**–40**	–40.0	8.3	**47**	116.6	49	**120**	248	349	**660**	1220
–37.2	**–35**	–31.0	8.9	**48**	118.4	54	**130**	266	354	**670**	1238
–34.4	**–30**	–22.0	9.4	**49**	120.2	60	**140**	284	360	**680**	1256
–31.7	**–25**	–13.0	10.0	**50**	122.0	66	**150**	302	366	**690**	1274
–28.9	**–20**	–4.0	10.6	**51**	123.8	71	**160**	320	371	**700**	1292
–26.1	**–15**	5.0	11.1	**52**	125.6	77	**170**	338	377	**710**	1310
–23.3	**–10**	14.0	11.7	**53**	127.4	82	**180**	356	382	**720**	1328
–20.6	**–5**	23.0	12.2	**54**	129.2	88	**190**	374	388	**730**	1346
–17.8	**0**	32.0	12.8	**55**	131.0	93	**200**	392	393	**740**	1364
–17.2	**1**	33.8	13.3	**56**	132.8	99	**210**	410	399	**750**	1382
–16.7	**2**	35.6	13.9	**57**	134.6	100	**212**	414	404	**760**	1400
–16.1	**3**	37.4	14.4	**58**	136.4	104	**220**	428	410	**770**	1418
–15.6	**4**	39.2	15.0	**59**	138.2	110	**230**	446	416	**780**	1436
–15.0	**5**	41.0	15.6	**60**	140.0	116	**240**	464	421	**790**	1454
–14.4	**6**	42.8	16.1	**61**	141.8	121	**250**	482	427	**800**	1472
–13.9	**7**	44.6	16.7	**62**	143.6	127	**260**	500	432	**810**	1490
–13.3	**8**	46.4	17.2	**63**	145.4	132	**270**	518	438	**820**	1508
–12.8	**9**	48.2	17.8	**64**	147.2	138	**280**	536	443	**830**	1526
–12.2	**10**	50.0	18.3	**65**	149.0	143	**290**	554	449	**840**	1544
–11.7	**11**	51.8	18.9	**66**	150.8	149	**300**	572	454	**850**	1562
–11.1	**12**	53.6	19.4	**67**	152.6	154	**310**	590	460	**860**	1580
–10.6	**13**	55.4	20.0	**68**	154.4	160	**320**	608	466	**870**	1598
–10.0	**14**	57.2	20.6	**69**	156.2	166	**330**	626	471	**880**	1616
–9.4	**15**	59.0	21.1	**70**	158.0	171	**340**	644	477	**890**	1634
–8.9	**16**	60.8	21.7	**71**	159.8	177	**350**	662	482	**900**	1652
–8.3	**17**	62.6	22.2	**72**	161.6	182	**360**	680	488	**910**	1670
–7.8	**18**	64.4	22.8	**73**	163.4	188	**370**	698	493	**920**	1688
–7.2	**19**	66.2	23.3	**74**	165.2	193	**380**	716	499	**930**	1706
–6.7	**20**	68.0	23.9	**75**	167.0	199	**390**	734	504	**940**	1724
–6.1	**21**	69.8	24.4	**76**	168.8	204	**400**	752	510	**950**	1742
–5.6	**22**	71.6	25.0	**77**	170.6	210	**410**	770	516	**960**	1760
–5.0	**23**	73.4	25.6	**78**	172.4	216	**420**	788	521	**970**	1778
–4.4	**24**	75.2	26.1	**79**	174.2	221	**430**	806	527	**980**	1796
–3.9	**25**	77.0	26.7	**80**	176.0	227	**440**	824	532	**990**	1814
–3.3	**26**	78.8	27.2	**81**	177.8	232	**450**	842	538	**1000**	1832
–2.8	**27**	80.6	27.8	**82**	179.6	238	**460**	860	566	**1050**	1922
–2.2	**28**	82.4	28.3	**83**	181.4	243	**470**	878	593	**1100**	2012
–1.7	**29**	84.2	28.9	**84**	183.2	249	**480**	896	621	**1150**	2102
–1.1	**30**	86.0	29.4	**85**	185.0	254	**490**	914	649	**1200**	2192
–0.6	**31**	87.8	30.0	**86**	186.8	260	**500**	932	677	**1250**	2282
0.0	**32**	89.6	30.6	**87**	188.6	266	**510**	950	704	**1300**	2372
0.6	**33**	91.4	31.1	**88**	190.4	271	**520**	968	732	**1350**	2462
1.1	**34**	93.2	31.7	**89**	192.2	277	**530**	986	760	**1400**	2552
1.7	**35**	95.0	32.2	**90**	194.0	282	**540**	1004	788	**1450**	2642
2.2	**36**	96.8	32.8	**91**	195.8	288	**550**	1022	816	**1500**	2732

The formulas below may also be used for converting Centigrade or Fahrenheit degrees into the other scale

Degrees Centigrade, $°C = \frac{5}{9}(°F + 40) - 40$ Degrees Fahrenheit, $°F = \frac{9}{5}(°C + 40) - 40$

APPENDIX 5

Water Sample Description

Field: ____________ Lease: ____________

County: ____________ Well: ____________

State:

Date Sample Taken:

Person Taking Sample:

Sample Point Location:

Sample Description

Source: ____________ (Geologic Formation, River, etc.)

Color:

Odor:

Suspended Solids:

Oil Scum:

System Operation at Time of Sampling (Check One)

Normal:

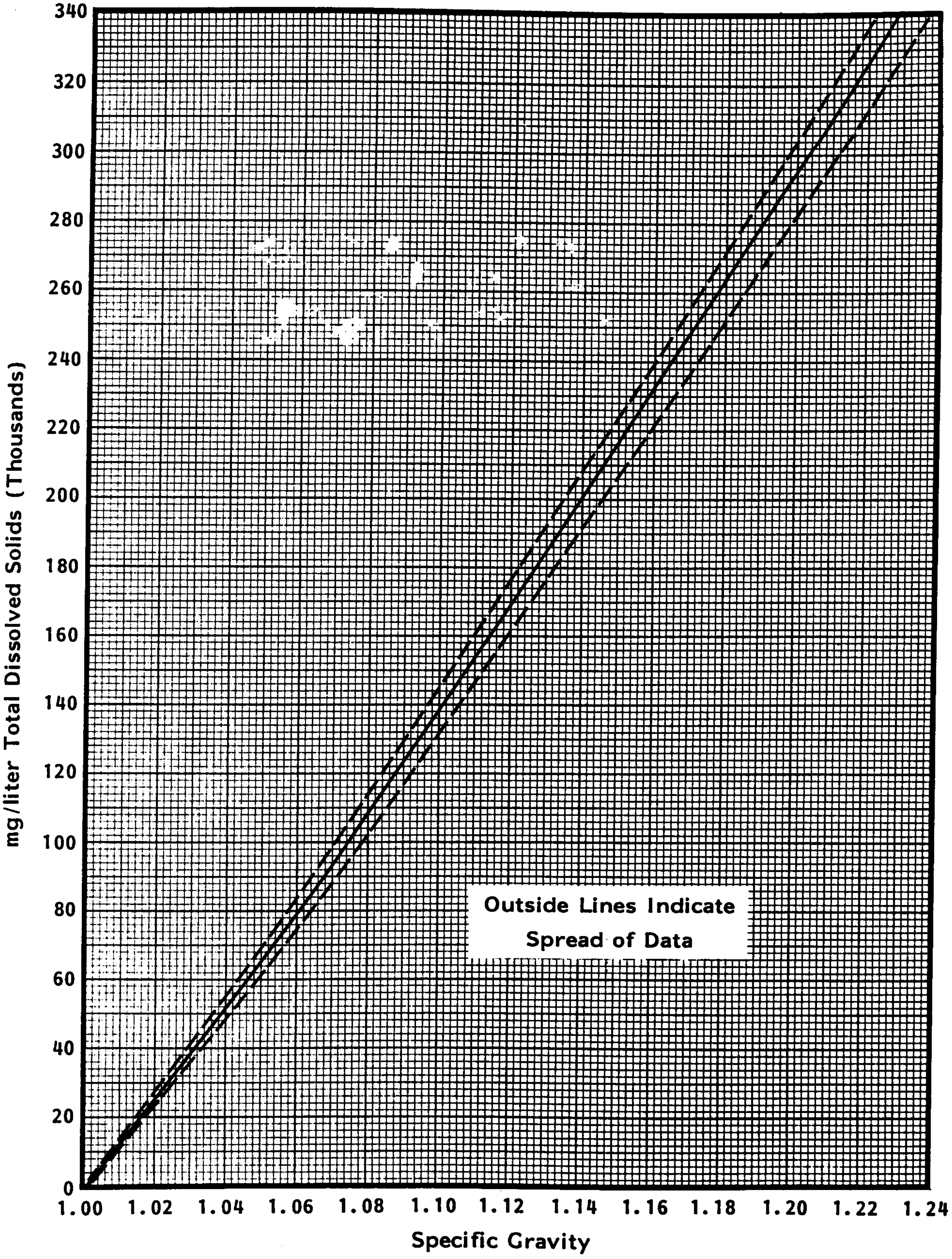
Abnormal (Describe):

Shut-Down:

Analyses Performed On-Site(List):

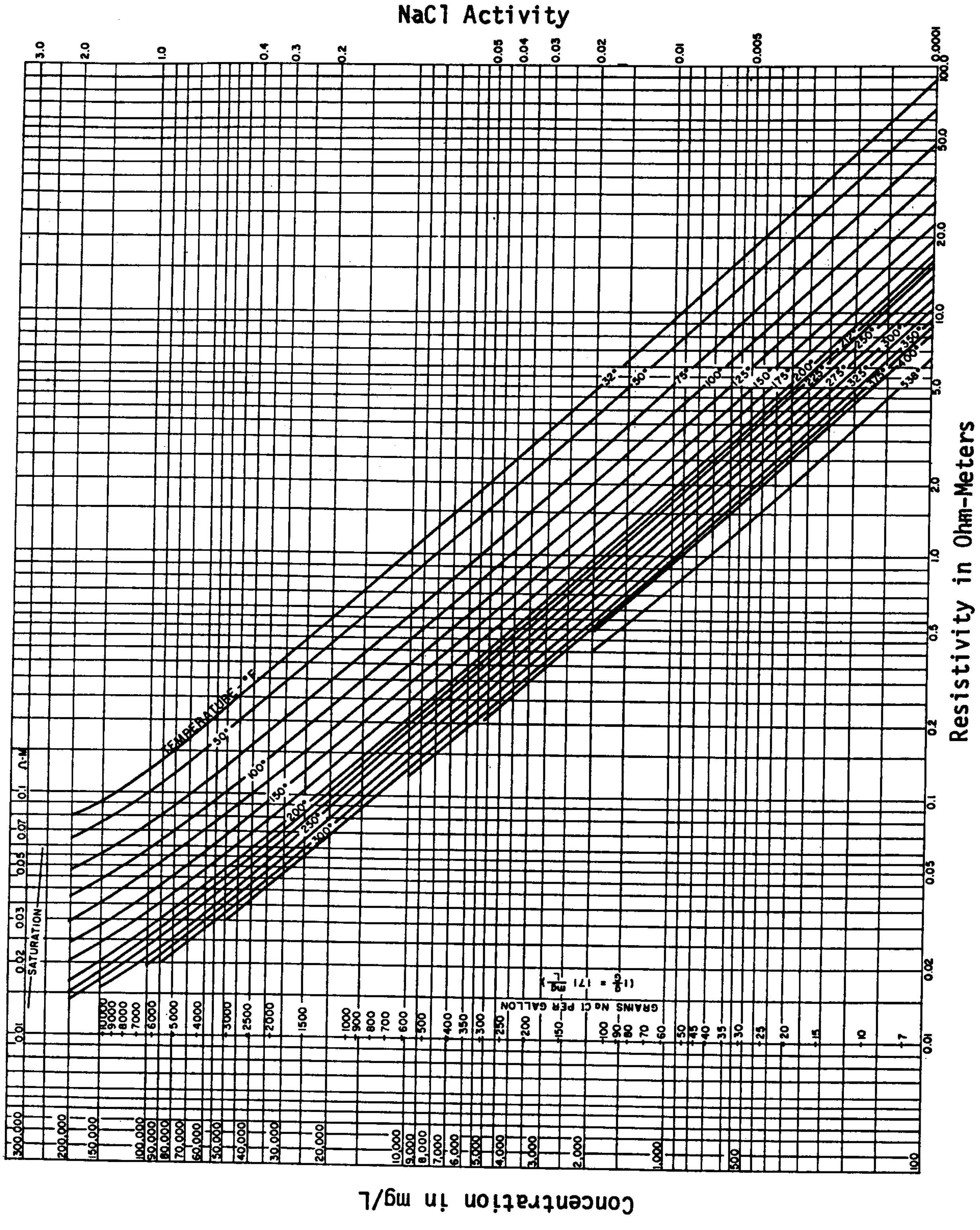
APPENDIX 6

Specific Gravity vs. Total Dissolved Solids



APPENDIX 7

Resistivity as a Function of Salinity and Temperature for NaCl Solutions



APPENDIX 8

Calcium Carbonate Conversion Factors

To Convert From	To	Ion	Multiply By
ppm as $CaCO_3$	ppm of the Ion	Ca^{++}	0.400
		Mg^{++}	0.243
		K^{+}	0.782
		Na^{+}	0.460
		Ba^{++}	1.374
		Sr^{++}	0.876
		Fe^{++}	0.558
		Fe^{+++}	0.372
		Cl^{-}	0.709
		HCO_3^{-}	1.220
		OH^{-}	0.340
		$SO_4^{=}$	0.960
		$CO_3^{=}$	0.600

$$\text{Conversion Factor} = \frac{\text{Equivalent Wt. of Ion}}{\text{Equivalent Wt. of } CaCO_3} = \frac{\text{Equivalent wt. of Ion}}{50}$$

APPENDIX 9

Water Analysis Reports

PRODUCTION PROFITS, INC.

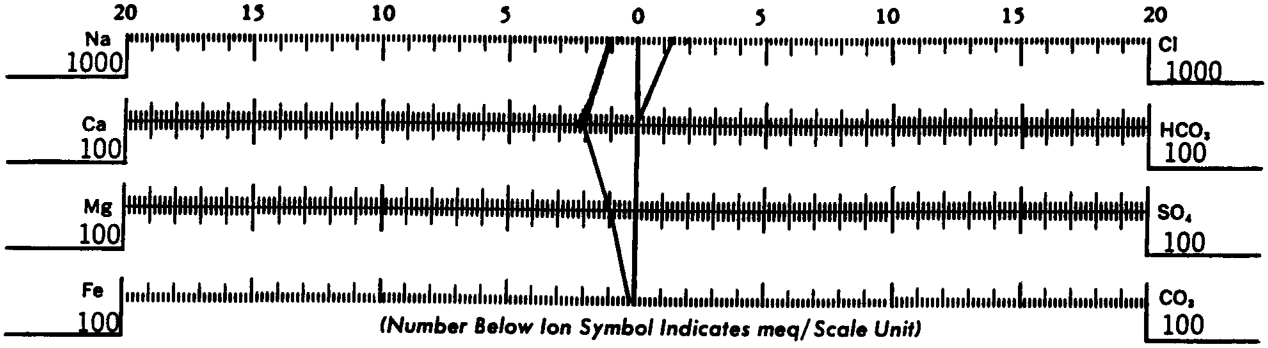
Petroleum Service Laboratory
DALLAS, TEXAS

Client
County State
Field Lease Well No.
Formation Depth Perf.
Source of Sample Injection Pump Discharge (Produced)
Date Collected 12/4/86 by PPI

REPORT OF WATER ANALYSIS

Lab. Number G1 4014 Specific Gravity 1.0632 pH (Lab) 6.5
Total Dissolved Solids 84,155 Resistivity (Ohmmeters at 68° F.) 0.098 Hydrogen Sulfide Absent

DISSOLVED MINERAL ANALYSIS PATTERN



(Number Below Ion Symbol Indicates meq/Scale Unit)

DISSOLVED SOLIDS ANALYSIS

	mg/L	meq/L
Total Solids (Calc.)	84,155	
Sodium (Calc.)	26,400	1145.8
Iron (Dissolved)	16	0.6
Barium	6	0.1
Calcium	4350	217.1
Magnesium	1250	102.8
Chloride	51,700	1457.9
Bicarbonate	115	1.9
Carbonate	0	0
Sulfate	318	6.6

TOTAL IRON 25

PRECIPITATED AND SUSPENDED SOLIDS ANALYSIS

mg/L
Total Undissolved Solids
Oil (Solvent Soluble)
Acid Solubles
Iron as
Calcium as
Magnesium as
Sulfate as
Organic (Ignition Loss)
Acid Insolubles
Sand & Clay
Barium Sulfate (Quan.)
(Qual.)

SOLUBILITY CALCULATIONS

Calcium Carbonate Stability Index at 77° F -0.68 Scaling Tendency Neg
Calcium Sulfate Stability at 95°F
Concentration 6.6 meq/L Calc. Solubility 40.1 meq/L Percent Saturation 16.45
Barium Sulfate Stability at 95° F
Concentration 0.1 meq/L Calc. Solubility 0.01 meq/L Percent Saturation 100

REMARKS
Sodium by AA: 29,390 Oil and Grease: 0 mg/L

APPENDIX 9

Water Analysis Reports (Cont'd.)

Requested By:			Sample No. GL 4014	Date Sampled 12/4/86
Field		Legal Description	Province	
Lease or Unit	Well	Depth	Formation	Rate B/D 1000
Type of Water (Produced, Supply, etc.) Produced		Sampling Point (Treater, Tank, etc) Injection Pump Discharge		Sampled By: PPI

Sample Appearance Clear ☒ Cloudy ☐ Colored ☐ ________

Suspended Solids ☐ Oil Present ☐ Odor ☐ ________

Remarks (Any other relevant information)

DISSOLVED SOLIDS

CATIONS	mg/L	me/L
Sodium, Na(calc)	26,347	1145.5
Calcium, Ca	4350	217.1
Magnesium, Mg	1250	102.8
Barium, Ba	6	0.1
Iron, Fe (Total)	25	0.9

ANIONS	mg/L	me/L
Cloride, Cl	51,700	1457.9
Sulfate, SO_4	318	6.6
Carbonate, CO_3	0	0
Bicarbonate HCO_3	115	1.9

Total Dissolved Solids (calc.) 84,155

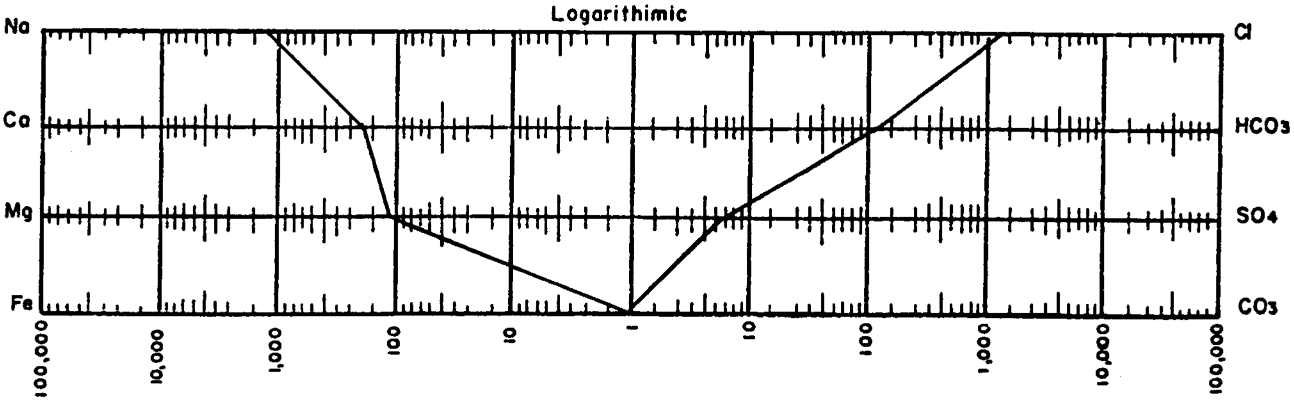
OTHER PROPERTIES

pH	6.5
Specific Gravity, 60/60F	1.0632
Resistivity(ohm-meters) F	0.098
Sulfide as H_2S mg/L	Absent

REMARKS & RECOMMENDATIONS

Analysis By: ________

WATER PATTERNS — me/L



APPENDIX 10

Use of Syringes

1. Remove the needle from the end of the syringe, immerse the tip of the syringe into the solution, and draw in a bit more solution than you plan to use.

2. Withdraw the syringe from the solution and orient it with the tip pointing up.

3. Tap the side of the syringe with your finger until all gas bubbles rise to the tip of the syringe.

4. Move the syringe plunger just far enough to displace the gas from the syringe, plus a few drops of liquid.

5. Replace the needle if necessary, and move the plunger sufficiently to force a drop or two of liquid out of the tip of the needle.

6. Move the plunger index to the desired volume and then dispense the sample or begin titration, whichever is desired.

7. Always use at least half of the syringe volume, whether measuring a sample or titrating. If less volume is required, use a smaller syringe. This is necessary to maintain the needed accuracy.

APPENDIX 11

Nomograph for Determination of Ryznar and Langelier Scaling Indexes

Example:

Given the following data, find the values of both the Langelier and the Ryznar Indexes:

pH = 6.9

Temp. = 70°F

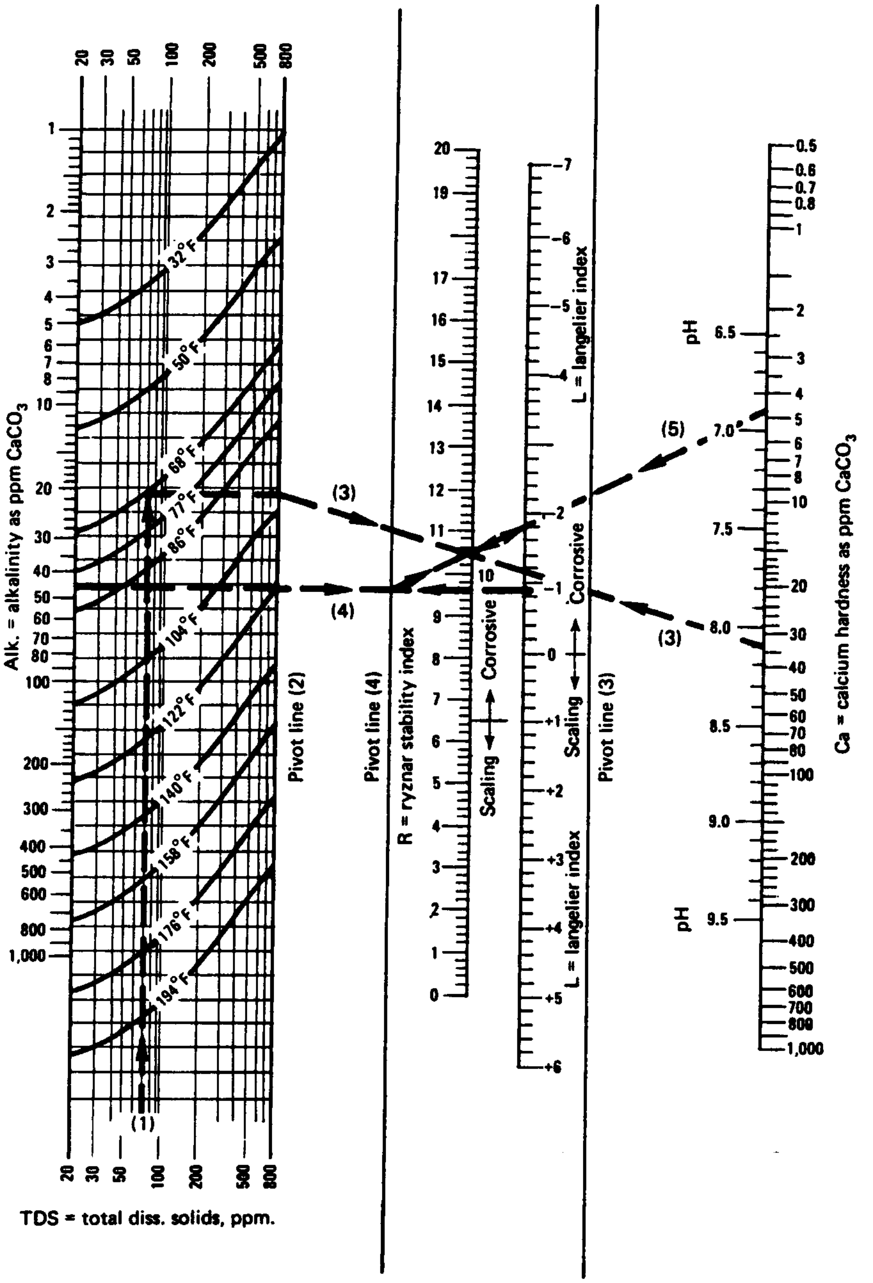
TDS = 72 ppm

Calcium hardness as
$CaCO_3$ = 34 ppm

Methyl orange alkalinity as
$CaCO_3$ = 47 ppm

Solution:

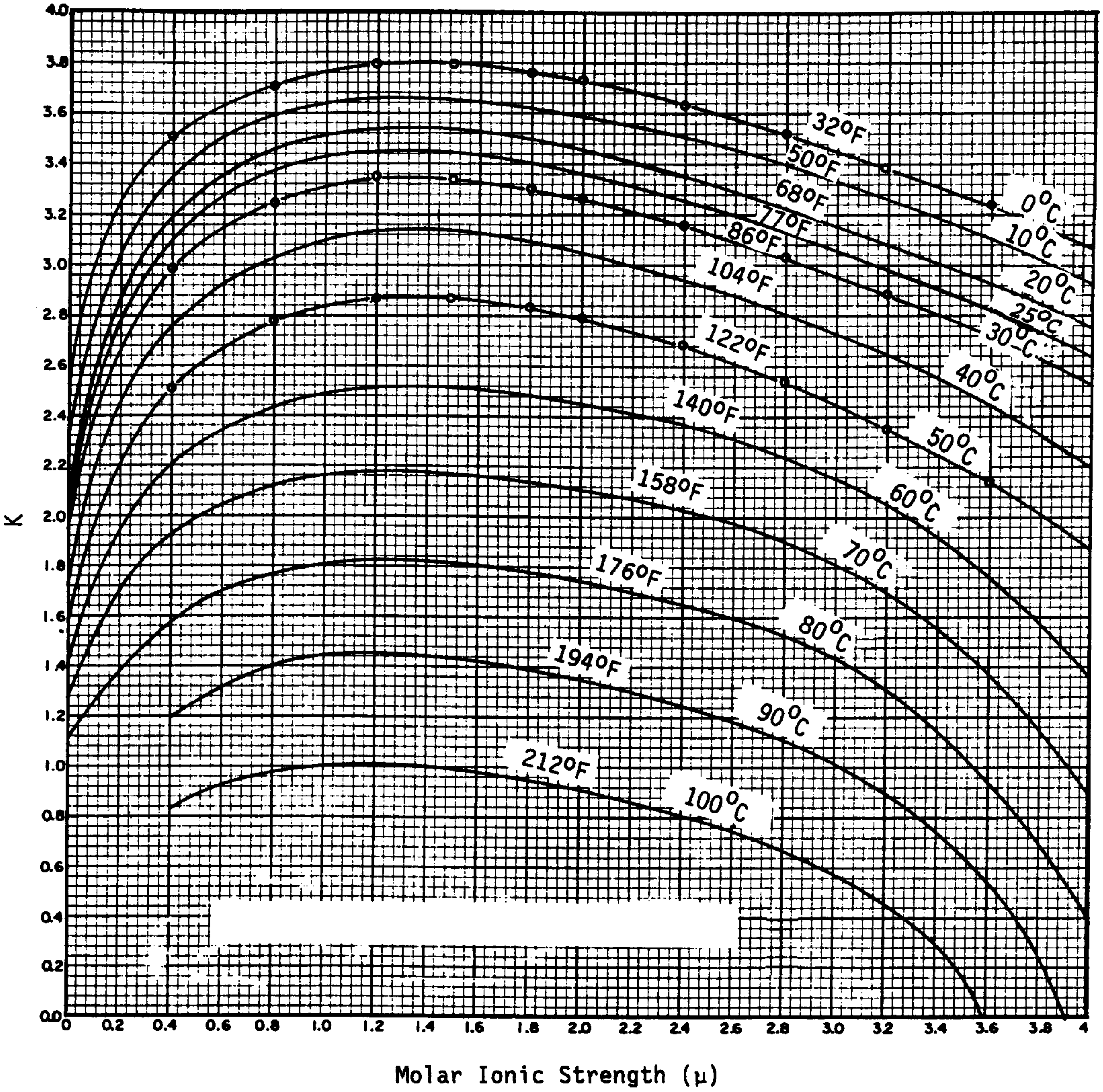
1. Reading at the bottom of the left-hand side, find TDS = 72 and note the intersection of this reading with the curved 70°F line.
2. Carry this intersection horizontally to pivot line 2.
3. Connect that point with Ca hardness = 34 on the right-hand scale.
4. Note the intersection with pipot line 3.
5. Connect that point with alkalinity = 47 on the left-hand scale.
6. Note the intersection on pivot line 4. Connect this intersection to pH = 69.
7. The Langelier Index = −1.8 and the Ryzner Index = 10.5. This water would be said to be very corrosive.



Ref: Caplan, F.: "Is Your Water Scaling or Corrosive?," *Chemical Engineering* (Sept. 1, 1975) 129.

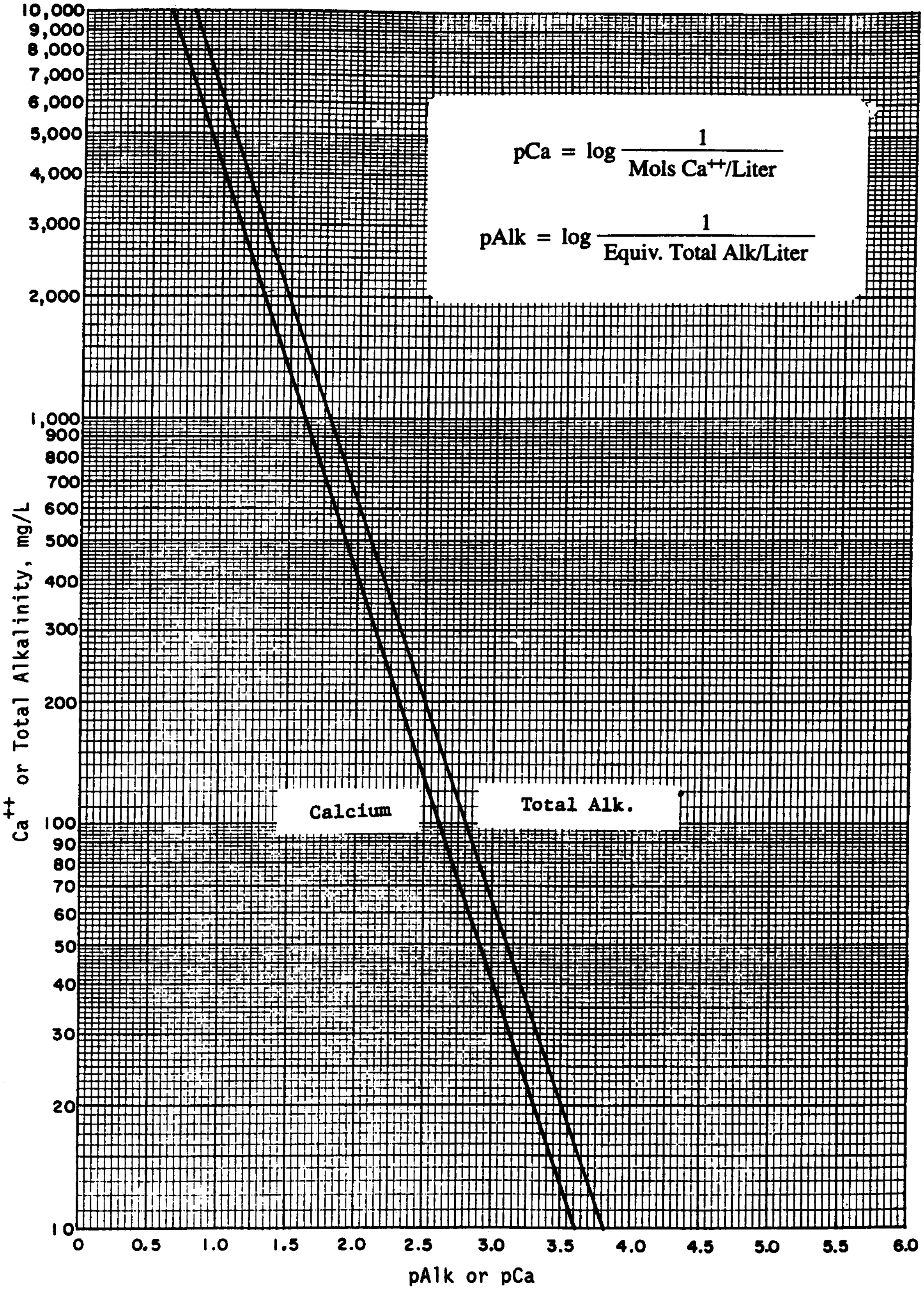
APPENDIX 12

Values of Stiff & Davis "K" for $CaCO_3$ Scale Calculations



APPENDIX 13

Conversion of mg/L Calcium and Alkalinity into pCa and pAlk



APPENDIX 14

Example Scale Calculations

Ionic Strength, $CaCO_3$ Scaling Index and $CaSO_4$ Solubility

Water Analysis		Ionic Strength Calculation		
Ion	Concentration (mg/L)	Conversion Factor		
Na^+	7559	2.2×10^{-5}	=	$16\,630 \times 10^{-5}$
Ca^{++}	877	5.0×10^{-5}	=	4385×10^{-5}
Mg^{++}	239	8.2×10^{-5}	=	1960×10^{-5}
Cl^-	12 294	1.4×10^{-5}	=	$17\,212 \times 10^{-5}$
$CO_3^=$	0	3.3×10^{-5}	=	0×10^{-5}
HCO_3^-	556	0.82×10^{-5}	=	456×10^{-5}
SO_4^-	1740	2.1×10^{-5}	=	3654×10^{-5}
		Total Ionic Strength = μ	=	$44\,297 10^{-5}$
		μ	=	0.44

Temperature = 60°C ; pH = 7.04

Calcium Carbonate Scaling Index Calculation

$K = 2.24$ (from Appendix 12)
$pCa = 1.67$ (from Appendix 13)
$pAlk = 2.05$ (from Appendix 13)

$$SI = pH - (K + pCa + pAlk) = 7.04 - (2.24 + 1.67 + 2.05) = +1.08$$

$SI > 0$, so CaCO3 scale is likely.

Calcium Sulfate Solubility Calculation

$K_c = 9.2 \times 10^{-4}$ (from Appendix 15)
$4\,K_c = 36.8 \times 10^{-4}$

Ion	Concentration (mg/L)	Conversion Factor	M (moles/L)
Ca^{++}	877	2.5×10^{-5}	2192.5×10^{-5}
$SO_4^=$	1740	1.04×10^{-5}	$1809. \times 10^{-5}$
			$X = \Delta M = 382.9 \times 10^{-5}$

$$S = 1000\left[((0.146 + 36.8) \times 10^{-4})^{0.5} - 382.9 \times 10^{-5}\right] = 57 \text{ meq/L}$$

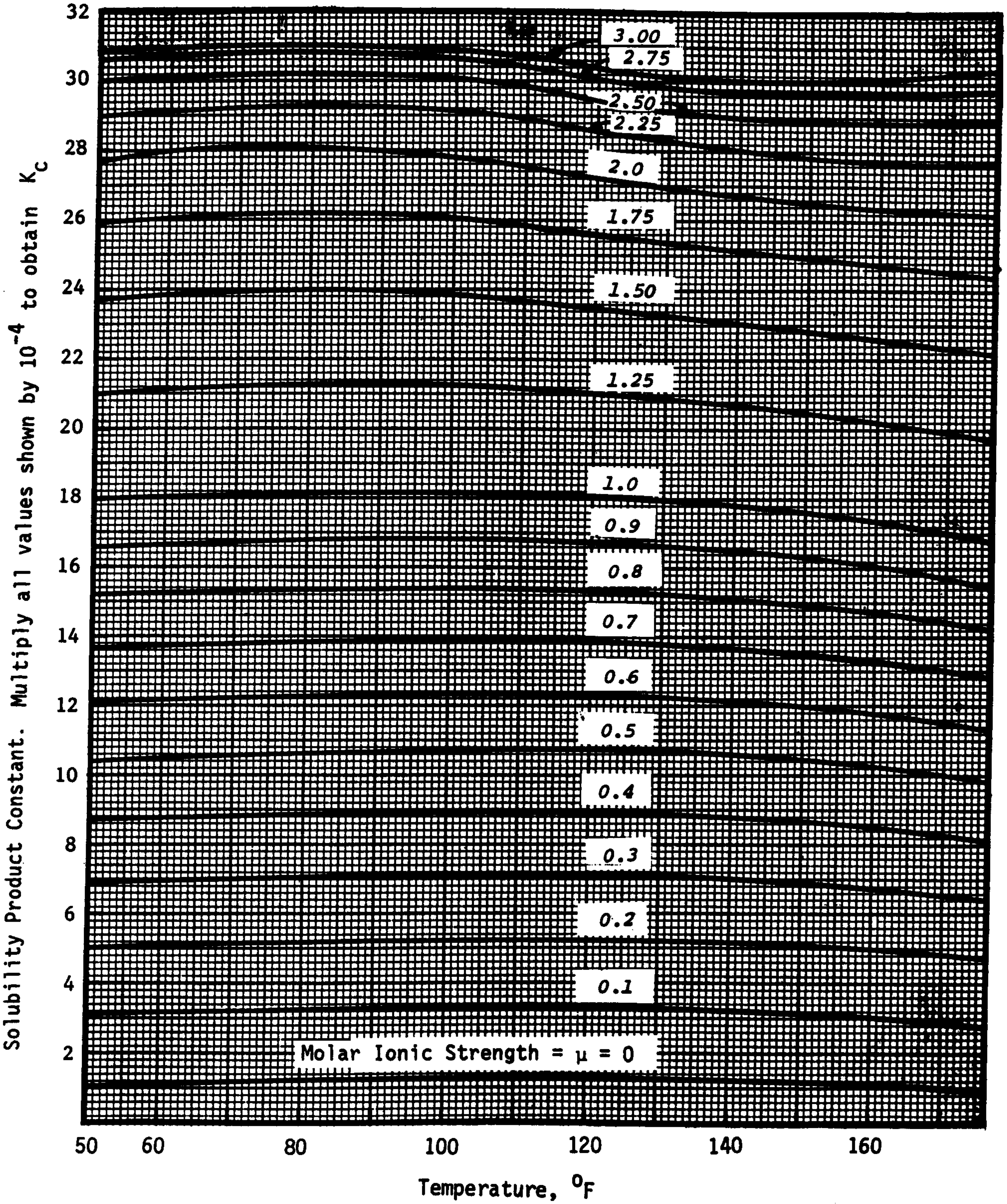
Ion	Concentration (mg/L)	Equivalent Weight	Concentration (meq/L)
Ca^{++}	877	20	43.9
$SO_4^=$	1740	48	36.3

Actual $CaSO_4$ Concentration = 36.3 meq/L

S > Actual, so $CaSO_4$ scale is unlikely.

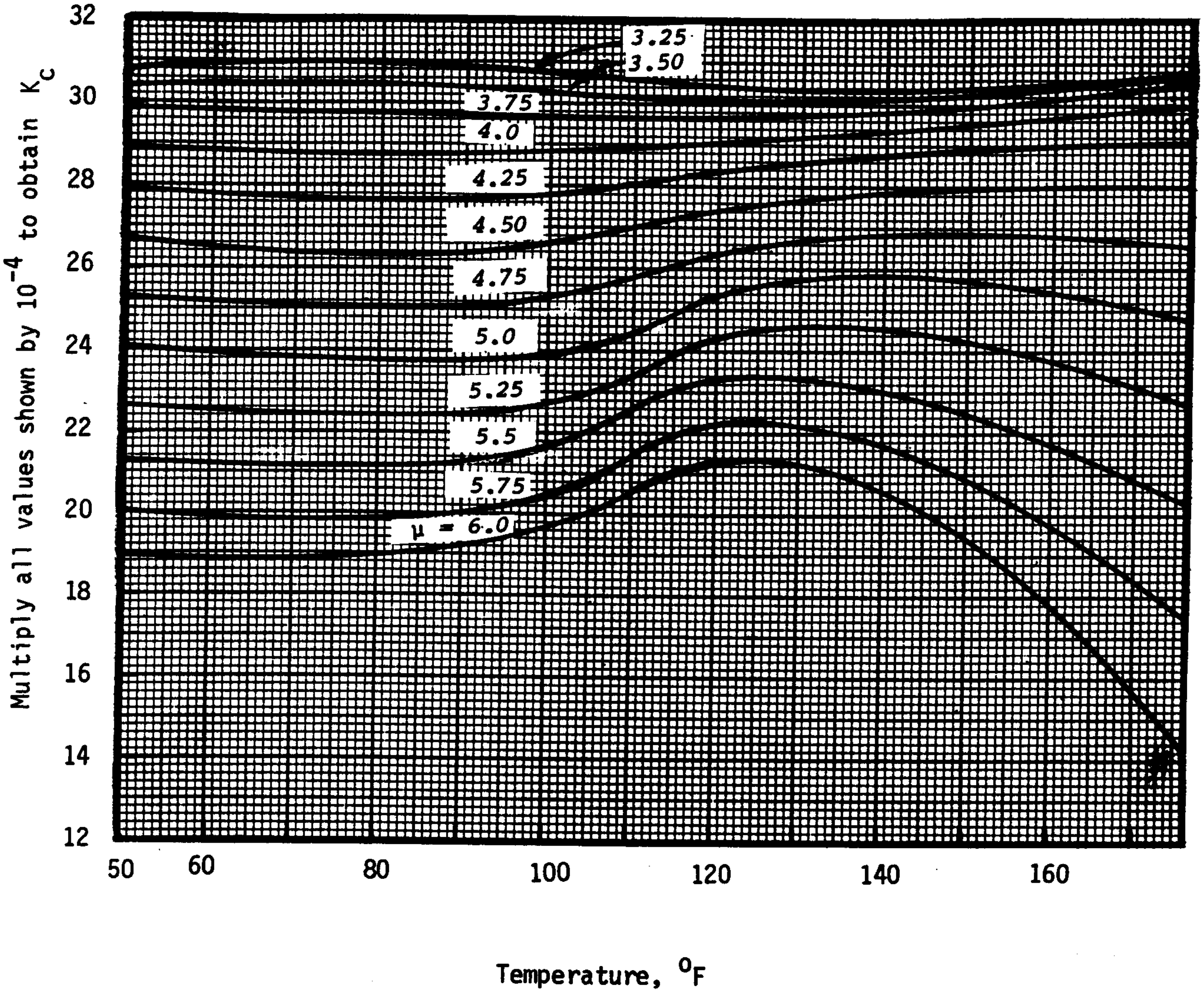
APPENDIX 15

Calcium Sulfate (Gypsum) Conditional Solubility Product Constants



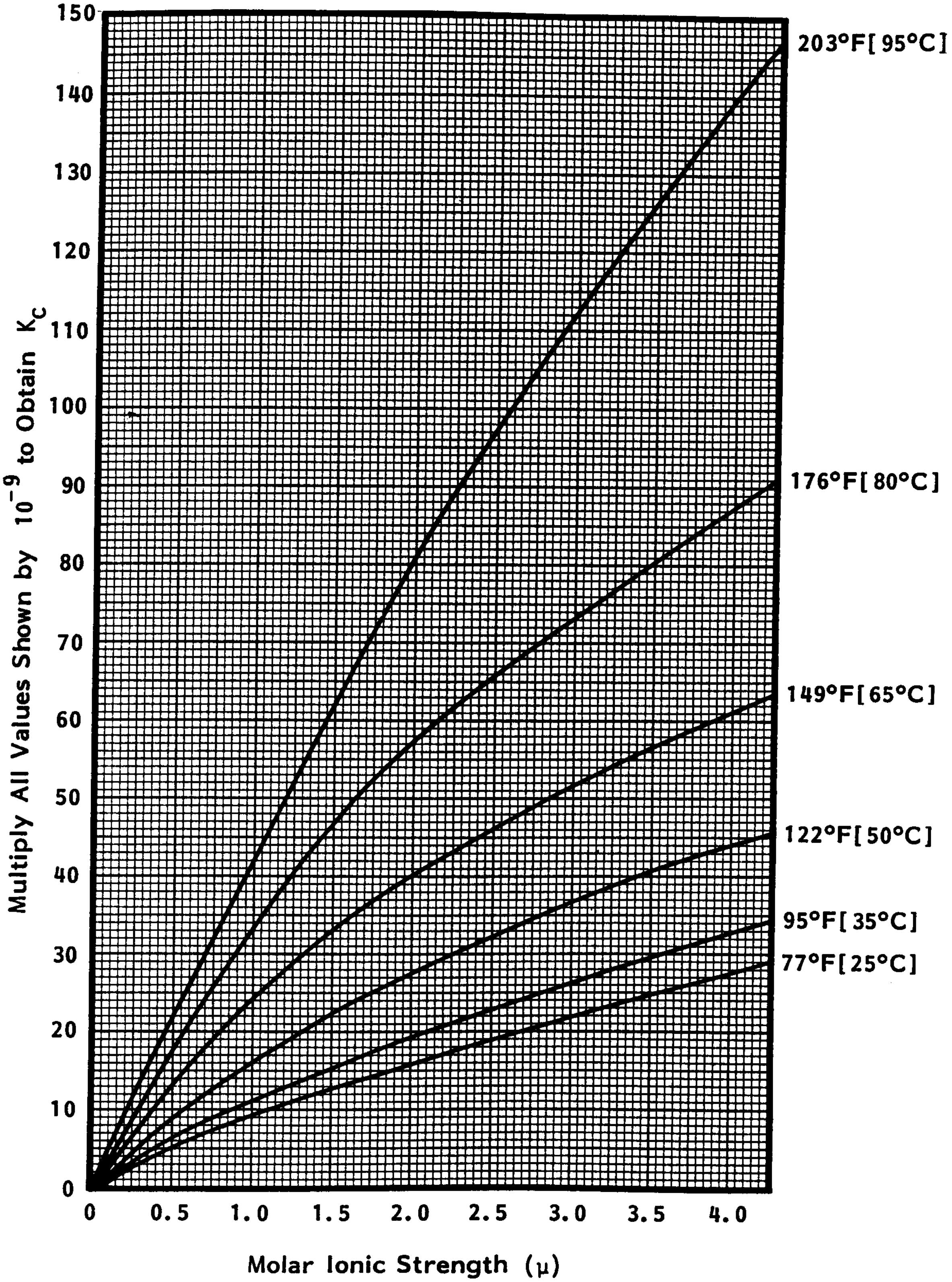
APPENDIX 15

Calcium Sulfate (Gypsum) Conditional Solubility Product Constants (Cont'd.)



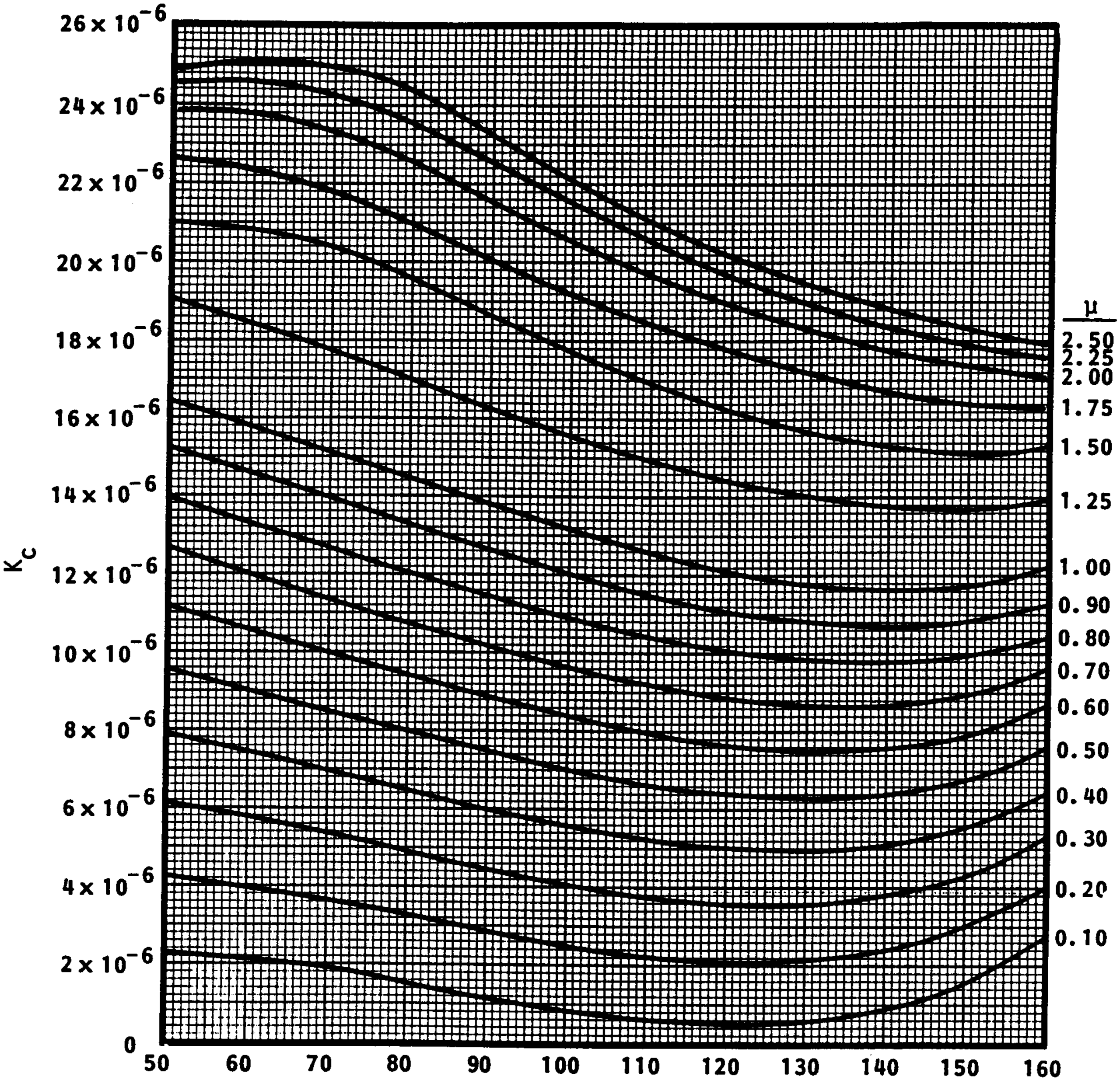
APPENDIX 16

Barium Sulfate Conditional Solubility Product Constants



APPENDIX 17

Strontium Sulfate Conditional Solubility Product Constants

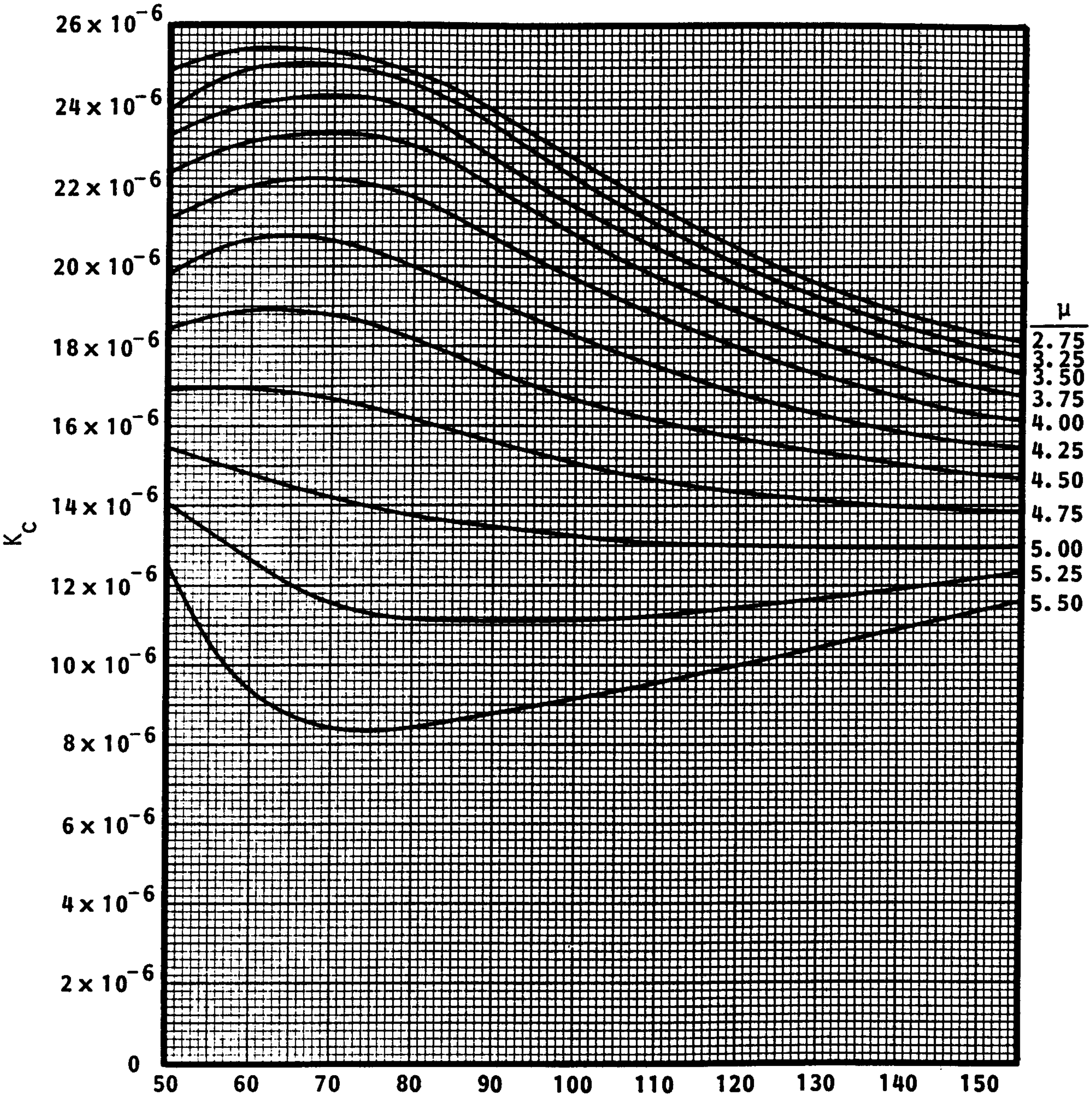


Temperature, °F

(µ is molar ionic strength)

APPENDIX 17

Strontium Sulfate Conditional Solubility Product Constants (Cont'd.)



(μ is molar ionic strength)

APPENDIX 18

Toxicity of Hydrogen Sulfide Gas

Concentration	Result
10 ppm	Can be smelled. Safe for 8 hours of exposure.
100 ppm	Kills smell in 3 to 15 minutes. May sting eyes and throat.
200 ppm	Kills smell quickly. Stings eyes and throat.
500 ppm	Loss of sense of reasoning and balance. Respiratory paralysis in 2 to 15 minutes. Prompt artificial resuscitation required.
700 ppm	Unconsciousness within 15 minutes (maximum). Cessation of breathing and death will result without immediate artifical resuscitation.
1000 ppm	Immediate unconsciousness. Permanent brain damage may result unless rescued promptly. May be fatal within 30 minutes.