Testing of Heavy Brines

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Suggested revisions are invited and should be submitted to the Standards Department, API, 1220 L Street, NW, Washington, DC 20005, standards@api.org.

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Introduction

API 13J covers the testing of heavy brines commonly used in petroleum and natural gas completion, fracturing, workover, and drill-in fluids. These brines can be purchased or rented from multiple sources and are available worldwide. No single source or limited source of supply is included, either by inference or reference.

Annexes A to E are given for information.

In this standard, quantities are expressed in the International System (SI) of units and are also, where practical, expressed in U.S. Customary (USC) units in parentheses for information.

NOTE The units do not necessarily represent a direct conversion of SI units to USC units, or of USC units to SI units.

This document uses a format for numbers that follows the examples given in *API Document Format and Style Manual*, First Edition, June 2007 (Editorial Revision, January 2009). This numbering format is different than that used in API 13J, Fourth Edition. In this document, the decimal mark is a period and separates the whole part from the fractional part of a number. No spaces are used in the numbering format. The thousands separator is a comma and is only used for numbers greater than 10,000 (i.e. 5000 items, 12,500 bags).

Consideration has been given to the precision of the instrument making the measurement. For example, thermometers are typically marked in one degree increments, thus temperature values have been rounded to the nearest degree. However, for certain critical measurements such as brine crystallization, thermometers are typically calibrated and used to 0.05 °C (0.1 °F).

Calibrating an instrument refers to assuring the accuracy of the measurement. Accuracy is the degree of conformity of a measurement of a quantity to its actual or true value. Accuracy is related to precision, or reproducibility of a measurement. Precision is the degree to which further measurements or calculations will show the same or similar results. Precision is characterized in terms of the standard deviation of the measurement. The results of calculations or a measurement can be accurate but not precise, precise but not accurate, neither, or both. A result is valid if it is both accurate and precise.

Testing of Heavy Brines

1 Scope

API 13J covers the physical properties, potential contaminants, and test procedures for heavy brine fluids manufactured for use in oil and gas well drilling, completion, fracturing, and workover fluids.

API 13J provides methods for assessing the performance and physical characteristics of heavy brines for use in field operations. It includes procedures for evaluating the density or specific gravity, the clarity or amount of particulate matter carried in the brines, the crystallization point or the temperature (both ambient and under pressure) at which the brines make the transition between liquid and solid, the pH, and iron contamination.

It also contains a discussion of gas hydrate formation and mitigation, brine viscosity, corrosion testing, buffering capacity, and a standardized reporting form (see Figure A.1).

API 13J is intended for the use of manufacturers, service companies, and end users of heavy brines.

2 Normative References

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

API Recommended Practice 13B-1, *Recommended Practice for Field Testing Water-based Drilling Fluids*

ASTM E77 [1], *Standard Test Method for Inspection and Verification of Thermometers*

NBS (NIST) Circular 555 [2], *Testing of Hydrometers*, October 22, 1954

NIST SRM 185h, *Potassium Hydrogen Phthalate, pH Standard*

NIST SRM 186g, *Potassium Dihydrogen Phosphate, pH Standard*

NIST SRM 191C, *pH Standards*

3 Terms, Definitions, Acronyms, Abbreviations, and Symbols

3.1 Terms and Definitions

For the purposes of this document, the following terms and definitions apply.

3.1.1
ACS reagent grade
Grade of chemical that meets purity standards as specified by the American Chemical Society (ACS).

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[1] ASTM International, 100 Barr Harbor Drive, West Conshocken, Pennyslvania 19428. www.astm.org.

[2] National Institute of Standards and Technology, 100 Bureau Drive, Stop 3460, Gaithersburg, Maryland 20899. www.nist.gov.

3.1.2
calculated density

Density of the brine at the reporting temperature of 20 °C in SI units or 70 °F in USC units, calculated from a measured brine density at a measurement temperature other than the reporting temperature using a brine density correction factor and/or conversion factor.

3.1.3
converted density

Density of the brine at the reporting temperature of 20 °C in SI units or 70 °F in USC units, calculated from a brine density measured at a temperature other than the reporting temperature using a density–temperature conversion factor (conversion factor).

3.1.4
corrected density or specific gravity

Measured density or specific gravity of the fluid corrected for glass expansion/contraction (correction factor) when the measurement is made at a temperature other than the sample reference temperature.

3.1.5
density
mass density

Mass of a specified material per volume of the specified material, at a specified temperature.

3.1.6
measured density

Density of a fluid at its measured temperature.

3.1.7
sample reference temperature

The temperature at which measurements made do not require a correction factor.

3.1.8
specific gravity
relative density

Density relative to the density of a reference substance, generally water at a specified temperature.

3.19
user

Manufacturer, service company, end user, or operator applying the testing of this part of API 13J.

3.2 Acronyms and Abbreviations

ACS	American Chemical Society, 1155 Sixteenth Street NW, Washington, DC 20036 www.acs.org
AISI	American Iron and Steel Institute, 1140 Connecticut Avenue NW, Washington, DC 20036 www.steel.org
bbl	one U.S. oilfield barrel, 42 gal
CAS	Chemical Abstracts Service, a division of American Chemical Society, 2540 Olentangy River Road, Columbus, OH 43202 www.cas.org
CRA	corrosion-resistant alloy
CW	cold-worked
DSS	duplex stainless steel
FCTA	first crystal to appear
LCTD	last crystal to dissolve
MIC	microbiologically induced corrosion

MSS	martensitic stainless steel
MTALC	maximum temperature after last crystal
NTU	nephelometric turbidity unit
PCT	pressure crystallization temperature
psi	pounds per square inch
SCC	stress corrosion cracking
SS	stainless steel
SSC	sulfide stress cracking
TCT	true crystallization temperature
TD	to deliver
V	volts

3.3 Symbols

B_{c}	the hydrometer-correction curve intercept
C	correction factor, in grams per milliliter per °C
C_{SI}	correction factor from Table 2
C_{USC}	correction factor from Table 2 or Equation (3)
C_{p}	pressure compensation factor, see Table 4
C_{θ}	temperature compensation factor, see Table 3
c_{B1}	first buffer concentration, in milliequivalents of acid per milliliter brine (meq$_{\mathrm{ACID}}$/ml$_{\mathrm{BRINE}}$)
c_{B2}	second buffer concentration, in milliequivalents of acid per milliliter of brine (meq$_{\mathrm{ACID}}$/ml$_{\mathrm{BRINE}}$)
c_{KHCO3}	concentration of titratable basic species, in kg/m^3 or lb/bbl of potassium bicarbonate
c_{K2CO3}	concentration of titratable basic species, in kg/m^3 or lb/bbl of potassium carbonate
c_{Na2CO3}	concentration of titratable basic species, in kg/m^3 or lb/bbl of sodium carbonate
c_{NaHCO3}	concentration of titratable basic species, in kg/m^3 or lb/bbl of sodium bicarbonate
$h_{\mathrm{TVD\text{-}SI}}$	true vertical depth, in meters
$h_{\mathrm{TVD\text{-}USC}}$	true vertical depth, in feet
M_{A}	molarity of the hydrochloric acid, in moles per liter
m_1	original mass of pan and filter paper, in milligrams
m_2	final mass of pan, filter paper and residue, in milligrams
m_3	total suspended solids, in milligrams per liter
m_4	mass of the porcelain evaporating dish and filter medium, in milligrams
m_5	mass of the porcelain evaporating dish and filtered sample after drying at 105 °C (220 °F), in milligrams
m_6	mass of the porcelain evaporating dish and filtered sample after auto-ignition at 550 °C (1000 °F), in milligrams
m_7	total nonvolatile solids or residue, in milligrams per liter
m_8	total volatile solids, in milligrams per liter
$P_{\mathrm{h\text{-}SI}}$	hydrostatic pressure, in kilopascal

$P_{\text{h-USC}}$	hydrostatic pressure, in pounds per square inch
R	hydrometer corrected reading for a 60 °F/60 °F hydrometer;
R_1	average hydrometer reading at the lower bath temperature
R_2	average hydrometer reading at the higher bath temperature
V_{A}	volume of hydrochloric acid used to the first endpoint or target pH, in milliliters
V_{B}	volume of hydrochloric acid used to reach the second endpoint or target pH, in milliliters
V_{S}	volume of undiluted brine, in milliliters
V_1	volume of the original sample, in milliliters
Z_{c}	hydrometer-correction curve slope, in (kg/m^3)/°C or (lb/gal)/°F
∇_{cf}	mud gradient, expressed in pounds per square foot calculated from density in pounds per cubic foot
∇_{SI}	SI mud gradient, in kiloPascals per meter
∇_{USC}	USC mud gradient, in pounds per square inch per foot (psi/ft), calculated from density expressed in pounds per gallon
$\theta_{\text{A-SI}}$	is the brine temperature, in °C, measured at the surface or assumed to be 20 °C
$\theta_{\text{A-USC}}$	is the brine temperature, in °F, measured at the surface or assumed to be 70 °F
$\theta_{\text{B-SI}}$	is the brine temperature, in °C, measured at bottom hole
$\theta_{\text{B-USC}}$	is the brine temperature, in °F, measured at bottom hole
θ_{m}	measured temperature, in °C or °F
$\theta_{\text{m-SI}}$	measured temperature, in °C
$\theta_{\text{m-USC}}$	measured temperature, in °F
θ_1	average temperature at the lower bath temperature, in °C or °F
$\theta_{\text{1-SI}}$	the lower temperature, in °C
$\theta_{\text{1-USC}}$	brine temperature, in °F, measured at the surface or assumed to be 70 °F
θ_2	average temperature at the higher bath temperature, either °C or °F
$\theta_{\text{2-SI}}$	the higher temperature, in °C
$\theta_{\text{2-USC}}$	brine temperature, in °F, measured at bottom hole, expressed in °F
ρ	density in SI units, in grams per milliliter
$\rho_{\text{A-SI}}$	corrected average brine density in the wellbore, in kilograms per cubic meter
$\rho_{\text{A-USC}}$	corrected average brine density in the wellbore, in pounds per gallon
ρ_{SI}	calculated density in SI units, in kilograms per cubic meter
$\rho_{\text{SI-20}}$	density at 20 °C, in kilograms per cubic meter
ρ_{USC}	density in USC units, in pounds per gallon
ρ_1	density at lower temperature, in grams per milliliter
$\rho_{\text{1-SI}}$	density at the surface, in kilograms per cubic meter
$\rho_{\text{1-USC}}$	density at the surface, in pounds per gallon
ρ_2	density at higher temperature, in grams per milliliter

ρ_{20}	density at 20 °C, in grams per milliliter
ρ_{70}	density at 70 °F, in pounds per gallon
$\rho_{\theta m}$	hydrometer corrected density reading at measured temperature expressed in g/ml or kg/m^3

4 Requirements

4.1 Quality Control Instructions

All quality control work shall be controlled by documented instructions that include appropriate methodology and quantitative acceptance criteria.

4.2 Records Retention

All records specified in API 13J shall be maintained for a minimum of one year from the date of preparation.

5 Calibration of Equipment

5.1 General Requirements

5.1.1 Laboratory equipment and reagents shall be calibrated at periodic intervals and by specified calibration procedures. For laboratory items not listed, the user shall develop procedures where deemed appropriate.

5.1.2 The user shall control, calibrate, verify, and maintain the laboratory equipment and reagents used in API 13J for measuring product conformance.

5.1.3 The user shall maintain and use laboratory equipment and reagents in a manner such that measurement uncertainty is known and meets required measurement capability.

5.1.4 The user shall document and maintain calibration procedures, including details of laboratory equipment and reagent type, identification number, frequency of checks, acceptance criteria, and corrective action to be taken when results are unsatisfactory.

5.1.5 The user shall establish and document responsibility for administration of the calibration program and responsibility for corrective action.

5.1.6 The user shall document and maintain calibration records for laboratory equipment and reagents; shall periodically review these records for trends, sudden shifts, or other signals of approaching malfunction; and shall identify each item with a suitable indicator or approved identification record to show calibration status.

5.2 Reagents and Materials for Calibration and Verification

5.2.1 Chemicals and Solutions

ACS reagent grade, or equivalent, is recommended. Shelf life shall not exceed the manufacturer's recommendation or six months after opening if no recommendation is stated.

5.2.2 Distilled or Deionized Water

The user shall develop, document and implement a method to determine hardness of water, such as ASTM D1126 or equivalent. The water shall not be used if hardness is greater than 5 µg/ml calcium ion concentration.

5.3 General Requirements for Calibration of Particular Apparatus

5.3.1 Volumetric Glassware

Laboratory volumetric glassware used for testing, including flasks and pipettes, are usually calibrated by the supplier. Users of products in accordance with API 13J shall document evidence of glassware calibration prior to use. Supplier certification is acceptable. Calibration may be checked gravimetrically. Periodic recalibration is not required.

5.3.2 Laboratory Temperature-measuring Devices

The user shall calibrate all laboratory temperature-measuring devices used in measuring product conformance against a secondary reference temperature-measuring device. The secondary reference temperature-measuring device shall show evidence of calibration as performed against NIST certified master instruments in accordance with ASTM E77 and NBS (NIST) Circular 555.

If NBS (NIST) cannot be obtained (i.e. international use of this standard), the secondary reference temperature measuring device shall show evidence of calibration as performed against a certified and traceable master instrument to a national/international standard body, such as ISO or equivalent body.

5.3.3 Laboratory Balances

The user shall calibrate laboratory balances periodically in the range of use with ASTM Class 1, 4, or 6 or better weights, depending on balance accuracy and in accordance with good laboratory practices, good management practices, or ISO quality management standards, and shall service and adjust balances whenever calibration indicates a problem.

If ASTM cannot be obtained (i.e. international use of this standard), the secondary weights shall show evidence of calibration as performed against a certified and traceable master instrument to a national/international standard body, such as ISO or equivalent body.

5.3.4 Hydrometers

The user shall calibrate each hydrometer with fluids of known density referenced and traceable to a standard.

5.3.5 Density Meter

The user shall calibrate each density meter to a known national/international standard that is traceable and according to the equipment manufacturer's recommendations.

5.4 Frequency of Calibration Verification

5.4.1 General

Any instrument subjected to movement that will affect its calibration shall be recalibrated prior to use.

5.4.2 Temperature-measuring Devices

Calibrate each temperature-measuring device before it is put into service. After calibration, mark each temperature-measuring device with an identifying number that ties it to its corresponding correction chart. Check calibration as required and stated by manufacturer, against the secondary reference temperature-measuring device. Calibration periodicity should be user specified.

5.4.3 Laboratory Balances

Calibrate each balance prior to being put into service. Check calibration at least annually, or more frequently as stated by manufacturer. Calibration periodicity should be user specified.

5.4.4 Hydrometers

Calibrate each hydrometer prior to being put into service. After calibration, note and record each hydrometer identifying number that ties it to its correction chart. Before each use, inspect for damage, and if needed recalibrate or discard. Calibration periodicity should be user specified.

5.4.5 Density Meter

Calibrate each density meter prior to being put into service. Calibration periodicity should be according to manufacturer recommendations.

5.5 Calibration Verification

5.5.1 Temperature-measuring Devices

5.5.1.1 Place the temperature-measuring devices to be calibrated side-by-side with a secondary reference temperature-measuring device in a constant-temperature water bath or suitable container of 4 L (1 gal) or more, filled with water, on a counter in a constant-temperature room. Allow to equilibrate for at least 1 h.

5.5.1.2 Read and record the temperature indicated by each temperature-measuring device.

5.5.1.3 Repeat the readings at 1 h intervals to obtain a minimum of four readings.

5.5.1.4 Calculate the average and the range of readings for each temperature-measuring device. The difference between the ranges of readings for each temperature-measuring device shall not exceed 0.1 °C (0.2 °F), or the smallest scale division on the temperature-measuring device being calibrated.

5.5.1.5 If the manufacturer of the temperature-measuring device recommends test calibration at multiple temperatures, repeat 5.5.1.1 through 5.5.1.4 in water baths set at various temperatures.

5.5.1.6 Calculate the average deviation of each temperature-measuring device reading from the secondary reference temperature-measuring device reading. Calculate and document correction for each temperature-measuring device. Discard the temperature-measuring device, if appropriate.

5.5.2 Hydrometers

5.5.2.1 Calibrate each hydrometer to be used using the same solution as the NIST or other national/international traceable standard hydrometer, at temperatures spanning the anticipated test temperatures, and by reading the bottom of the meniscus. Calibrate each hydrometer using the method given in 5.5.2.2 through 5.5.2.9.

5.5.2.2 Prepare 1 L of test solution of the relevant density.

5.5.2.3 Place the test solution into a sedimentation cylinder. Then place the cylinder in a constant-temperature bath. Set bath temperature to the lowest expected temperature for any actual test. Allow to reach equilibrium ± 0.2 °C (± 0.5 °F). Insert the traceable standard hydrometer and wait at least 5 min for the hydrometers and solution to reach the bath temperature, as measured by equilibrium of the solution temperature.

5.5.2.4 Read and record the bottom of the meniscus as the hydrometer reading. Read and record the reading obtained by the temperature-measuring device. Repeat readings at least 5 min apart to obtain a minimum of four readings.

5.5.2.5 Repeat 5.5.2.3 through 5.5.2.4 using the hydrometer to be calibrated.

5.5.2.6 Calculate the average hydrometer reading and designate this R_1. Calculate the average temperature reading and designate it as θ_1.

5.5.2.7 Repeat 5.5.2.3 through 5.5.2.4, with the bath temperature set to the highest expected test temperature. Calculate average hydrometer and temperature readings, and designate these readings as R_2 and θ_2.

5.5.2.8 Calculate the hydrometer-correction curve slope as follows:

$$Z_c = 1000 \frac{\left(R_1 - R_2\right)}{\theta_2 - \theta_1} \tag{1}$$

where

Z_c is the hydrometer-correction curve slope, expressed in (kg/m^3)/°C or (lb/gal)/°F;

R_1 is the average hydrometer reading at the lower bath temperature;

R_2 is the average hydrometer reading at the higher bath temperature;

θ_1 is the average temperature at the lower bath temperature, either °C or °F;

θ_2 is the average temperature at the higher bath temperature, either °C or °F.

Temperature may be measured in either degrees Celsius or degrees Fahrenheit as long as all measurements and calculations are consistent in units.

5.5.2.9 Calculate the hydrometer-correction curve intercept as follows:

$$B_c = \left(Z_c \times \theta_1\right) + \left[1000\left(R_1 - 1\right)\right] \tag{2}$$

where

B_c is the hydrometer-correction curve intercept;

NOTE B_c is provided for reference in the permanent calibration record.

Z_c hydrometer-correction curve slope, expressed in (kg/m^3)/°C or (lb/gal)/°F;

R_1 is the average hydrometer reading at the lower bath temperature;

θ_1 is the average temperature at the lower bath temperature, expressed in either °C (°F).

5.5.2.10 Record Z_c, B_c, and hydrometer serial number in a permanent calibration record.

6 Density

6.1 General

6.1.1 The density of brine is determined by its salt type and concentration. Moreover, the brine density decreases as the temperature increases. The amount of decrease depends on the brine composition. Conversely, the brine density increases as the pressure on the brine increases. Therefore, the brine density at ambient atmospheric conditions is not a reliable indicator of brine density downhole because the brine density changes with temperature, hydrostatic pressure, and applied pressure.

6.1.2 The density of brine is the mass of brine per unit of volume. In the SI system, density is expressed in kilograms per cubic meter (kg/m^3). The use of derived units, grams per cubic centimeter (g/cm^3) and grams per milliliter (g/ml), is acceptable. Density may also be expressed in terms of specific gravity (relative density) or pressure gradient. Specific gravity of brine is the density of the brine at a specified temperature relative to the density of the hydrometer reference material at its reference temperature. The density of a brine when measured at the reference temperature of the hydrometer can be calculated by multiplying the specific gravity by the density of the reference material at its reference temperature.

NOTE 1 In USC units, density is expressed in pounds per gallon (lb/gal) or pounds per cubic foot (lb/ft^3).

NOTE 2 It is considered that one milliliter is equal to one cubic centimeter.

NOTE 3 The reference material for hydrometers most commonly used for heavy brine is air-free distilled water [density 999 kg/m^3 (8.337 lb/gal) at 15.56 °C (60 °F)].

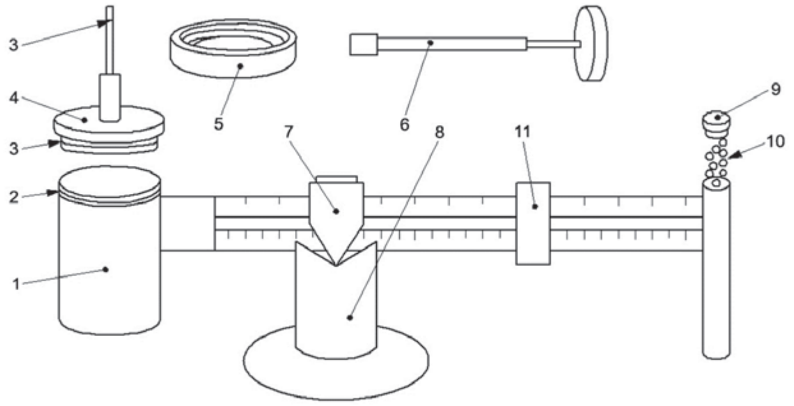
Pressure gradient is the hydrostatic pressure exerted by the brine per unit depth. In SI system, pressure gradient is expressed in kilopascal per meter (kPa/m). In USC units, it is expressed in pounds per square inch per foot (psi/ft).

6.1.3 The reference temperature for reporting brine density in SI units is 20 °C. The reference temperature in USC units is 70 °F. The reported/calculated density at 20 °C or 70 °F is not used to determine hydrostatic pressure. Instead, the actual measured density at surface temperature (measured density read or calculated from the hydrometer reading at surface temperature) is used to calculate an estimated hydrostatic pressure. A more accurate value can be obtained by integrating the density changes due to temperature and pressure increase along the brine column.

6.1.4 The measurement of the density of brines is affected by entrapped gases. If gas entrainment is a problem, it is recommended that the procedures outlined in API 13B-1 be used to remove the entrained gas. These procedures use a pressurized fluid density (mud) balance and/or deaerator to aid in the density measurement. The pressurized mud balance is shown in Figure 1 and the atmospheric balance in Figure 2.

6.1.5 The pressurized (see Figure 1) and atmospheric (see Figure 2) mud balances are useful for determining density trends (increases or decreases) in the field but are not sufficiently accurate for absolute determination of brine density. For purposes of absolute density determination, a set of calibrated hydrometers or calibrated density meter shall be used instead of a mud balance. For the use of mud balances, follow the procedures specified in API 13B-1.

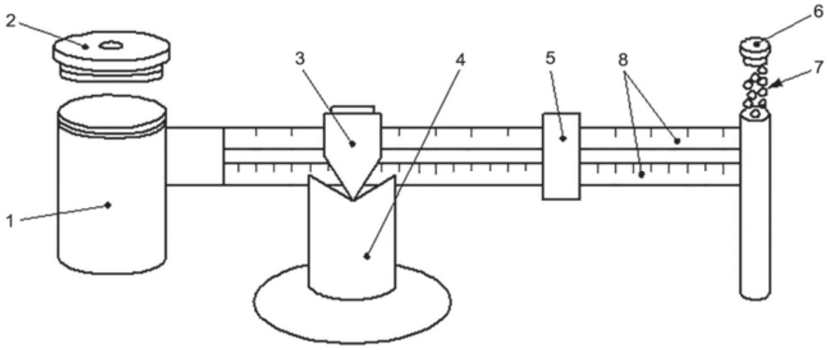
6.1.6 Any instrument of sufficient precision to permit measurement to within ± 5 kg/m^3 (± 0.005 g/ml; ± 0.05 lb/gal) and reportable to within ± 10 kg/m^3 (± 0.01 g/ml; ± 0.1 lb/gal) may be used. Generally, this requires the use of hydrometers or density meter for fluid density measurements. An atmospheric or pressurized mud balance may be used but lacks sufficient precision to meet the requirements of this clause for reporting brine density (see 6.2.1 through 6.2.3).



Key

1 sample cup
2 threaded edge to sample cup
3 O-ring seals
4 pressurized lid
5 retaining ring for securing lid
6 pressurization device
7 knife edge with level
8 base with fulcrum
9 weight adjustment screw cover
10 scale calibration material
11 rider for reading scales

Figure 1—Pressurized Mud Balance



Key

1 sample cup
2 lid for cup
3 knife edge with level
4 base with fulcrum
5 rider for reading scale
6 weight adjustment screw cover
7 scale calibration material
8 scales

Figure 2—Atmospheric Mud Balance

6.2 Apparatus

6.2.1 Set of glass hydrometers, which cover the density or specific gravity range encountered in heavy brine applications with graduations not greater than 0.002 in density units expressed in grams per cubic centimeter (or grams per milliliter) or in specific gravity units (dimensionless).

NOTE Hydrometers graduated in kg/m^3 are not common oilfield apparatuses. Specific gravity hydrometers graduated in lb/gal are also not common apparatuses.

The hydrometer is a weighted bulb with a graduated stem. Two types of hydrometers (density meter) can be used: density hydrometers and specific gravity hydrometers (relative density). The depth to which the hydrometer sinks in a fluid is determined by the density of the fluid and temperature (Archimedes' Law); therefore, the brine temperature should be recorded to apply temperature correction and/or conversion factors if required.

Two temperatures are identified with each type of hydrometer:

1) the reference temperature at which the measurement is made, called the sample reference temperature; and

2) the reference temperature at which the reference material was specified, called the reference material reference temperature.

These are typically displayed as, for example, 60 °F/60 °F, wherein the upper temperature is the sample reference temperature and the lower temperature is the reference material reference temperature. Other hydrometer reference temperatures are 20 °C/4 °C and 20 °C/20 °C (often with one temperature written directly above the other).

NOTE 1 Hydrometer reference temperatures are (Sample Reference Temperature)/(Reference Material Reference Temperature).

NOTE 2 Most specific gravity hydrometers used in the oilfield are 60 °F/60 °F hydrometers and the reference material is deaerated water. Therefore, the calculations reported herein are based on these 60 °F/60 °F specific gravity hydrometers.

NOTE 3 For density hydrometers provided by suppliers where only one temperature, called the density meter calibration temperature, is marked on the apparatus, the user should verify that the temperature is both the reference temperature and the reference material temperature.

Any oil present in the sample will interfere with the measurement, and the use of freshly filtered samples is recommended.

At least, the following information shall be permanently, legibly, and unequivocally marked with the hydrometer.

1) The basis of the scale [e.g. g/cm^3, dimensionless specific gravity (relative density hydrometer)].

2) The sample reference temperature for the hydrometer measurement (e.g. 20 °C, 60 °F) and the reference temperature for the reference standard (e.g. 15.56 °C, 60 °F). For some density hydrometers, only one temperature called the apparatus reference or calibration temperature is recorded.

3) A particular surface tension expressed in millinewtons per meter (e.g. 75 mN/m), or a surface tension category (e.g. high or low surface tension), when known.

4) An identification number; the first two digits of which may indicate the year of manufacturing (e.g. 11xxxxx).

5) The series identification (e.g. M50), related to accuracy of the hydrometer.

6.2.1.1 Density Hydrometer

The scale shall indicate density (mass per unit of volume) with graduations in grams per milliliter (or grams per cubic centimeter) not greater than 0.002 g/ml (0.002 g/cm^3). At the same time, brine temperature should be recorded to apply temperature correction and/or conversion factors if needed. The density of a brine when measured at the sample reference temperature of the density hydrometer is the density read directly from the density hydrometer. At temperatures other than the sample reference temperature, correction and conversion factors for temperature are required.

Since the hydrometer is constructed of glass, a correction factor due to the thermal volumetric expansion (or contraction) of glass is applied first to the measurement whenever the measurement is made at a temperature different from the sample reference temperature.

When converting the measured density of brine to a temperature different from the measured temperature, a conversion factor shall be applied based on the thermal volume expansion (or contraction) of the specific brine composition.

6.2.1.2 Specific Gravity (Relative Density) Hydrometer

Specific gravity (relative density) hydrometers are widely used, for which the sample reference temperature and the reference material reference temperature are typically 15.56 °C (60 °F). Specific gravity hydrometers are similar to density hydrometers and have a graduated stem with dimensionless graduations in specific gravity units not greater than 0.002. At the same time, brine temperature should be recorded to apply temperature correction and/or conversion factors if needed.

Since the hydrometer is constructed of glass, a correction factor due to the thermal volumetric expansion (or contraction) of glass is applied first to the measurement whenever the measurement is made at a temperature different from the sample reference temperature.

The measurement is the specific gravity (relative density) of a brine at the measurement temperature relative to the density of the reference material at its reference temperature. Then, the density of a brine at the measured temperature is calculated by multiplying the specific gravity at the measured temperature by the density of the reference material at the reference material reference temperature. The density of the reference material, deaerated distilled water, for the most popular specific gravity hydrometer (60 °F/60 °F) used for oilfield brine measurements is 0.999 g/ml (8.337 lb/gal).

When converting the measured specific gravity of brine into density at a temperature different from the measured temperature, a conversion factor shall be applied based on the thermal volume expansion (or contraction) of the specific brine composition.

6.2.2 Cylindrical sample container, plastic or glass.

For convenience in pouring, the cylinder may have a lip on the rim. The inside diameter of the cylinder shall be at least 2.54 cm (1.0 in) greater than the outside diameter of the hydrometer used. The height of the cylinder shall be such that the hydrometer floats in the sample fluid with at least 2.54 cm (1.0 in) clearance between the bottom of the hydrometer and the bottom of the cylinder.

6.2.3 Temperature-measuring device, range 0 °C to 105 °C (32 °F to 220 °F), with accuracy of ± 1 °C (± 2 °F).

6.2.4 Filter paper.

6.3 Measurement of Specific Gravity or Density Using a Hydrometer

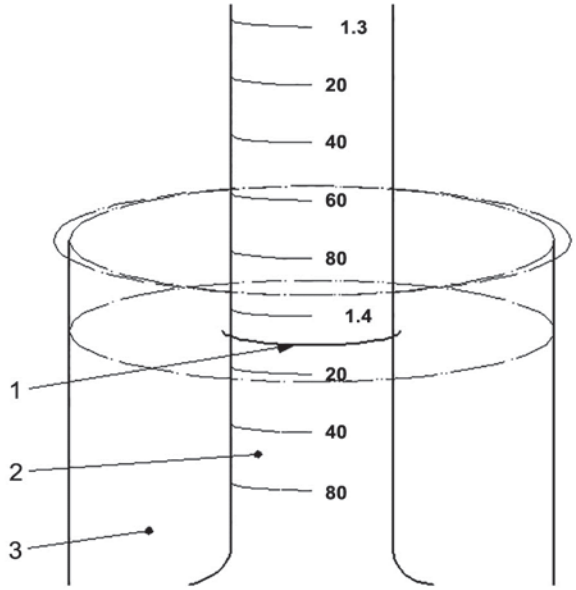
6.3.1 This procedure is applicable for both density and relative density hydrometers.

6.3.2 Pour the sample fluid into the clean, dry cylinder without splashing. Splashing can entrain air bubbles in the fluid. Remove any air bubbles adhering to the surface by touching them with a piece of clean filter paper.

6.3.3 Place the cylinder in a location that is free from air currents.

6.3.4 Place the hydrometer vertically in the sample fluid and spin the hydrometer to center the device.

6.3.5 After the hydrometer has come to rest and floats freely away from the walls of the cylinder, take the hydrometer reading as the point at which the surface of the sample fluid appears to cut the hydrometer scale (bottom of the meniscus) as shown in Figure 3.



Key

1 reading at bottom of meniscus

2 hydrometer

3 sample

Figure 3—Reading at Bottom of Meniscus

6.3.6 Determine the temperature of the sample fluid immediately following reading the hydrometer.

6.3.7 Ideally, the measurement temperature should be 20 °C ± 2 °C for SI units and 70 °F ± 5 °F for USC units in order to minimize measurement uncertainties and the application of correction and/or conversion factors. The following measurement scenarios exist.

6.3.7.1 When the measurement is made at the hydrometer sample reference temperature, no correction for glass thermal expansion/contraction or brine thermal expansion/contraction is required.

The brine thermal expansion/contraction factor (conversion factor) can then be used to obtain the density or specific gravity of the brine at some other temperature.

6.3.7.2 When the measured brine temperature is different from the hydrometer sample reference temperature, correction for glass expansion/contraction is required to obtain the density or specific gravity of the brine at the measured temperature, if significant.

The brine thermal expansion/contraction factor (conversion factor) can then be used to obtain the density or specific gravity of the brine at some other temperature.

6.4 Density Corrections for Hydrometers and Brines

6.4.1 Temperature Corrections for Hydrometer Readings

6.4.1.1 Density from Hydrometer Readings

If the hydrometer reading is taken at a temperature reading other than the sample reference temperature for the hydrometer, then the reading will be in error because there is a change in volume of the hydrometer between the two temperatures due to the thermal expansion or contraction of the glass from which the hydrometer is made.

Appropriate corrections making allowance for the thermal glass expansion/contraction effect are given in Table 1. When positive in sign, the temperature correction is to be added to the hydrometer reading. Conversely when negative in sign, the temperature correction is to be subtracted from the hydrometer reading. The table is computed using a nominal coefficient of cubical thermal expansion for the glass of the hydrometer having a value of 25×10^{-6} °C^{-1} (13.9×10^{-6} °F^{-1}). In the worst cases for measuring temperatures dramatically different from the hydrometer sample reference temperature, the glass expansion/contraction factors affect only digits that are estimated from the hydrometer reading. Hydrometer readings corrected for glass expansion/contraction are labeled hydrometer corrected readings.

6.4.1.2 Specific Gravity and Density by Specific Gravity Hydrometer

If the specific gravity hydrometer reading is taken at a temperature reading other than the sample reference temperature for the hydrometer, then the reading will be in error because there is a change in volume of the hydrometer between the two temperatures due to the thermal expansion or contraction of the glass from which the hydrometer is made.

As for density hydrometers, appropriate corrections making allowance for the thermal glass expansion/contraction effect are given in Table 1. When positive in sign, the temperature correction is to be added to the hydrometer reading. Conversely when negative in sign, the temperature correction is to be subtracted from the hydrometer reading. The table is computed using a nominal coefficient of cubical thermal expansion for the glass of the hydrometer having a value of 25×10^{-6} °C^{-1} (13.9×10^{-6} °F^{-1}). In the worst cases for measuring temperatures dramatically different from the hydrometer sample reference temperature, the glass expansion/contraction factors affect only digits that are estimated from the hydrometer reading. Hydrometer readings corrected for glass expansion/contraction are labeled hydrometer corrected readings.

Table 1—Temperature Correction Factors for Hydrometers due to Glass Expansion and Contraction

Change in Measuring Temperature		**Specific Gravity or Density Reading** Dimensionless or expressed in g/ml (10^{-3} kg/m^3)						
°C	°F	**1.0**	**1.2**	**1.4**	**1.6**	**1.8**	**2.0**	**2.2**
−20	−36	0.0005	0.0006	0.0007	0.0008	0.0009	0.0010	0.0011
−15	−27	0.0004	0.0005	0.0005	0.0006	0.0007	0.0008	0.0008
−10	−18	0.0003	0.0003	0.0004	0.0004	0.0005	0.0005	0.0006
−5	−9	0.0001	0.0002	0.0002	0.0002	0.0002	0.0003	0.0003
Hydrometer Sample Reference Temperature		**0**	**0**	**0**	**0**	**0**	**0**	**0**
5	+9	−0.0001	−0.0002	−0.0002	−0.0002	−0.0002	−0.0003	−0.0003
10	+18	−0.0003	−0.0003	−0.0004	−0.0004	−0.0005	−0.0005	−0.0006
15	+27	−0.0004	−0.0005	−0.0005	−0.0006	−0.0007	−0.0008	−0.0008
20	+36	−0.0005	−0.0006	−0.0007	−0.0008	−0.0009	−0.0010	−0.0011
25	+45	−0.0006	−0.0008	−0.0009	−0.0010	−0.0010	−0.0011	−0.0014

NOTE 1 These corrections when applied to the hydrometer reading at a measured temperature give the specific gravity or density (g/ml) at the measured temperature. They are based on the equation

$C_g = 0.000025R(\theta_{Ref} - \theta_m)$

where

C_g is the correction for glass expansion/contraction in g/ml for density or dimensionless specific gravity;

R is the density hydrometer reading in g/ml or dimensionless specific gravity;

θ_m is the temperature of the liquid to be measured in °C;

θ_{Ref} is the sample reference temperature of the hydrometer in °C.

NOTE 2 Cubical volume expansion factor for glass is 0.000025 per °C (0.0000139 per °F).

Density of a brine, $\rho_{\theta m}$, at measurement temperature, θ_m, can be calculated using appropriate equations according to the desired unit:

$\rho_{\theta m}$, expressed in g/ml, using Equation (3) based on the hydrometer corrected specific gravity reading, R, at measured temperature $\theta_{m,}$ 0.999 is the density of deaerated distilled water at 15.56 °C (60 °F) expressed in g/ml:

$$\rho_{\theta m} = 0.999 \times R \tag{3}$$

$\rho_{\theta m\text{-}SI}$, expressed in kg/m^3, using Equation (4) based on the hydrometer corrected specific gravity reading, R, at measured temperature θ_m, 999 is the density of deaerated water at 15.56 °C (60 °F) expressed in kg/m^3:

$$\rho_{\theta m\text{-}SI} = 999 \times R \tag{4}$$

$\rho_{\theta\text{m-USC}}$, expressed in lb/gal, using Equation (5) based on the hydrometer corrected specific gravity reading, R, at measured temperature θ_m, 8.337 is the density of deaerated water at 15.56 °C (60 °F) expressed in lb/gal:

$$\rho_{\theta\text{m-USC}} = 8.337 \times R \tag{5}$$

R is the specific gravity hydrometer corrected reading for thermal glass expansion/contraction at measured temperature

6.4.2 Temperature Corrections for Brine

The calculated density of a brine sample shall be corrected to 20 °C for SI units and to 70 °F for USC units if the hydrometer measurement was taken at any other measurement temperature. This brine volume expansion/contraction factor is due to the fact that the volume of brine changes as the temperature of the brine changes. Therefore, brine density must be corrected for brine volume changes when converting from one temperature to another. The conversion factor shall be read from Table 2, which is an estimate of the conversion factor, or from the appropriate Equation (6), Equation (7), Equation (8), Equation (9), or Equation (10) having the measurement/units of interest.

a) For SI derived units expressed in g/ml, C can be calculated using Equation (6):

$$C = 10^{-3} \times \left[(-0.12868) + (1.4999 \times \rho_{\theta\text{m}}) - \left(1.036 \times \rho^2_{\theta\text{m}}\right) + \left(0.2727 \times \rho^3_{\theta\text{m}}\right) \right] \tag{6}$$

where

$\rho_{\theta\text{m}}$ is the hydrometer corrected density reading at measured temperature expressed in g/ml;

C is the brine density conversion factor in g/ml per °C.

b) For SI units expressed in kg/m^3, C_SI can be calculated using Equation (7):

$$C_\text{SI} = \left[(-0.12868) + (1.4999 \times \rho_{\theta\text{m}}) - \left(1.036 \times \rho^2_{\theta\text{m}}\right) + \left(0.2727 \times \rho^3_{\theta\text{m}}\right) \right] \tag{7}$$

where

$\rho_{\theta\text{m}}$ is the hydrometer corrected density reading at measured temperature expressed in g/ml;

C_SI is the brine density conversion factor in kg/m^3 per °C;

or using Equation (8):

$$C_\text{SI} = \left[(-0.12868) + \left(1.4999 \times 10^{-3} \times \rho_{\theta\text{m-SI}}\right) - \left(1.036 \times 10^{-6} \times \rho^2_{\theta\text{m-SI}}\right) + \left(0.2727 \times 10^{-9} \times \rho^3_{\theta\text{m-SI}}\right) \right] \tag{8}$$

where

$\rho_{\theta\text{m-SI}}$ is the hydrometer corrected density reading at measured temperature expressed in kg/m^3;

C_SI is the brine density conversion factor in kg/m^3 per °C.

c) For USC units, C_{USC} can be calculated using Equation (9):

$$C_{\text{USC}} = 10^{-3} \times \left[(-0.59659) + (0.83411 \times \rho_{\theta\text{m-USC}}) - \left(0.06904 \times \rho^2_{\theta\text{m-USC}}\right) + \left(0.00218 \times \rho^3_{\theta\text{m-USC}}\right) \right] \quad (9)$$

where

$\rho_{\theta\text{m-USC}}$ is the hydrometer corrected density reading at measured temperature expressed in lb/gal;

C_{USC} is the brine density conversion factor in lb/gal per °F;

or directly from corrected hydrometer specific gravity reading using Equation (10):

$$C_{\text{USC}} = 10^{-3} \times \left[(-0.59659) + (6.954 \times R) - \left(4.799 \times R^2\right) + \left(1.263 \times R^3\right) \right] \quad (10)$$

where

R is the hydrometer corrected reading for a 60 °F/60 °F hydrometer expressed in specific gravity;

C_{USC} is the brine density conversion factor in lb/gal per °F.

Using the conversion factor from either Equations (6) to (10) or Table 2, calculate the corrected density at 20 °C for SI units or 70 °F for USC units.

a) If temperature measurement is given in degrees Celsius, use Equation (11) to find the corrected density in g/ml:

$$\rho_{20} = \rho_{\theta\text{m}} + \left[(\theta_{\text{m-SI}} - 20) \times C \right] \quad (11)$$

where

ρ_{20} is the density at 20 °C, expressed in grams per milliliter;

$\rho_{\theta\text{m}}$ is the hydrometer corrected density reading at measured temperature expressed in g/ml;

NOTE $\rho_{\theta\text{m}}$ can be calculated using Equation (3) and a corrected specific gravity hydrometer reading.

$\theta_{\text{m-SI}}$ is the measured temperature, in °C;

C is the brine thermal expansion/contraction factor from Table 2 or Equation (3).

Table 2—Estimated Brine Thermal Expansion/Contraction Factors (Conversion Factors)

Hydrometer Corrected Density Hydrometer Reading $\rho_{\theta m}$ g/ml	Hydrometer Corrected Specific Gravity 60 °F/60 °F Hydrometer Reading R dimensionless	Brine Density at Measured Temperature		Brine Thermal Expansion/Contraction Factors		
		$\rho_{\theta m}$ kg/m^3	$\rho_{\theta m}$ lb/gal	C g/ml per °C	C_{SI} kg/m^3 per °C	C_{USC} lb/gal per °F
1.020	1.021	1020	8.51	0.00061	0.61	0.00285
1.050	1.051	1050	8.76	0.00062	0.62	0.00288
1.100	1.101	1100	9.18	0.00063	0.63	0.00293
1.150	1.151	1150	9.60	0.00064	0.64	0.00298
1.200	1.201	1200	10.01	0.00065	0.65	0.00302
1.250	1.251	1250	10.43	0.00066	0.66	0.00307
1.300	1.301	1300	10.85	0.00067	0.67	0.00311
1.350	1.351	1350	11.26	0.00068	0.68	0.00315
1.400	1.401	1400	11.68	0.00069	0.69	0.00320
1.450	1.451	1450	12.10	0.00070	0.70	0.00325
1.500	1.502	1500	12.52	0.00071	0.71	0.00330
1.550	1.552	1550	12.94	0.00072	0.72	0.00336
1.600	1.602	1600	13.36	0.00074	0.74	0.00342
1.650	1.652	1650	13.77	0.00075	0.75	0.00349
1.700	1.702	1700	14.19	0.00077	0.77	0.00356
1.750	1.752	1750	14.61	0.00078	0.78	0.00365
1.800	1.802	1800	15.02	0.00080	0.80	0.00374
1.850	1.852	1850	15.44	0.00083	0.83	0.00384
1.900	1.902	1900	15.86	0.00085	0.85	0.00396
1.950	1.952	1950	16.27	0.00088	0.88	0.00409
2.000	2.002	2000	16.69	0.00091	0.91	0.00423
2.050	2.052	2050	17.11	0.00094	0.94	0.00438
2.100	2.102	2100	17.52	0.00098	0.98	0.00455
2.150	2.152	2150	17.94	0.00102	1.02	0.00473
2.200	2.202	2200	18.36	0.00106	1.06	0.00493
2.250	2.252	2250	18.78	0.00111	1.11	0.00515
2.300	2.302	2300	19.19	0.00116	1.16	0.00539

NOTE 1 When the measured temperature is not at the hydrometer sample reference temperature, the hydrometer reading is corrected for glass expansion/contraction by applying the appropriate hydrometer correction factor found in Table 1.

NOTE 2 When the measured temperature is not the reporting temperature of 20 °C for SI units or 70 °F for USC units, then brine density thermal expansion/contraction factors (conversion factors) are applied to the corrected hydrometer reading.

b) If temperature measurement is given in degrees Celsius, use Equation (12) to find the corrected density in kg/m^3:

$$\rho_{\text{SI-20}} = \rho_{\theta\text{m-SI}} + \left[\left(\theta_{\text{m-SI}} - 20 \right) \times C_{\text{SI}} \right] \tag{12}$$

where

$\rho_{\text{SI-20}}$ is the density at 20 °C, expressed in kilograms per cubic meter;

$\rho_{\theta\text{m-SI}}$ is the hydrometer corrected density reading at measured temperature expressed in kg/m^3;

NOTE $\rho_{\theta\text{m-SI}}$ can be calculated using Equation (4) and a corrected specific gravity hydrometer reading.

$\theta_{\text{m-SI}}$ is the measured temperature, in °C;

C_{SI} is the brine thermal expansion/contraction factor from Table 2 or Equation (4).

c) If the temperature measurement is given in degrees Fahrenheit, use Equation (13) or Equation (14) to find the corrected density in lb/gal. The coefficient of 8.337 is the deaerated distilled water density at 15.56 °C (60 °F) in lb/gal:

$$\rho_{70} = 8.337R + \left[\left(\theta_{\text{m-USC}} - 70 \right) \times C_{\text{USC}} \right] \tag{13}$$

or, using Equation (5) to calculate $\rho_{\theta\text{m-USC}}$:

$$\rho_{70} = \rho_{\theta\text{m-USC}} + \left[\left(\theta_{\text{m-USC}} - 70 \right) \times C_{\text{USC}} \right] \tag{14}$$

where

ρ_{70} is the density at 70 °F, expressed in pounds per gallon;

R is the hydrometer corrected reading for a 60 °F/60 °F hydrometer expressed in specific gravity;

$\rho_{\theta\text{m-USC}}$ is the hydrometer corrected density reading at measured temperature expressed in lb/gal;

$\theta_{\text{m-USC}}$ is the measured temperature, expressed in °F;

C_{USC} is the brine thermal expansion/contraction factor from Table 2 or Equation (10).

6.4.3 The conversion factor for a particular brine can be also calculated by measuring the density of the brine at two or more widely separated temperatures. Measurement can be either done with a density hydrometer or a relative density hydrometer. In both cases, the measured densities should be corrected using the method described in 6.4.1. The conversion factor is then calculated using Equation (15), illustrated for C expressed in g/ml per °C:

$$C = \frac{\rho_1 - \rho_2}{\theta_{\text{2-SI}} - \theta_{\text{1-SI}}} \tag{15}$$

where

C is the brine thermal expansion/contraction factor, expressed in grams per milliliter per °C;

ρ_1 is the density at lower temperature, expressed in grams per milliliter;

ρ_2 is the density at higher temperature, expressed in grams per milliliter;

$\theta_{1\text{-SI}}$ is the lower temperature, expressed in °C;

$\theta_{2\text{-SI}}$ is the higher temperature, expressed in °C.

6.4.4 An additional field method for conversion of brine density utilizes a curve developed to compare the measured brine densities at various temperatures. The curve may then be used for density conversion to 20 °C for SI units or 70 °F for USC units. This curve will be specific for the particular brine being tested and cannot be applied to any other fluid, nor can it be applied to the fluid after its composition has been altered (i.e. dilution, increase in density, etc.).

6.4.5 Regardless of the method selected, care shall be taken to accurately measure the density and the temperature of the brine. Minor variations in either of these measurements lead to errors in the calculation or graphs used for density correction.

These methods shall be used to correct the density measured at surface, and are not intended for use to calculate the required density downhole nor the effective hydrostatic pressure exerted by a column of the fluid.

6.5 Calculation of Density in Units Other Than kg/m^3

6.5.1 Convert the density in kg/m^3 to other common units by the following equations:

$$\rho_{\text{USC}} = \rho_{\text{SI}} \times 0.008345 \tag{16}$$

where

ρ_{USC} is the density in USC units, expressed in pounds per gallon;

ρ_{SI} is the calculated density in SI units, expressed in kilograms per cubic meter;

or

$$\rho_{\text{USC}} = \rho_{\text{SI}} \times 0.06243 \tag{17}$$

where

ρ_{USC} is the density in USC units, expressed in pounds per cubic foot;

ρ_{SI} is the calculated density in SI units, expressed in kilograms per cubic meter;

or

$$\rho = \rho_{\text{SI}} \times 0.001 \tag{18}$$

where

ρ is the density in derived SI units, expressed in grams per milliliter;

ρ_{SI} is the calculated density in SI units, expressed in kilograms per cubic meter.

6.5.2 Calculate the mud gradient from the density:

$$\nabla_{\mathrm{SI}} = \frac{\rho}{0.10197} \tag{19}$$

where

∇_{SI} is the SI mud gradient, expressed in kilopascals per meter;

ρ is the density in derived SI units, expressed in grams per milliliter;

or

$$\nabla_{\mathrm{USC}} = \rho_{\mathrm{USC}} / 19.24 \tag{20}$$

$$\nabla_{\mathrm{USC}} = \rho / 2.3056 \tag{21}$$

where

∇_{USC} is the USC mud gradient, expressed in pounds per square inch per foot (psi/ft), calculated from density expressed in pounds per gallon;

ρ_{USC} is the density in USC units, expressed in pounds per gallon;

ρ is the density in derived SI units, expressed in grams per milliliter;

or

$$\nabla_{\mathrm{cf}} = \rho_{\mathrm{USC}} / 144 \tag{22}$$

where

∇_{cf} is the mud gradient, expressed in pounds per square foot calculated from density expressed in pounds per cubic foot;

ρ_{USC} is the density in USC units, expressed in pounds per cubic foot.

NOTE The results from Equation (18) and Equation (20) are equivalent.

6.6 Calculation for Pressure and Temperature Compensation

6.6.1 Brine fluid density is a function of temperature and pressure. As brine temperature increases, its density decreases. As the pressure on brine increases, its density increases. To determine the actual density of brine in a wellbore, the density must be corrected for its temperature expansion and pressure compression. The total hydrostatic pressure is then calculated with the temperature- and pressure-corrected density at true vertical depth.

NOTE Most completion brine service companies and fluid engineers have sophisticated computer models to calculate the average brine density in the wellbore. These models typically divide the wellbore into 20 or more slices and iterate the changes to the density caused by temperature and pressure at each wellbore interval. The calculations provided in this divide the well into two parts.

Deepwater wells require that these calculations be done for different sections of the well—initially in the riser section where the column density increases (inverse function of temperature gradient) and finally in the subsea section where the column density decreases (mudline to true vertical depth).

Deepwater well calculations should compensate for the warm-to-cool temperature gradient in the riser, then combine that value with the conventional calculation of cool-to-warm temperature gradient in the wellbore.

6.6.2 Calculate the average brine density in the wellbore, in SI units of kg/m^3:

$$\rho_{\text{A-SI}} = \frac{\left\{\left[2000 - \left(0.0098 \times C_{\text{p-SI}} \times h_{\text{TVD-SI}}\right)\right]\rho_{\text{1-SI}}\right\} + \left[10 C_{\theta} \times \left(\theta_{\text{A-SI}} - \theta_{\text{B-SI}}\right)\right]}{\left[2000 - \left(0.01962 \times C_{\text{p-SI}} \times h_{\text{TVD-SI}}\right)\right]} \tag{23}$$

where

$\rho_{\text{A-SI}}$	corrected average brine density in the wellbore, expressed in kilograms per cubic meter;
$C_{\text{p-SI}}$	pressure compensation factor, see Table 4;
$h_{\text{TVD-SI}}$	true vertical depth, expressed in meters;
$\rho_{\text{1-SI}}$	density at the surface, expressed in kilograms per cubic meter;
C_{θ}	temperature compensation factor, see Table 3;
$\theta_{\text{A-SI}}$	is the brine temperature, in °C, measured at the surface or assumed to be 20 °C;
$\theta_{\text{B-SI}}$	is the brine temperature, in °C, measured at bottom hole.

Table 3—Temperature Compensation Factor in SI

Brine Type	Density ρ_{SI} kg/m^3	Vol/Vol/°C × 10^{-4}	Temperature Compensation Factor $C_{\theta\text{-SI}}$ kg/m^3/100 °C
NaCl	1.137	4.57	52.0
$CaCl_2$	1.373	4.30	59.1
NaBr	1.495	4.81	71.9
$CaBr_2$	1.714	4.19	71.9
$ZnBr_2/CaBr_2/CaCl_2$	1.918	4.09	78.4
$ZnBr_2/CaBr_2$	2.309	4.57	105.6

NOTE Expansibility of heavy brine was measured at 82,740 kPa (12,000 psig) from 22.44 °C to 92.22 °C (76 °F to 198 °F) (see Bibliography Reference [16]).

Table 4—Pressure Compensation Factor in SI

Brine Type	Density ρ_{SI} kg/m^3	Vol/Vol/kPa × 10^{-6}	Pressure Compensation Factor $C_{p\text{-}SI}$ (kg/m^3)/MPa
NaCl	1.137	0.287	0.327
$CaCl_2$	1.373	0.218	0.299
NaBr	1.496	0.242	0.362
$CaBr_2$	1.714	0.222	0.380
$ZnBr_2/CaBr_2/CaCl_2$ (less than 2.1 specific gravity)	1.919	0.202	0.387
$ZnBr_2/CaBr_2$ (greater than 2.1 specific gravity)	2.309	0.238	0.549

NOTE Compressibility of heavy brine was measured at 198 °F from 6895 kPa (1000 psig) to 68,950 kPa (10,000 psig) (see Bibliography Reference [16]).

6.6.3 Calculate the average brine density in the wellbore in SI units of kg/m^3:

$$\rho_{A\text{-SI}} = 119.83 \times \rho_{A\text{-USC}} \tag{24}$$

where

$\rho_{A\text{-USC}}$ is the corrected average brine density in the wellbore, expressed in pounds per gallon;

$\rho_{A\text{-SI}}$ is the corrected average brine density in the wellbore, expressed in kilograms per cubic meter.

6.6.4 Calculate the average brine density in the wellbore, in USC units of lb/gal:

$$\rho_{A\text{-USC}} = \frac{\left\{\left[2000-\left(0.052\times C_{p\text{-USC}}\times h_{TVD\text{-USC}}\right)\right]\rho_{1\text{-USC}}\right\}+\left[10C_{\theta}\times\left(\theta_{A\text{-USC}}-\theta_{B\text{-USC}}\right)\right]}{\left[2000-\left(0.104\times C_{p\text{-USC}}\times h_{TVD\text{-USC}}\right)\right]} \tag{25}$$

where

$\rho_{A\text{-USC}}$ is the correct average brine density in the wellbore, expressed in pounds per gallon;

$\rho_{1\text{-USC}}$ is the density at the surface, expressed in pounds per gallon;

$\theta_{A\text{-USC}}$ is the brine temperature, in °F, measured at the surface or assumed to be 70 °F;

$\theta_{B\text{-USC}}$ is the brine temperature, in °F, measured at bottom hole;

C_{θ} is the temperature compensation factor, see Table 5;

$C_{p\text{-USC}}$ is the pressure compensation factor, see Table 6;

$h_{TVD\text{-USC}}$ is the true vertical depth, in feet.

Table 5—Temperature Compensation Factors in USC Units

Brine Type	**Density** ρ_{USC} lb/gal	**Vol/Vol/°F $\times$ 10^{-4}**	**Temperature Compensation Factor** C_θ lb/gal/100 °F
NaCl	9.49	2.54	0.24
$CaCl_2$	11.46	2.39	0.27
NaBr	12.48	2.67	0.33
$CaBr_2$	14.30	2.33	0.33
$ZnBr_2/CaBr_2/CaCl_2$	16.01	2.27	0.36
$ZnBr_2/CaBr_2$	19.27	2.54	0.48

NOTE Expansibility of heavy brine was measured at 82,737 kPa (12,000 psig) from 22.44 °C to 92.22 °C (76 °F to 198 °F) (see Bibliography Reference [16]).

Table 6—Pressure Compensation Factors in USC Units

Brine Type	**Density** ρ_{USC} lb/gal	**Vol/Vol/psi-$\times$ 10^{-6}**	**Pressure Compensation Factor** C_p (lb/gal)/kpsi [a]
NaCl	9.49	1.98	0.019
$CaCl_2$	11.46	1.50	0.017
NaBr	12.48	1.67	0.021
$CaBr_2$	14.30	1.53	0.022
$ZnBr_2/CaBr_2/CaCl_2$ (less than 2.1 specific gravity)	16.01	1.39	0.022
$ZnBr_2/CaBr_2$ (greater than 2.1 specific gravity)	19.27	1.64	0.031

NOTE Compressibility of heavy brine was measured at 198 °F from 6894.8 kPa (1000 psig) to 68,948 kPa (10,000 psig) (see Bibliography Reference [16]).

[a] 1 kpsi = 1000 psi

6.6.5 Calculate the average hydrostatic pressure in the wellbore in SI units of kilopascal using the temperature and pressure corrected average brine density:

$$P_{\text{h-SI}} = 6.8948 \times P_{\text{h-USC}} \tag{26}$$

where

$P_{\text{h-SI}}$ is the hydrostatic pressure, expressed in kilopascal;

$P_{\text{h-USC}}$ is the hydrostatic pressure, expressed in pounds per square inch.

6.6.6 Calculate the average hydrostatic pressure in the wellbore in SI units of kilopascal using the temperature and pressure corrected average brine density:

$$P_{\text{h-SI}} = 0.009807 \times \rho_{\text{A-SI}} \times h_{\text{TVD-SI}} \tag{27}$$

where

$P_{\text{h-SI}}$ is the hydrostatic pressure, expressed in kilopascals;

$\rho_{\text{A-SI}}$ is the density, expressed in kilograms per cubic meter;

$h_{\text{TVD-SI}}$ is the true vertical depth, expressed in meters.

6.6.7 Calculate the average hydrostatic pressure in the wellbore in USC units of lb/in.^{2} using the temperature and pressure corrected average brine density:

$$P_{\text{h-USC}} = 0.052 \times \rho_{\text{A-USC}} \times h_{\text{TVD-USC}} \tag{28}$$

where

$P_{\text{h-USC}}$ is the hydrostatic pressure, expressed in pounds per square inch;

$\rho_{\text{A-USC}}$ is the corrected average brine density in the wellbore, expressed in pounds per gallon;

$h_{\text{TVD-USC}}$ is the true vertical depth, expressed in feet.

7 Crystallization Temperature

7.1 Principle

7.1.1 This clause describes a method for the measurement of crystallization temperatures of brines used in completion, workover, fracturing, and drilling operations.

7.1.2 Three different crystallization temperatures are often quoted for the same brine because of the nature of the brine cooling curve. The following defines the three crystallization temperatures, discusses the practical significance of each crystallization temperature, and explains the difference between crystallization of salt crystals from a brine and the freezing of water from a brine.

7.1.3 The actual crystallization temperature of brine is that temperature at which a solid will begin to form from the solution if given sufficient time and proper nucleating conditions. The solid can be either salt or fresh water (ice).

7.1.4 The crystallization temperature for normally formulated brine is the temperature at which the brine is saturated with one or more components that it contains. At this temperature, the solubility of the least soluble component is exceeded and it crystallizes as the salt or salt hydrate, or ice. Cooling the brine below the crystallization temperature results in formation of additional salt crystals or ice. Brine having a crystallization temperature below the lowest anticipated operating temperature is recommended, in order to prevent crystallization of the brine during use.

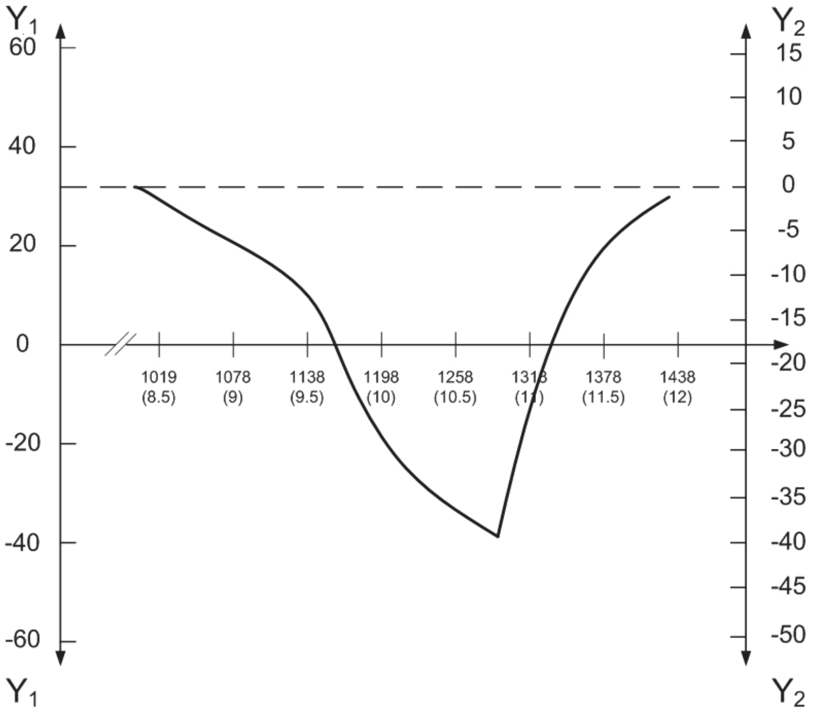
7.1.5 Precipitation of salt crystals or ice in brine at or below the crystallization temperature can lead to a number of problems. Rapid plugging of filtration units can occur. If salt crystals settle in the tank, the density of the brine pumped downhole can be insufficient to control formation pressures, or if ice crystallizes, the brine density sent downhole might exceed fracture gradient. As additional crystals form, brine viscosity can increase. The viscosity can become so high that the brine appears to be a frozen solid. This can cause line plugging, fluid in tanks becoming solid, and pump seizures. Sufficient heating and agitation of the brine redissolves the crystals with no permanent change in the brine properties.

7.1.6 Since salt crystals should have a smaller specific volume than the brine, the brine will not expand in volume during crystallization and should not cause ruptured lines, valves, or pump heads, which can occur when water freezes. However, solutions from which ice crystallizes, especially those containing low concentrations of salt, will expand and can lead to equipment failure.

7.1.7 The crystallization temperature of a multi-salt brine at a given density can be varied by adjusting the concentrations and composition of the salts in the brine. Consequently, a brine of a given density can be formulated with numerous crystallization temperatures. Generally, multi-salt brines with lower crystallization temperatures will be more costly. A lower-cost brine with an excessively high crystallization temperature can lead to problems caused by crystallization of the fluid in the pumps, lines, filtration units, and tanks.

7.1.8 With dilute brine (e.g. seawater), the salt in the water depresses the crystallization temperature or the freezing point of the brine. The salts reduce the temperature at which fresh-water ice will form.

7.1.9 Figure 4 and Table 7 show the crystallization temperature of calcium chloride solution as a function of concentration. Table 8 shows the concentration of sodium chloride solution as a function of concentration. The tables and figure show the true crystallization temperature, TCT, and is given as an example.



Key

X density, kg/m^3 (lb/gal)

Y_1 temperature, °F

Y_2 temperature, °C

Figure 4—Calcium Chloride Crystallization Temperature

Table 7—Calcium Chloride Solutions—Crystallization Temperature [23]

Density (60 °F; 15.56 °C) lb/gal	**Specific Gravity** (60 °F; 15.56 °C)	**$CaCl_2$** %	**Calcium Ion** [a] mg/l	**Chloride Ion** [a] mg/l	**Crystallization Temperature** [b]	
					°F	°C
8.4	1.008	1.0	3636	6434	31	−0.6
8.5	1.020	2.0	7359	13,020	30	−1.1
8.6	1.032	3.4	12,658	22,395	28	−2.2
8.7	1.044	5.1	19,208	33,983	26	−3.3
8.8	1.056	6.0	22,857	40,439	25	−3.9
8.9	1.068	7.6	29,282	51,805	23	−5.0
9.0	1.080	9.3	36,234	64,105	21	−6.1
9.1	1.092	10.8	42,546	75,272	19	−7.2
9.2	1.104	12.2	48,589	85,964	17	−8.3
9.3	1.116	13.6	54,754	96,870	15	−9.4
9.4	1.128	15.0	61,040	107,991	12	−11.1
9.5	1.140	16.3	67,035	118,599	9	−12.8
9.6	1.152	17.6	73,144	129,406	6	−14.4
9.7	1.164	18.9	79,364	140,412	3	−16.1
9.8	1.176	20.2	85,698	151,617	0	−17.8
9.9	1.188	21.4	91,715	162,263	−4	−20.0
10.0	1.200	22.6	97,836	173,092	−8	−22.2
10.1	1.212	23.8	104,062	184,106	−13	−25.0
10.2	1.224	25.0	110,391	195,303	−18	−27.8
10.3	1.236	26.1	116,378	205,896	−23	−30.6
10.4	1.248	27.2	122,460	216,656	−29	−33.9
10.5	1.261	28.3	128,740	227,766	−36	−37.8
10.6	1.273	29.4	135,017	238,871	−43	−41.7
10.7	1.285	30.5	141,389	250,145	−51	−46.1
10.8	1.297	31.5	147,388	260,759	−59	−50.6
10.9	1.309	32.5	153,474	271,526	−40	−40.0
11.0	1.321	33.5	159,646	282,446	−22	−30.0
11.1	1.333	34.5	165,905	293,520	−11	−23.9
11.2	1.345	35.5	172,251	304,747	0	−17.8
11.3	1.357	36.7	179,662	317,859	13	−10.6
11.4	1.369	37.6	185,696	328,533	27	−2.8
11.5	1.381	38.5	191,807	339,346	35	1.7
11.6	1.393	39.6	199,002	352,074	44	6.7

[a] Composition of the brine is calculated based on a pure calcium chloride solution without the presence of other salts such as sodium chloride.

[b] Crystallization points are given as an approximation. The true crystallization point can vary greatly with contaminants or impurities in the brine.

The crystallization temperature of the brine decreases to as low as –46.0 °C (–50.8 °F) at a mass fraction of 30 % $CaCl_2$ or 1280 kg/m^3 (1.28 specific gravity, 10.7 lb/gal). For densities less than 1280 kg/m^3 (10.7 lb/gal), temperatures just below the crystallization temperature result in the crystallization of fresh-water ice, producing brine with a higher salt concentration and lower crystallization temperature.

Brines with calcium chloride mass fractions above 30 % (above 1280 kg/m^3, 10.7 lb/gal) exhibit an increase in the crystallization temperature. This portion of the curve represents the solubility limit of calcium chloride in water. The crystallization temperature increases with increasing calcium chloride concentration. Therefore, as calcium chloride precipitates out of solution upon cooling, the resulting brine will have a reduced salt concentration and density, and also have a lower crystallization temperature.

A similar table for sodium chloride (NaCl) is presented in Table 8.

Table 8—Sodium Chloride Solutions—Crystallization Temperature [23]

Density (60 °F; 15.56 °C) lb/gal	**Specific Gravity** (60 °F; 15.56 °C)	**NaCl** %	**Sodium Ion [a]** mg/l	**Chloride Ion [a]** mg/l	**Crystallization Temperature [b]** °F	°C
8.4	1.008	1.04	4120	6353	31	-0.6
8.5	1.020	2.66	10,663	16,442	29	−1.7
8.6	1.032	4.44	18,007	27,768	27	−2.8
8.7	1.044	6.01	24,658	38,024	26	−3.3
8.8	1.056	7.53	31,249	48,188	24	−4.4
8.9	1.068	9.22	38,698	59,673	22	−5.6
9.0	1.080	10.74	45,584	70,292	19	−7.2
9.1	1.092	12.36	53,043	81,794	17	−8.3
9.2	1.104	13.91	60,350	93,063	14	−10.0
9.3	1.116	15.54	68,155	105,098	11	−11.7
9.4	1.128	17.05	75,582	116,550	9	−12.8
9.5	1.140	18.51	82,927	127,876	6	−14.4
9.6	1.152	19.96	90,364	139,345	3	−16.1
9.7	1.164	21.53	98,487	151,871	−1	−18.3
9.8	1.176	22.99	106,250	163,871	3	−16.1
9.9	1.188	24.36	113,731	175,377	5	−15.0
10.0	1.200	25.69	121,151	186,820	25	−3.9

[a] Composition of the brine is calculated based on a pure sodium chloride solution without the presence of other salts such as potassium or calcium chloride.

[b] Crystallization points are given as an approximation. The true crystallization point can vary greatly with contaminants or impurities in the brine.

7.1.10 The crystallization profile of a brine is characterized by the following four temperature parameters.

a) First crystal to appear (FCTA)—the temperature corresponding to a minimum inflection point in a plot of temperature during cooling, or the temperature at which visible crystals start to form. FCTA will generally include some super-cooling effect (cooling below the actual crystallization temperature without crystals being observed).

b) True crystallization temperature (TCT)—the temperature corresponding to the maximum temperature reached following the super-cooling minimum. In a plot of temperature during cooling cycle, TCT is the maximum temperature reached following the super-cooling minimum, or the inflection point in cases with no super-cooling. If there is no super-cooling, TCT will equal FCTA. TCT is the measured crystallization temperature nearest the temperature at which a brine will naturally crystallize in pumps, lines, filtration units, and tanks.

c) Last crystal to dissolve (LCTD)—the temperature corresponding to the temperature plot, at which crystals disappear, or the inflection point during the heating curve. LCTD is the measured crystallization temperature nearest the temperature at which crystals that have formed will re-dissolve.

d) Maximum temperature after last crystal (MTALC)—the maximum temperature at which the second and subsequent cooling cycles begin. The MTALC should not be more than 1.1 °C (2.0 °F) above the LCTD.

7.1.11 Experimental methods for measuring the crystallization temperatures of brine involve alternately cooling and heating the brine. Figure 5 is a representative cooling/heating curve for brine with the four points identified. The accuracy of the testing method depends on several factors. Most important is controlling super-cooling. Super-cooling can be minimized by slow cooling rates and nucleation of crystals with selected solid surfaces.

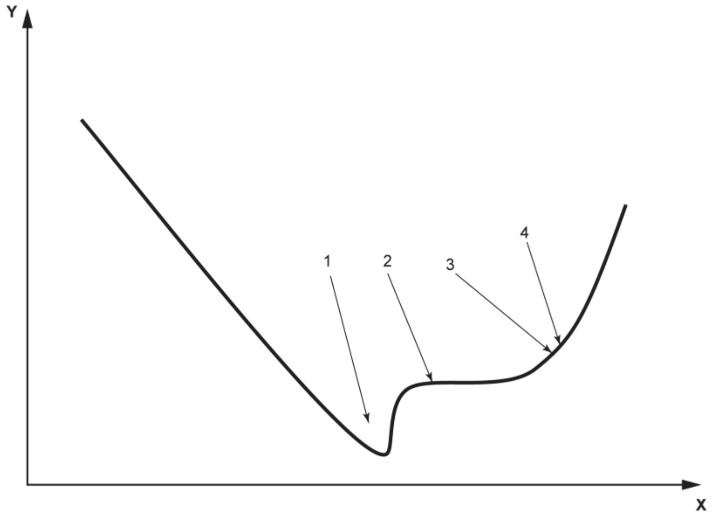
7.1.12 When a brine is cooled below its actual crystallization temperature, crystals may not form spontaneously due to lack of nucleation sites and other kinetic factors. This is the super-cooling effect. The use of selected solid surfaces can initiate the nucleation of crystals. Barium oxide, barium hydroxide, calcium carbonate, and bentonite have been found to be effective nucleates for brines. Only trace amounts are required to reduce the magnitude of super-cooling.

7.1.13 As crystals begin to form at the FCTA, the heat released by the crystallization process increases the temperature of the brine. The maximum temperature following super-cooling is the actual TCT of the brine. If significant super-cooling occurs [i.e. TCT exceeds FCTA by 3 °C (5 °F) or more], the measurements should be repeated at a slower cooling rate. Investigators have found that samples that super-cool on the first cycle often super-cool only slightly or not at all on subsequent cycles. Minimizing the super cooling effect will increase the accuracy of the measured TCT.

7.1.14 The heat of dissolution is responsible for the inflection point at LCTD that can be observed as a crystallized solution is warmed. As the brine is heated, crystals absorb thermal energy when dissolving, thus slowing the heating rate of the solution. When all the crystals have re-dissolved at LCTD, the brine will warm more rapidly. The work group studying the measurement of brine pressure crystallization (PCT) has determined that the most accurate crystallization measurements were obtained when the maximum temperature after the LCTD was not more than 1.0 °C (2.0 °F) above the LCTD.

NOTE 1 The heat of dissolution for NaCl is positive so no inflection point is found.

NOTE 2 The maximum temperature after last crystal can also be noted as MTALC.



Key

X time

Y temperature

1 first crystal to appear (FCTA)

2 true crystallization temperature (TCT)

3 last crystal to dissolve (LCTD)

4 maximum temperature after last crystal (MTALC)

Figure 5—Typical Crystallization Curve for Brine

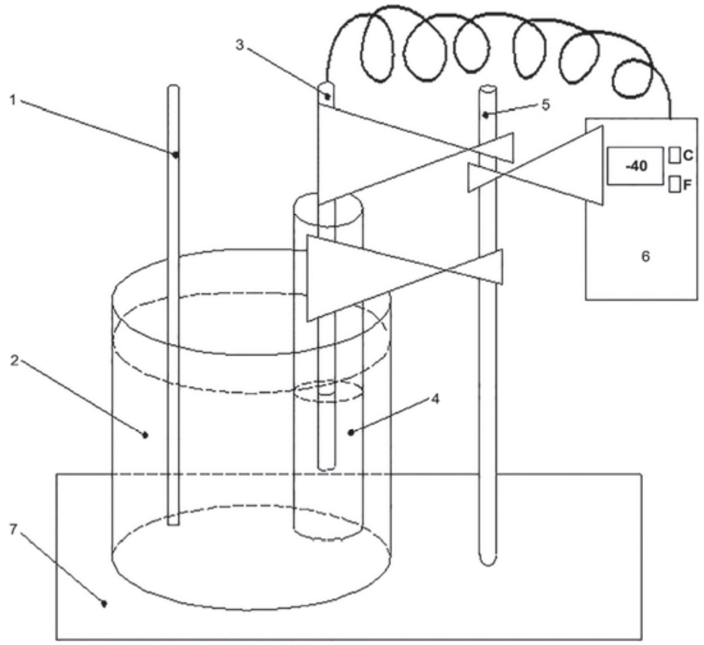
7.1.15 When measuring the crystallization temperature of brine, one should be aware that minor components can precipitate from solution before the TCT. For example, both sodium chloride and potassium chloride are less soluble than calcium chloride, calcium bromide, or zinc bromide. If brine is contaminated with sodium chloride, the small amount of sodium chloride can crystallize and turn the brine cloudy at a temperature much higher than the TCT. Reformulation of the brine to reduce the faulty TCT could prove costly.

7.1.16 In summary, the best measure of the crystallization temperature of a brine is the TCT. This measured crystallization temperature best represents the temperature at which crystals will precipitate from a brine. FCTA and LCTD may also be specified. FCTA is generally lower than TCT, and LCTD is generally higher than TCT. The difference between FCTA and TCT represents the degree of super-cooling, and if this difference exceeds 3 °C (5 °F), repeat the measurements at a slower cooling rate.

7.2 Apparatus

7.2.1 Digital temperature-measuring device with thermistor or RTD probe, having an indicating range of –45 °C to 40 °C (–50 °F to 100 °F) with a resolution of 0.05 °C (0.1 °F).

A typical crystallization temperature-measuring system is shown in Figure 6.



Key

1	thermometer
2	heating and cooling bath
3	RTD probe/thermistor
4	sample
5	laboratory stand
6	digital thermometer
7	laboratory base

Figure 6—Typical Crystallization Temperature Measurement Setup

7.2.2 Container, minimum capacity 25 ml.

A suitable container for the brine is a 2.0 cm × 15.0 cm (0.75 in. × 6.0 in.) test tube that will fit inside a 2.5 cm × 15.0 cm tube (1.0 in. × 6.0 in.). The outer container is used to slow the cooling rate of the brine sample.

7.2.3 Cooling Bath

The cooling bath should be no more than 10 °C (20 °F) below the FCTA temperature. Ideally, the cooling rate should be less than 0.5 °C (1 °F) per minute. This can be achieved through the use of an electronic cooling system or through the use of one or more of the following.

a) Ice/water slurry (1:1 volume ratio ice to water). The temperature of the bath will be 0 °C (32 °F). Use if FCTA temperature is in the range of 2 °C to 5 °C (35 °F to 40 °F).

b) Ice/saltwater slurry [1:1 volume ratio ice to saltwater; NaCl solution should contain 30 g NaCl (CAS No. 7647-14-5) in 90 g water]. The temperature of the bath will be –15 °C to –12 °C (5 °F to 10 °F). Use if the FCTA temperature is approximately –12 °C to 4 °C (10 °F to 40 °F).

c) Ice/$CaCl_2$ slurry [1:1 volume ratio crushed ice to $CaCl_2$ solution; $CaCl_2$ solution should contain 50 g $CaCl_2$ (CAS No. 10043-52-4) in 50 g water]. The temperature of the bath will approach –40 °C (–40 °F) as the ice melts.

d) Refrigerated cool plate or cool bath device. The temperature of the bath should be 10 °C (20 °F) less than the FCTA point.

When using an electronic cooling system, follow the manufacturer's recommended test procedure.

7.2.4 Seeding material, 0.1 % mass fraction of an inert, insoluble nucleating agent or less, or crystals that are precipitated in situ from the brine.

See 7.1.12. Use approximately 0.03 g seeding material, equivalent to a few grains of salt, for 25 ml of brine.

7.2.5 Organic seeding, organic seeding materials include 3 µm to 5 µm $CaCO_3$ (ground marble), carbon black and crystals that are precipitated in situ from brine containing organic salts.

7.3 Determination of Crystallization Point

7.3.1 Measure approximately 25 ml of the brine to be tested into the sample container. Add the nucleating agent to the sample. Place the sample container inside the outer container and place both in the cooling bath with the temperature-measuring device probe inserted in the brine.

7.3.2 Cool the sample slowly to minimize super-cooling. Stir the brine and observe the temperature of the sample as it decreases. The temperature of the brine will decrease steadily until crystals begin to form. Record the minimum temperature reached when the first crystal is observed as the FCTA temperature.

7.3.3 Record the maximum temperature achieved immediately after crystallization has occurred, as the TCT. The temperature should stabilize briefly (10 s to 20 s). If the temperature does not stabilize, or if a large amount of super-cooling is evident [TCT minus FCTA is greater than 3 °C (5 °F)], repeat the test on the same sample. For the repeat test, the sample should be warmed above the LCTD point, but the maximum temperature after the last crystal to dissolve (MTALC) shall be no more than 1.0 °C (2.0 °F) higher than the LCTD point.

7.3.4 Discontinue cooling the sample by removing the sample container from the bath or increasing the temperature setting of the cooling plate or bath. Allow the sample to warm at the rate of 0.5 °C (1.0 °F) per minute, while observing for the dissolution of crystals. When all crystals have dissolved, record the temperature as the LCTD.

7.3.5 Repeat 7.3.2 through 7.3.4 at least three times using the same sample. The sample should be warmed above the LCTD but no more than 1.0 °C (2.0 °F) higher than the LCTD point.

7.4 Calculation of Crystallization Point

Calculate average readings of the three or more tests from 7.3.5. Do not include any data in which super-cooling exceeds 3 °C (5 °F) below the TCT point. Report the temperatures for FCTA, TCT, LCTD, and MTALC.

8 Brine Clarity

8.1 Principle

8.1.1 Solids contamination in a brine fluid can greatly affect the productivity of a well. Accumulation of insoluble particles can cause significant formation damage. Quantifying total suspended solids in brine is critical.

8.1.2 Clarity is a relative expression referring to the turbidity of brine due to the presence of suspended insoluble or immiscible matter.

8.1.3 The method described here for measurement of brine clarity relies upon the nephelometric (light scatter and absorption) measurement of a liquid in a cuvette (sample container) of fixed volume and dimensions.

8.1.4 The method gives a nephelometric turbidity unit (NTU) as compared with that of a standard sample of known NTU value. Definition of minimum and/or maximum limits of NTU values is left to the supplier and user.

NOTE No conclusions on the effect of the particle size or concentration of the solids on formation damage are intended or implied from any detail of this procedure.

8.1.5 Measurements of solids content in brine, under field conditions with traditional tools such as particle counters and gravimetric analysis, are difficult and not reliable. The volume and size of particles in suspension are frequently very small, and visual inspection of the fluid does not provide a reliable method of determining suitability.

8.1.6 NTU measurement of solids content provides a relative value that can be used to determine suitability of the brine for use. NTU values do not reflect a specific milligrams per liter (or parts per million) solids level in suspension. Variables such as total particle count, particle size, particle type, and trace amounts of other chemicals in the brine affect the NTU value of a particular sample; 1 mg/l can represent as little as one (1) particle or many millions of finely divided particles. In general, the higher the total number of particles in suspension, the higher the NTU value. Nephelometric measurement does not indicate the size or milligrams per liter of solids in suspension.

8.1.7 The user should be aware of the effects that damaged filtration equipment, high loads of very finely divided solids (particles smaller than the size-cut of the filter system), and chemical additives can have on the NTU values obtained. Careful monitoring of equipment and fluid properties is an essential part of NTU value interpretation.

8.2 Apparatus

8.2.1 **NTU meter**, available from a number of manufacturers.

Follow the manufacturer's recommendations for use and maintenance.

8.2.2 **Standard NTU reference cuvettes.**

8.2.3 **Sample cuvettes.**

Sample cuvettes should be maintained in a clean and dry state. Residue or films that cannot be removed or scratches on the cuvette walls will cause artificially higher NTU readings. Damaged cuvettes should be discarded in appropriate waste receptacles, in accordance with local, state, and federal regulations.

8.2.4 **Mild cleaning solution.**

8.2.5 Distilled or deionized water.

8.2.6 Lint free cleaning cloth.

8.2.7 Container, clean, dry and of sufficient volume to collect a representative sample of the brine.

8.3 Determination of Brine Clarity

8.3.1 Collect a sample of brine to be measured in the container.

8.3.2 Fill a sample cuvette to the appropriate level.

The sample liquid should be free of entrained gases or gas bubbles on the cuvette walls. If deaeration is needed, it may be necessary to invert the sealed cuvette several times before measurement **to ensure uniform dispersion of suspended solids.**

8.3.3 Clean the exterior of the sample cuvette with mild cleaning solution, then rinse with distilled or deionized water. Dry with a lint-free cloth.

8.3.4 Switch on the NTU meter**.**

8.3.5 Insert an appropriate standard cuvette, and adjust the readout to the standard cuvette value.

8.3.6 Insert the sample cuvette and allow meter reading to stabilize**.**

8.3.7 Record the reading for the sample cuvette, and report in NTU units.

9 Solids Evaluation by Gravimetric Procedure

9.1 Principle

9.1.1 Heavy brine is composed of salt dissolved in water but can contain impurities. These impurities are either inorganic or organic and could include contamination products, formation solids, field organic material, and salt precipitates. The categorization of mixture components shall be accomplished by a series of procedures including filtration, drying, and ignition testing.

9.1.2 The brine salt is soluble and nonvolatile, and it passes through a filtration medium.

9.1.3 At room temperature, all impurities can be identified as soluble (behaving like the brine) or suspended (solids in suspension). The differentiation is carried out by filtration and drying of the filtration residue, and noted as total suspended solids.

9.1.4 Impurities can also be volatile or nonvolatile, and they would indicate organic and inorganic species. This differentiation is accomplished by measuring loss on ignition, which can be done on the total sample, the soluble portion, or the filtered residue from drying. Brines are reported as total volatile solids and total nonvolatile solids following ignition.

9.1.5 All nonrepresentative particulates, such as leaves, sticks, or paper, shall be excluded from the brine prior to testing.

9.1.6 Samples with a high level of filterable residue (dissolved solids), such as brines and saline water, can be subject to a positive interference. Care shall be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids minimizes this potential interference.

9.1.7 Samples with high concentrations of calcium, magnesium, chloride, and/or bromide can be hygroscopic and require prolonged procedure times.

9.1.8 Samples with entrained gas must be deaerated or discarded.

9.1.9 Preservation of brine samples is not practical. Analyses should begin as soon as possible. Refrigeration or icing to 4 °C (40 °F) minimizes microbiological decomposition of solids.

9.2 Apparatus

9.2.1 **Muffle furnace**, regulated to 550 °C (1000 °F).

9.2.2 **Oven**, regulated to 105 °C ± 1 °C (220 °F ± 2 °F).

9.2.3 **Glass-fiber filters** without organic binder, 4.8 cm ($1\ {}^{7}/_{8}$ in.) in diameter, available from several suppliers.

NOTE Because of the physical nature of glass-fiber filters, their absolute pore size cannot be controlled or measured. Terms such as "pore size," collection efficiencies, and effective retention are used to define glass-fiber filters. Values for these parameters vary depending on the filter manufacture.

9.2.4 **Membrane filter support**, such as a glass or ceramic fritted disk available from several suppliers with coarse (40 µm to 60 µm) openings.

9.2.5 **Vacuum filtration device**, including funnel with suction flask and reservoir of capacity 1 l (1 qt).

9.2.6 **Graduated cylinder** [to deliver (TD)], 100 ml.

9.2.7 **Balance**, readability of 0.1 mg and repeatability of 0.1 mg.

9.2.8 **Forceps** or **tongs**, with handle of sufficient length to remove samples from oven or furnace.

9.2.9 **Desiccator**, with absorbent drier such as anhydrous calcium chloride (CAS No. 10043-52-4), calcium sulfate (CAS No. 10101-41-4), or silica gel (CAS No. 112926-00-8).

9.2.10 **Distilled water or deionized water**

9.2.11 **Pipette**, 20 ml, with large open tip.

9.2.12 **Aluminum weighing pans**.

9.2.13 **Porcelain evaporating dishes**.

9.2.14 **Hydrochloric acid, 0.1 mol/l solution (0.1N) (CAS No. 7647-01-0).**

9.3 Preparation of Glass-fiber Filter Disk

9.3.1 Place the glass-fiber filter on the membrane filter apparatus or insert into the bottom of a suitable Gooch crucible with wrinkled surface up.

9.3.2 Apply a vacuum to the filtration device, and wash the disk three times using 20 ml distilled or deionized water for each wash.

9.3.3 Continue to apply vacuum until all traces of water have been removed.

9.3.4 Remove the filter from the membrane filter apparatus or remove both crucible and filter.

9.3.5 Dry in the oven for 1 h.

9.3.6 Remove to the desiccator and cool to room temperature. Store filter disk in desiccator until needed.

9.4 Selection of Sample Volume

9.4.1 Assemble the filtration device and place a pre-weighed filter paper disk on the fritted surface with the rough side up.

9.4.2 Wet the paper with a small amount of distilled or deionized water to seat it against the fritted support.

9.4.3 Using vacuum, filter 100 ml of brine through the filter paper. Wash the graduated cylinder, filter, nonfilterable residue, and filter funnel wall with three portions of distilled or deionized water. Allow complete drainage between washings.

9.4.4 Remove the filter paper, dry, and reweigh.

9.4.5 The mass of residue remaining shall be no less than 1.0 mg. If the mass of residue remaining is less than 1.0 mg, increase the sample volume to provide at least 1.0 mg of residue.

If filters of other than 4.8 cm (1 $^7/_8$ in.) diameter are used, start with a sample volume equal to 7 ml per square centimeter of filter area. Collect at least a mass of residue proportional to the 1.0 mg stated.

9.4.6 If during filtration of this initial volume the filtration rate drops rapidly, or if filtration time exceeds 10 min, the following scheme is recommended.

a) Use an un-weighed glass-fiber filter of choice affixed in the filter assembly.

b) Add a known volume of sample to the filter funnel and record the time elapsed after selected volumes have passed through the filter. These increments are suggested to be twenty 5-ml aliquots with each aliquot timed for filtration rate.

c) Continue to record the time and volume increments until filtration rate drops rapidly.

d) Add additional sample if the filter funnel volume is inadequate to reach a reduced rate.

e) Plot the observed time versus volume filtered.

f) From the plot, select the proper filtration volume as that just before the time a significant change in filtration rate occurred.

9.5 Determination of Total Suspended Solids

9.5.1 Repeat the drying cycle on a prepared glass-fiber filter disk, or Gooch crucible with disk, until constant mass is obtained, i.e. until the mass difference is less than 0.5 mg on successive measurements.

9.5.2 Weigh the filter or crucible/filter immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only.

9.5.3 Mark three aluminum pans with individual identifying numbers or letters. Weigh the pans with the filter paper or crucible/filter paper and record the mass to 0.1 mg.

9.5.4 Assemble the filter apparatus and place the filter on the frit. Wet the filter paper with a small volume of distilled or deionized water to seat it against the fritted support.

9.5.5 Shake the sample vigorously and quantitatively transfer the predetermined sample volume (see 9.4) using a wide-mouth pipette.

9.5.6 Using vacuum, filter the volume of fluid in the graduated cylinder through the prepared glass-fiber filter, and then wash the graduated cylinder, filter, residue, and filter funnel wall with three portions of distilled or deionized water, allowing complete drainage between washings. Remove all traces of water by continuing to apply vacuum to the glass fiber filter.

NOTE 1 Total volume of wash-water used should equal approximately 30 ml for a 4.8 cm (1 $^7/_8$ in.) filter.

NOTE 2 For zinc containing brines only, adjust the pH (measured with an appropriate pH meter) of the distilled or deionized water to between 4 to 5 with HCl 0.1N solution to prevent precipitation of zinc during washing.

9.5.7 Carefully remove the filter disk from the filter support and place in a pre-weighed aluminum pan. Repeat 9.5.5 through 9.5.6 two additional times.

9.5.8 Dry aluminum pans with filters or crucible/filter for a minimum of 1 h at 105 °C (220 °F).

9.5.9 Remove the pans to a desiccator and cool. Reweigh and repeat the drying cycle until a constant mass is obtained, i.e. until the mass difference is less than 0.5 mg on successive measurements.

9.5.10 Record the mass of pan with filter paper for each sample.

9.6 Calculation of Total Suspended Solids

Calculate the total suspended solids using Equation (29):

$$m_3 = \frac{m_2 - m_1}{V_1} \times 1000 \tag{29}$$

where

m_1 is the original mass of pan and filter paper, expressed in milligrams;

m_2 is the final mass of pan, filter paper, and residue, expressed in milligrams;

V_1 is the volume of the original sample, expressed in milliliters;

m_3 is the total suspended solids, expressed in milligrams per liter.

NOTE Total suspended solids are also known as filterable residue.

9.7 Calculation of Precision and Bias

In studies by 2 analysts of 4 sets of 10 determinations each, the standard deviation was 5.2 mg/l (coefficient of variation 33 %) at 15 mg/l, 24 mg/l (10 %) at 242 mg/l, and 13 mg/l (0.76 %) at 1.707 mg/l.

Single laboratory duplicate analyses of fifty samples of water and wastewater were made with a standard deviation of differences of 2.8 mg/l.

Bias data on actual samples cannot be obtained.

9.8 Determination of Volatile and Nonvolatile Solids

9.8.1 Mark each porcelain evaporating dish with an individual identifying number. Clean the evaporating dishes by heating in the muffle furnace for 1 h at 550 °C (1000 °F), then cooling in a desiccator. Store in desiccator until ready for use.

9.8.2 Remove from desiccator and weigh. Record mass.

9.8.3 Follow procedure in 9.5 but substitute the porcelain evaporating dish for the aluminum pan, including drying for 1 h at 105 °C (220 °F). Cool in a desiccator.

9.8.4 Reweigh following the drying procedure, and record the mass of dish with fiber filter.

9.8.5 Place the porcelain evaporating dishes in a muffle furnace for 1 h at 550 °C (1000 °F). Remove and cool in desiccator.

9.8.6 Reweigh the porcelain evaporating dishes and record the masses.

9.9 Calculation of Nonvolatile and Volatile Solids

Use Equation (30) and Equation (31) to calculate the total nonvolatile and volatile solids, respectively:

$$m_7 = \frac{m_6 - m_4}{V_1} \times 1000 \tag{30}$$

$$m_8 = \frac{m_5 - m_6}{V_1} \times 1000 \tag{31}$$

where

m_4 is the mass of the porcelain evaporating dish and filter medium, expressed in milligrams;

m_5 is the mass of the porcelain evaporating dish and filtered sample after drying at 105 °C (220 °F), expressed in milligrams;

m_6 is the mass of the porcelain evaporating dish and filtered sample after auto-ignition at 550 °C (1000 °F), expressed in milligrams;

V_1 is the volume of the original sample, expressed in milliliters;

m_7 is the total nonvolatile solids or residue, expressed in milligrams per liter;

m_8 is the total volatile solids, expressed in milligrams per liter.

10 pH

10.1 Principle

10.1.1 Field measurement of brine fluid pH and adjustments to the pH are fundamental to fluid control. Solubility of various components and contaminants and effectiveness of additives can be dependent on pH, as is the control of acidic and sulfide corrosion processes.

10.1.2 pH is a thermodynamic value equal to the negative logarithm of the hydrogen ion activity, $[H^+]$, in aqueous solutions:

$$pH = -\log [H^+]$$

10.1.3 For pure water at 24 °C (75 °F), the hydrogen ion activity is 10^{-7} mol/l and pH = 7. This system is neutral because the hydroxyl ion activity $[OH^-]$ is also 10^{-7} mol/l. In aqueous systems at 24 °C (75 °F), the ion product, $[H^+] \times [OH^-]$, is 10^{-14} (a constant). Consequently, an increase in $[H^+]$ corresponds with a like decrease in $[OH^-]$. A change in pH of one unit indicates a 10-fold change in both $[H^+]$ and $[OH^-]$. Solutions with pH less than 7 are termed acidic, and those with pH greater than 7 are termed basic or alkaline.

10.1.4 Activity and concentration are equal only in very dilute solutions. Oilfield brines are not dilute solutions but are comprised of highly concentrated salts in solution. Consequently, the measured pH value should be used in a relative sense, and the changes in pH are more useful than absolute values.

10.1.5 Equipment recommended for pH measurement of brine fluid is a glass-electrode pH meter. This method is accurate and gives reliable pH values, being free of interferences if a high-quality electrode system is used with a properly designed instrument. Rugged pH instruments are available that automatically compensate the slope for temperature, and they are preferred over the manually adjusted instruments.

NOTE Color-matching pH paper and sticks are not recommended.

10.2 Reagents and Materials

10.2.1 Buffer solutions, to calibrate and set the slope of the pH meter prior to sample measurement.

Three solutions of pH = 4.0, pH = 7.0, and pH = 10.0 are standard pH buffer fluids. It is recommended that buffers be pre-made solutions or a dry powder package obtained from chemical supply houses. These buffer solutions shall meet the requirements of NIST SRM 185h, NIST SRM 186g, and NIST SRM 191C, as appropriate (see Section 2). The shelf life shall not exceed the manufacturer's recommendation or six months after opening. Bottles shall be kept tightly sealed.

NOTE If NIST standards are not available (i.e. international work), use an equivalent national/international standard, as appropriate.

If buffers must be prepared from composite chemicals, the following solution compositions are provided for informational purposes.

a) **Buffer solution pH = 4.0**—Potassium hydrogen phthalate (CAS No. 877-24-7) at 0.05 mol/l in water gives a 4.0 pH at 24 °C (75 °F).

b) **Buffer solution pH = 7.0**—Potassium di-hydrogen phosphate (CAS No. 7778-77-0) at 0.020 66 mol/l and disodium hydrogen phosphate (CAS No. 7558-79-4) at 0.029 34 mol/l in water gives a 7.0 pH at 24 °C (75 °F).

c) **Buffer solution pH = 10.0**—Sodium carbonate (CAS No. 497-19-8) at 0.025 mol/l and sodium bicarbonate (CAS No. 144-55-8) at 0.025 mol/l in water gives a 10.01 pH at 24 °C (75 °F).

10.2.2 Distilled or deionized water, preferably in a wash or spray bottle.

NOTE Deionization exchange resins are available.

10.2.3 Mild liquid detergent.

10.2.4 Sodium hydroxide solution, (CAS No. 1310-73-2), 0.1 mol/l, to recondition electrode.

10.2.5 Hydrochloric acid solution, (CAS No. 7647-01-0), 0.1 mol/l, to recondition electrode.

10.3 Apparatus

10.3.1 pH meter, millivolt (mV) range potentiometer calibrated to show pH units for measuring the potential between a glass-membrane electrode and a standard “reference” electrode. The instrument should be water-, shock-, and corrosion-resistant, and portable.

Specifications are as follows:

a) pH range: 0 to 14;

b) electronics type: solid state, recommended;

c) power source: batteries, recommended;

d) operating temperature range: 0 °C to 66 °C (32 °F to 150 °F);

e) readout: digital, recommended;

f) resolution: 0.1 pH unit;

g) accuracy: ± 0.1 pH unit;

h) repeatability: ± 0.1 pH unit;

i) meter adjustments:

  1) temperature compensation of electrode system, recommended;

  2) slope of electrode system, recommended;

  3) calibration setting of readout.

10.3.2 Electrode System

A combination system of a glass electrode for sensing H^+ ions and a standard-voltage reference electrode, constructed as a single electrode is recommended. The body of this probe should be constructed of durable material. A waterproof connection to the meter is recommended.

NOTE The use of solid-state ion-selective field effect transistor electrodes (ISFET) is not addressed in this method. The perceived advantages of these probes include robustness, no moist storage requirements, and shock resistance. One set of measurements using a specific ISFET probe resulted in lower pH values. The use of these electrodes needs to be evaluated further prior to inclusion in a standard procedure.

10.3.3 Soft tissues, preferably lint-free and static-free, to blot electrodes.

10.3.4 Temperature-measuring device, range: 0 °C to 105 °C (32 °F to 220 °F); accuracy ± 1 °C (± 2 °F).

10.3.5 Volumetric pipettes (TD) or syringes, 10 ml.

10.3.6 Beaker or equivalent container, 50 ml.

10.3.7 Blotting tissue or soft-bristle test tube brush, to clean electrode.

10.3.8 Electrode storage vial, capable of allowing immersion of electrode in storage solution.

10.4 Measurement of pH

10.4.1 Obtain and prepare a sample of the fluid to be tested, using one of the following methods.

a) Method 1—neat (undiluted) sample. Place 20 ml of the brine into a clean, dry 50-ml beaker or equivalent bowl. Stir thoroughly. Heat or chill the sample so that the temperature reaches 24 °C ± 3 °C (75 °F ± 5 °F).

b) Method 2—1:1 dilution. Prepare a 1:1 dilution by placing 10.0 ml of distilled/deionized water into a clean, dry 50 ml beaker or equivalent container. Add 10.0 ml of the sample, and mix thoroughly. Allow dilution to reach 24 °C ± 3 °C (75 °F ± 5 °F).

If the sample temperature deviates more than 10 °C (20 °F) from the calibration temperature, temperature calibration is required.

1:10 dilutions of inorganic brines in distilled/deionized water are neither suitable nor recommended, and they lead to imprecise results. Such high dilutions for any brine can result in a pH value at least one pH unit lower than the true pH value for the brine.

10.4.2 Allow the buffer solutions to reach the same temperature as the fluid to be tested.

NOTE For accurate pH measurement, the test fluid, buffer solution, and reference electrode must be at the sample temperature. The pH of the buffer solution indicated on the container label is the correct value only at 24 °C (75 °F). If calibration is carried out at another temperature, the actual pH of the buffer at this temperature is used. Tables of buffer pH values at various temperatures are available from the buffer suppliers.

10.4.3 Clean the electrodes by washing them with distilled/deionized water, and blot dry.

10.4.4 Follow the equipment manufacturer's recommended calibration procedure.

10.4.4.1 Dispense 20 ml of the pH 7.0 buffer in a suitable container and immerse the probe. Calibrate the equipment to pH 7.0.

10.4.4.2 Repeat 10.4.4.1, using a pH 4.0 buffer for an acidic sample and pH 10.0 buffer for an alkaline sample.

NOTE Older meters require manual setting of slope and/or temperature during the calibration procedure.

10.4.4.3 Check the meter with the pH 7.0 buffer again. Recalibrate if necessary. If the meter does not calibrate properly, recondition or replace the electrodes, see 10.6.

10.4.4.4 Calibrate the meter using two or preferably three buffers daily or before each use of the meter. Check the meter with the pH 7.0 buffer every 3 h when in continuous use. Use fresh buffer solutions for calibration every day.

10.4.5 When the meter is properly calibrated, rinse the electrode with distilled/deionized water, and blot dry. Place the electrode in the sample to be tested and stir gently while allowing the reading to stabilize. Generally, stabilization should occur within 2 min. Leave the probe in the brine no longer than 5 min.

10.4.6 Record the sample temperature and pH to the nearest 0.1 pH unit.

10.4.7 Carefully clean the electrode in accordance with the manufacturers' procedures, in preparation for the next use. Store in a vial of pH 4 buffer or as recommended by the probe manufacturer. NEVER let the probe tip become dry, and do not leave the probe in the test brine. Avoid storing the instrument at extreme temperatures [below 0 °C (32 °F) or above 50 °C (120 °F)].

10.5 Precision Statement

For neat brines and similarly for 1:1 diluted brines, the inter-laboratory reproducibility (standard deviation) of these pH assays was in a range between 0.1 pH and 0.4 pH units, depending on the type of brine being evaluated. Many brands of pH probes were used in the round-robin testing, and are most likely responsible for the observed deviations.

10.6 Care of the Electrode

10.6.1 Cleaning the electrode is necessary periodically, especially if oil or clay particles coat the face of the glass electrode.

10.6.2 Reconditioning the electrode may be necessary if plugging becomes severe, as indicated by slow response, drifting of readings or if the slope and calibration cannot be mutually set. Check the owner's manual of the electrode to determine the best procedure for reconditioning it.

10.6.3 General care of the electrode involves the following steps:

a) clean the electrode with a blotting tissue or soft-bristle brush and a mild detergent;

b) the electrode can be reconditioned by soaking it in 0.1 mol/l HCl (CAS No. 7647-01-0) for 10 min, rinsing in water, then soaking in 0.1 mol/l NaOH (CAS No. 1310-73-2) for 10 min, and rinsing it again in water;

c) check the electrode for response by performing a calibration, see 10.4.2 through 10.4.7;

d) replace the electrode system if the preceding steps a) through c) fail to recondition it.

11 Iron Contamination

11.1 Principle

11.1.1 Accumulation of insoluble iron salts in a brine completion fluid can cause significant formation damage and greatly affect the productivity of a well. In addition, iron can cause cross-linking and gelling of polymers and increase the stabilization of crude/brine emulsions. Iron salts are problematic in oilfield brines. Quantifying total iron in brine is critical.

11.1.2 Iron contamination in oilfield brines typically is a result of processes of corrosion of iron-containing metallic components and equipment. This can occur in both aerobic and anaerobic environments and can be electrochemically and microbiologically induced. Metallic iron (Fe) is first converted to Fe(II) [the ferrous cationic species] with the loss of two electrons. Fe(II) can be converted to Fe(III) [the ferric cationic species] with the loss of an additional electron. The electron acceptor depends on the environment and the configuration of the system. Generally, Fe(II) salts are water-soluble, and Fe(III) salts are water-insoluble.

11.1.3 A robust colorimetric, semi-quantitative method has been developed to determine the total iron content in brine, based on chemistry involving acidification, peroxide oxidation, and thiocyanate complex formation. The resulting colored complexes are compared to standards. Commonly used brine additives at typical concentrations minimally impact the method.

NOTE Control and remediation of iron contamination are not addressed in this method.

11.1.4 The method reports total iron content, expressed in milligrams per liter (mg/l). By simply dividing the measured mg/l by the density of the brine reported in kg/l, the mg/kg (sometimes referred to as parts per million) value can be obtained. This method does not distinguish between the species of iron.

11.2 Reagents and Materials

11.2.1 **Distilled or deionized water**, iron-free, preferably in a wash or spray bottle.

NOTE Deionization exchange resins are available.

11.2.2 **Acid solution**, 6.0 mol/l HCl.

11.2.3 **Hydrogen peroxide** (CAS No. 7722-84-1) solution, 3.0 % volume fraction.

11.2.4 **Ammonium thiocyanate** (CAS No. 71762-95-4) solution, 30 % mass fraction.

11.2.5 **Iron Standard Reference Material**, matrix 5 % to 10 % HNO_3, 1000 mg/l, traceable to NIST Standard Reference Material 3126a, Iron Standard Solution.

NOTE If NIST standards are not available (i.e. international work), use an equivalent national/international standard, as appropriate.

The shelf life shall not exceed the manufacturer's recommendation or six months after opening. The expiration date of standard reference material shall be shown on bottles used in the field. Bottles shall be kept tightly sealed.

11.3 Apparatus

NOTE Self-filling ampoule and measured reagent test kits are commercially available. Ensure that the test kit used is specifically designed for measuring iron in brine, that is, iron in heavy density brine.

11.3.1 **Volumetric flasks** or equivalent, 50 ml.

11.3.2 **Caps**, for volumetric flask, capable of sealing the flasks.

11.3.3 **Syringe**, capacity 1.0 ml.

11.3.4 **Syringes**, capacity 3.0 ml.

11.3.5 **Transfer pipettes, disposable**.

11.3.6 **Test tubes**, capacity 5 ml, clear, colorless glass.

11.3.7 **Timer**, range 1 s to 5 min.

11.3.8 **Soft tissues**, preferably lint-free.

11.3.9 **Natural or white light source**.

NOTE Fluorescent lighting can skew colorimetric interpretation.

11.4 Preparation of Colorimetric Standards

11.4.1 Colorimetric standards shall be prepared for comparison of the test sample of brine.

11.4.2 Using iron-free water, prepare dilutions of an NIST-traceable Iron Standard Reference Material. The iron concentrations of these standards shall bracket the iron concentration of the test brine. It is generally recommended to prepare iron concentrations in 10 mg/l increments in the range 0 mg/l to 100 mg/l. Above 100 mg/l, it is recommended to prepare iron concentrations in 100 mg/l increments.

11.4.3 Transfer 0.5 ml of the brine reference sample into a 50 ml volumetric flask via the 1.0 ml syringe.

11.4.4 Transfer 1.0 ml of the acid solution via a 3.0 ml syringe.

11.4.5 Add 0.25 ml (five drops) of the aqueous hydrogen peroxide solution via the transfer pipette. Swirl briefly to mix the contents. Wait 2.0 min, but not more than 3.0 min.

11.4.6 Fill the volumetric flask to the 50 ml mark with the iron-free water. Cap the flask and shake briefly to mix the contents. Remove the cap.

11.4.7 Transfer 1.0 ml of the solution from 11.4.6 into the test tube via a 3.0 ml syringe.

11.4.8 Transfer 0.5 ml of the aqueous ammonium thiocyanate solution into the test tube via a 3.0 ml syringe. Swirl the content to ensure mixing. Wait 1 min.

The color stability of these complexes has not been determined. It is recommended that the standards that bracket the iron concentration of the test brine be developed simultaneously with the test brine sample.

11.5 Measurement of Iron Contamination

11.5.1 Obtain a sample of the fluid to be tested. As the brine may contain particulates, agitate the brine to ensure complete and even dispersion. Nonsuspended solids shall not be included with the sample.

11.5.2 Transfer 0.5 ml of the brine sample into a 50 ml volumetric flask via the 1.0 ml syringe.

11.5.3 Transfer 1.0 ml of the acid solution via a 3.0 ml syringe.

11.5.4 Add 0.25 ml (five drops) of the aqueous hydrogen peroxide solution via the transfer pipette. Swirl briefly to mix the contents. Wait 2.0 min, but not more than 3.0 min.

NOTE The presence of significant amount (greater than 0.5 volume %) of oxidizable organic additives can lead to inaccurate, low readings. This can be remedied by adding more of the oxidant hydrogen peroxide in 11.5.4.

11.5.5 Fill the volumetric flask to the 50 ml mark with the iron-free water. Cap the flask and shake briefly to mix the contents. Remove the cap.

11.5.6 Transfer 1.0 ml of the solution from 11.5.5, into the test tube via a 3.0 ml syringe.

11.5.7 Transfer 0.5 ml of the aqueous ammonium thiocyanate solution into the test tube via a 3.0 ml syringe. Swirl the content to ensure mixing. Wait 1 min.

11.5.8 Compare the color of the test tube solution with standard solutions under a source of white light. If the color of the test tube solution is between two color standards, a concentration estimate can be made.

Electronic single-analyte measuring devices may be used to evaluate the intensity of the colored complexes formed. These devices can be calibrated to give a direct reading of the iron levels in the brine. Use the manufacturers' recommended test and calibration procedures.

11.6 Precision Statement

11.6.1 The precision depends on the standards used to bracket the iron concentration of the test brine. The closer the incremental concentrations of the standards are, the tighter is the precision.

11.6.2 For low concentrations of iron (less than 100 mg/l) using standards with incremental iron concentration increases of 10 mg/l, the inter-laboratory reproducibility (standard deviation) of the method was shown to be 10 mg/l. The variance (accuracy) compared to single atomic spectroscopy analyses was –12.7 %.

11.6.3 For high concentrations of iron (range 100 mg/l to 600 mg/l) using standards with incremental iron concentration increases of 100 mg/l, the inter-laboratory reproducibility (standard deviation) of the method was shown to be 87 mg/l. The variance (accuracy) compared to single atomic spectroscopy analyses was +3.0 %.

11.6.4 The inter-laboratory reproducibility and variance have not been determined for brines containing greater than 600 mg/l iron contamination.

12 Daily Completion Fluid Test Report

12.1 Principle

12.1.1 The daily fluid report presents information to the operator necessary for the technical management, administration, and record documentation of key information concerning well operations as they relate to completion fluid activities.

12.1.2 Primary impact areas are:

a) well control,

b) formation damage potential,

c) materials accountability.

12.1.3 The daily fluid report is similar in nature to the daily drilling fluid report but is configured for the unique conditions and measurements that completion fluids and completion operations impose.

12.1.4 The daily fluid report is comprised of six (6) elements, each containing specific information. The elements are not exclusive; operators and vendors may add additional information, as desired. The six elements shall be:

a) well identification, geometry, and zone data,

b) system properties,

c) fluids accounting,

d) cost accounting,

e) daily commentary,

f) vendor representative identification.

12.1.5 Page size is at the discretion of the operator and supplier. Some page sizing may not easily accommodate all parts of the required information; 12.5 through 12.7 can be formatted onto a second page.

12.1.6 Annex A gives an example layout with sections of information stated. Arrangement of these sections is discretionary and should be agreed between operator and supplier.

12.2 Well identification, Geometry, and Zone Data

12.2.1 Well Identification—Operator, Contractor, Rig Description, Legal Description

Well identification includes the following information:

a) report date;

b) report number;

c) operator name;

d) supervisor name;

e) contractor;

f) rig name and number;

g) well name and number;

h) geographic location;

i) country, region/state, county/parish, block.

12.2.2 Geometry

Well geometry includes the following information:

a) API well number (if applicable);

b) casing dimensions and lengths;

c) drill pipe and tubular dimensions and lengths;

d) well volume, expressed as capacity, annular, pipe, and pipe in hole.

12.2.3 Zone Data

Well zone data include the following information,

a) name of current zone or zone of treatment,

b) bottomhole temperature of current zone,

c) bottomhole pressure of current zone,

d) true vertical depth of current zone.

12.3 System Properties

12.3.1 The system properties to be included in the daily completion fluid report are those tested in accordance with API 13J:

a) actual specific gravity or density at actual temperature, noting °C or °F;

b) density, converted to 20 °C or 70 °F;

c) pH at actual temperature, noting °C or °F;

d) NTU;

e) percent solids (volume fraction);

f) iron content, expressed in mg/l.

12.3.2 Additional blank lines should be included on the form to accommodate optional data.

12.4 Fluids Accounting

12.4.1 Fluids are identified by fluid type, density, and volume expressed in m^3 (bbl).

NOTE In USC units, completion fluids use the common oilfield definition of 1 bbl = 42 gal.

12.4.2 Fluids accounting consists of the following four elements.

a) Fluid volume brought to or created on location. This represents fluids purchased, brought from another location, existing fluids on location at the start of operations, and volume created from bagged material or water additions.

b) Physical inventory. This represents fluids that have been stated in 12.4.2 a). The fluids are located in the well, on the rig, and in/on other storage sites such as tanks, boats, and fluids returned to vendor plants.

NOTE This can be a detailed accounting or grouped into main locations.

c) Fluid loss. This comprises categorization of two major areas of fluid use: surface and well. Loss is tallied by day and also cumulatively for categories and sums of categories.

d) Fluid volume balance. This entails a comparison of all fluids brought to or generated at the well from all sources, balanced against the tabulation of fluids from physical inventory and fluid loss. The sum of fluids brought to or created must match the sum of the physical inventory plus fluid loss.

12.5 Cost Accounting

Cost accounting is a tabulation of all material and service costs done daily and cumulatively for the project.

The values may be given as:

a) simple total of day and cumulative cost;

b) a grouping by primary cost category by day and cumulative; or

c) a detailed account of each product/service that reports quantities used, by day and cumulatively.

12.6 Daily Commentary

The daily commentary is a textual section summarizing daily operations at the well. It includes a description of system performance and problems encountered.

12.7 Vendor Representative Identification

This portion of the daily completion fluids report includes:

a) representative names,

b) location of plant or stock point,

c) location of office with contact information.

13 Buffering Capacity of Brines

13.1 Principle

13.1.1 Aqueous buffers consist of blends of weak acids and their conjugate bases or of weak bases and their conjugate acids. Buffering minimizes changes to the pH value upon the addition of either acid or base. For purposes of this standard, buffering capacity is defined as that amount of acid or base in milliequivalents that one milliliter of brine tolerates before a specified threshold pH value is reached. The primary focus for buffer capacity of brine systems is dominated by promoting brine stability, controlling acid gas intrusion, and providing corrosion protection; therefore, the focus is on buffering brine to a pH value higher than the unbuffered brine.

13.1.2 An assessment of buffer concentration measures the capacity of the brine to absorb acidic or basic species while maintaining pH control. A common example of a buffer system in formate brines and monovalent halide brines is the blend of sodium carbonate and sodium bicarbonate. This buffer system is much less effective with divalent halide brines due to the precipitation of insoluble carbonate salts, i.e. $CaCO_3$ and $ZnCO_3$. For the divalent halide brines, examples of buffering agents are lime and magnesium oxide. Zinc-based halide brines have natural pH values ranging from pH 2 to pH 7, depending on the zinc ion concentration and density. Calcium-based halide brines have pH values of 6.0 to 7.5. Monovalent halide and formate brines have pH values about 7.5. The influx of CO_2 lowers the pH of all brine systems.

13.1.3 Determination of the buffer concentration in brines assists in determining the ability to withstand potential exposure to the acidic gases—carbon dioxide and hydrogen sulfide. Neutralizing the intrusion of acid gases and controlling corrosion are prime reasons for buffering brines and is especially useful when the pH is controlled to values greater than 7.0. Most brines may be buffered to various pH values. The buffer capacity of brine shall therefore be assessed in relation to functional requirements and/or pH limitations.

13.1.3.1 For operational concerns, the pH of formate brine is maintained at a pH value above pH 7.0 in order to maintain stability and reduce the impact of formic acid species. Therefore, the buffer capacity of formate brine is defined for a pH value above 7.5.

13.1.3.2 Monovalent halide brines may be buffered to a wider range of pH values from acidic to basic. The desired buffer capacity is then based on the functional requirements for the specific application. Most often, the desired buffer capacity and most useful application range are pH values greater than pH 7.5.

13.1.3.3 Depending on density and brine type, divalent calcium-based halide brines may be buffered up to pH values around 8.0, but generally much less than monovalent brine systems. Similarly, zinc-based brines may be buffered, but at pH values less than pH 7.0, depending on the zinc-ion concentration and density.

13.1.4 Alkalinity in the form of hydroxyl (OH^-), carbonate (CO_3^{-2}), and bicarbonate (HCO_3–), and other buffering species may be titrated potentiometrically either with a manual or automated procedure.

13.1.4.1 When titrating brines with a sodium carbonate/sodium bicarbonate buffer system and a pH greater than 10, the first endpoint includes the hydroxyl and carbonate ion concentrations along with other buffering materials that may have formed or been incorporated into the brine.

13.1.4.2 A second endpoint may be detected at a pH lower than pH 4.0, which includes the bicarbonate ion concentration. With formate brines, endpoints less than a pH about 7 are severely complicated by the conversion of formate ion to formic acid and are incorporated into and titrated by the procedure for buffer determination.

13.1.5 For halide and formate brines, the recommended measurements are conducted on neat brine or brine diluted 1:1 with deionized water. Errors caused by higher dilution ratios greater than 1:1 are a common problem that was observed during round robin testing of formate brine [27].

13.2 Equipment

13.2.1 **pH meter**, millivolt (mV) range potentiometer calibrated to show pH units for measuring the potential between a glass-membrane electrode and a standard "reference" electrode. The instrument should be water-, shock-, and corrosion-resistant.

Specifications are as follows:

a) pH range: 0 to 14;

b) electronics type: solid state, recommended;

c) power source: 12 V adaptor power supply, 110 V, 120 V, 220 V, or 240 V for laboratory use;

d) operating temperature range: 0 °C to 65 °C (32 °F to 150 °F);

e) readout: digital, recommended;

f) resolution: 0.1 pH unit;

g) accuracy: ± 0.1 pH unit;

h) repeatability: ± 0.1 pH unit;

i) meter adjustments:

    1) temperature compensation of electrode system, recommended;

    2) slope of electrode system, recommended;

    3) calibration setting of readout.

13.2.2 **Electrode system**—a combination system of a glass electrode for sensing hydrogen (H^+) ions and a standard voltage reference electrode, constructed as a single electrode, is preferred. The body of this probe should be constructed of a durable material. A waterproof connection to the meter is recommended.

13.2.3 **Soft tissues**, preferably lint-free, to dry electrodes.

13.2.4 **Temperature-measuring device,** range 0 °C to 105 °C (32 °F to 220 °F).

13.2.5 Pipettes, volumetric (TD), 10 ml ± 0.01 ml, 20 ml ± 0.01 ml, or appropriate size (accuracy ± 0.01 ml) for brine sample. Alternatively, sample with accurately known density can be weighed ± 0.01 g, and the volume can then be calculated.

13.2.6 Beaker, glass, 50 ml, 100 ml, or appropriate size.

13.2.7 Test tube brush, soft-bristle, to clean electrode.

13.2.8 Electrode storage vial, capable of allowing immersion of electrode in storage solution.

13.2.9 Filter paper, qualitative.

13.2.10 Burettes, 25 ml ± 0.01 ml, 50 ml ± 0.01 ml, or appropriate size with accuracy ± 0.01 ml, for titrations.

13.2.11 Magnetic stirrer.

13.2.12 Stirring bars.

13.3 Reagents and Materials

13.3.1 Buffer solutions, for pH calibration, three solutions to calibrate and set the slope of the pH meter prior to sample measurement. Solutions of pH 4.0, pH 7.0, and pH 10.0 are the standard pH buffer fluids. It is recommended that buffer be obtained from pre-made solutions or a dry powder package.

These buffer solutions shall meet NIST primary or secondary buffer standards. The shelf life shall not exceed the manufacturer's recommendation or six months after opening. Bottles shall be kept tightly sealed.

NOTE If NIST standards are not available (i.e. international work), use an equivalent national/international standard, as appropriate.

The slope of the pH meter when calibrating shall be 95.0 % or higher.

13.3.2 Distilled or deionized water.

13.3.3 Mild liquid detergent.

13.3.4 Sodium hydroxide (CAS number 1310-73-2), 0.1 M (mol/l), to recondition the electrode.

13.3.5 Sodium hydroxide (CAS number 1310-73-2), freshly standardized 0.5 M (mol/l) to 1.0 M (mol/l), for titration.

13.3.6 Hydrochloric acid (CAS number 7647-01-0), 0.1 mol/l (0.1N) to recondition the electrode.

13.3.7 Hydrochloric acid (CAS number 7647-01-0), freshly standardized 0.5 mol/l (0.5N) to 1.0 mol/l (1.0N), for titration.

13.4 Procedure—Determination of Buffer Concentration

13.4.1 Obtain and prepare a sample of the fluid to be tested.

13.4.2 Record sample integrity (clarity, color, suspended solids, etc.). Filter, as necessary.

13.4.3 Record the brine density, pH, and temperature at the time of measurements.

13.4.4 Titrate the undiluted sample.

13.4.4.1 Measure accurately two 10 ml to 20 ml samples of undiluted brine to beakers or proper titration vessels. Record as V_S. Alternatively, accurately weigh and record the sample of known density, then calculate and record its volume, as V_S.

13.4.4.2 Record the starting pH.

13.4.4.3 Titrate each of the two samples using a freshly standardized HCl (see 13.3.7) solution. Record pH versus ml acid added. If using a manual titration procedure, record the pH at every 0.5 ml acid added and monitor ΔpH/ΔV_{HCl} versus volume of HCl acid. When indicated by an increase in ΔpH/ΔV_{HCl} versus V_{HCl} (about pH 9 for 1:1 diluted brine or pH 10 for neat carbonate-buffered formate brine), start adding 0.1 ml to 0.2 ml hydrochloric acid until the first endpoint is passed. Record the volume of acid to reach the first endpoint as V_A.

13.4.4.4 Continue titrating to the desired target pH (about pH 6 for 1:1 diluted brine or about pH 7 for neat carbonate-buffered formate brine). Record the volume of acid to the second endpoint as V_B.

13.4.4.5 Plot the data using a computer-based or manual method, as shown in Figure 7. For a more accurate determination of endpoints, the recommended procedure is to plot and monitor ΔpH/ΔV_{HCl} versus V_{HCl}. The endpoint is the maximum value for the plotted curve. See Figure 8 for an example.

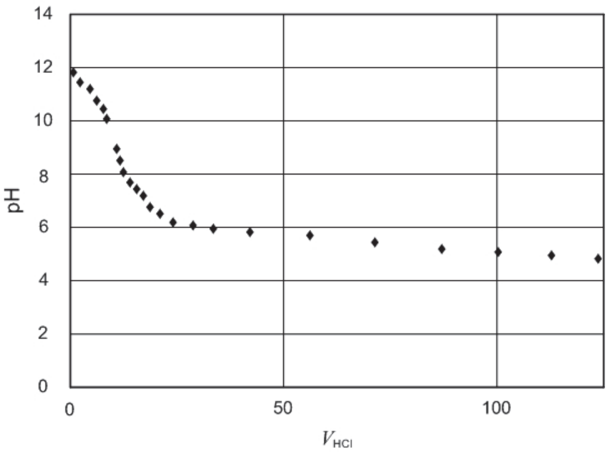


Figure 7—Example of pH versus Volume of HCl Acid Added

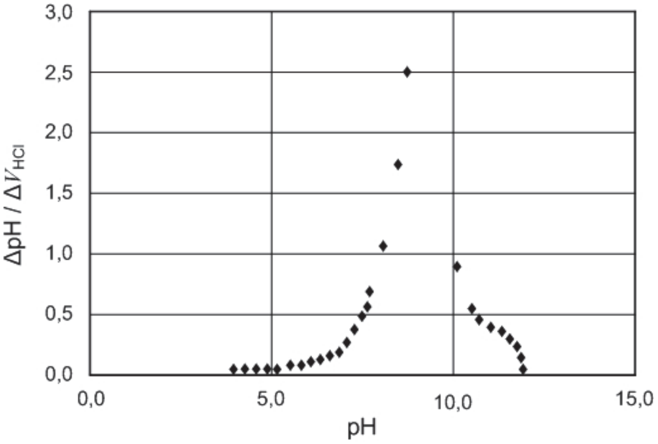


Figure 8—Example of ΔpH/ΔV_{HCl} versus Volume of HCl Acid Added, for More Accurate Determination of Titration Endpoint

13.4.4.6 Report all endpoints observed as milliliters of hydrochloric acid used.

13.4.4.7 Calculate the average milliequivalents of hydrochloric acid per milliliter of brine (meq_{ACID}/ml_{BRINE}) and report.

13.4.5 Titration of 1:1 Diluted Samples

13.4.5.1 Measure accurately two 10 ml to 20 ml aliquots of the undiluted brine to beakers or proper titrating vessels. Records as V_S. Alternatively, accurately weigh and record the sample of known density, then calculate its volume and record as V_S.

13.4.5.2 Measure and record the pH of the undiluted brine.

13.4.5.3 Dilute the brine with an equal volume of distilled or deionized water, mix well, and record the pH of the 1:1 diluted samples.

13.4.5.4 Follow 13.4.4.3 through 13.4.4.7. Report all endpoints observed as milliliters of hydrochloric acid used.

13.4.5.5 Calculate the average milliequivalents of hydrochloric acid per milliliter of brine (meq_{ACID}/ml_{BRINE}) and report.

13.5 Calculation—First Endpoint or Target pH

13.5.1 Calculate the buffer concentration in milliequivalents of hydrochloric acid per milliliter of brine:

$$c_{B1} = \frac{V_A \times M_A}{V_S} \tag{32}$$

where

c_{B1} is the buffer concentration, expressed in milliequivalents of acid per milliliter brine (meq_{ACID}/ml_{BRINE});

V_A is the volume of hydrochloric acid used to the first endpoint or target pH, expressed in milliliters;

M_A is the molarity of the hydrochloric acid used, expressed in moles per liter;

V_S is the volume of undiluted brine, expressed in milliliters.

13.5.2 Calculate the average of the duplicate titrations, (for either c_{Na2CO3} and c_{K2CO3}), and report the first endpoint in milliequivalents of acid per milliliter of brine (meq_{ACID}/ml_{BRINE}), or percentage. Repeat titrations if duplicate results differ by 5 % or more.

13.5.3 Calculate the concentration of titratable basic species, expressed as kg/m^3 or lb/bbl of sodium or potassium carbonate, as needed:

NOTE These calculations make the assumption that only Na_2CO_3 or K_2CO_3 contributed to acid consumption and totally ignores added NaOH or KOH and other buffering materials.

$$c_{Na2CO3} = \frac{53.00 \times V_A \times M_A}{V_S} \qquad \text{(in kg/m}^3\text{)} \tag{33}$$

$$c_{\mathrm{Na2CO3}} = \frac{18.58 \times V_{\mathrm{A}} \times M_{\mathrm{A}}}{V_{\mathrm{S}}} \quad \text{(in lb/bbl)} \tag{34}$$

$$c_{\mathrm{K2CO3}} = \frac{69.11 \times V_{\mathrm{A}} \times M_{\mathrm{A}}}{V_{\mathrm{S}}} \quad \text{(in kg/m}^3\text{)} \tag{35}$$

$$c_{\mathrm{K2CO3}} = \frac{24.22 \times V_{\mathrm{A}} \times M_{\mathrm{A}}}{V_{\mathrm{S}}} \quad \text{(in lb/bbl)} \tag{36}$$

where

c_{Na2CO3} is the concentration of titratable basic species, expressed as kg/m^3 or lb/bbl of sodium carbonate;

c_{K2CO3} is the concentration of titratable basic species, expressed as kg/m^3 or lb/bbl of potassium carbonate;

V_{A} is the volume of hydrochloric acid used to reach the first endpoint, expressed in milliliters;

M_{A} is the molarity of hydrochloric acid, expressed in moles per liter;

V_{S} is the volume of the undiluted brine, expressed in milliliters.

NOTE The molecular weight of Na_2CO_3 is 105.99, and the molecular weight of K_2CO_3 is 138.21.

13.6 Calculation—Second Endpoint or Target pH

13.6.1 Calculate the buffer concentration in milliequivalents of hydrochloric acid per milliliter of brine:

$$c_{\mathrm{B2}} = \frac{\left(V_{\mathrm{B}} - V_{\mathrm{A}}\right) \times M_{\mathrm{A}}}{V_{\mathrm{S}}} \tag{37}$$

where

c_{B2} is the second buffer concentration, expressed in milliequivalents of acid per milliliter of brine ($\mathrm{meq}_{\mathrm{ACID}}/\mathrm{ml}_{\mathrm{BRINE}}$);

V_{A} is the volume of hydrochloric acid used to the first endpoint or target pH, expressed in milliliters;

V_{B} is the volume of hydrochloric acid used to reach the second endpoint or target pH, expressed in milliliters;

M_{A} is the molarity of the hydrochloric acid, expressed in moles per liter;

V_{S} is the volume of undiluted brine, expressed in milliliters.

13.6.2 Calculate the average of the duplicate titrations, (for either c_{Na2HCO3} and c_{KHCO3}), and report the second endpoint in milliequivalents of acid per milliliter of brine ($\mathrm{meq}_{\mathrm{ACID}}/\mathrm{ml}_{\mathrm{BRINE}}$), or percentage. Repeat titrations if duplicate results differ by 5 % or more.

13.6.3 Calculate the concentration of titratable basic species between the two endpoints, expressed as kg/m^3 or lb/bbl sodium bicarbonate or potassium bicarbonate, as needed:

NOTE These calculations make the assumption that only $NaHCO_3$ or $KHCO_3$ contributed to acid consumption and totally ignores other buffering materials, inhibitors, etc.

$$c_{\mathrm{NaHCO3}} = \frac{84.01 \times V_{\mathrm{A}} \times M_{\mathrm{A}}}{V_{\mathrm{S}}} \quad \text{(in kg/m}^3\text{)} \qquad (38)$$

$$c_{\mathrm{NaHCO3}} = \frac{29.47 \times V_{\mathrm{A}} \times M_{\mathrm{A}}}{V_{\mathrm{S}}} \quad \text{(in lb/bbl)} \qquad (39)$$

$$c_{\mathrm{KHCO3}} = \frac{100.12 \times V_{\mathrm{A}} \times M_{\mathrm{A}}}{V_{\mathrm{S}}} \quad \text{(in kg/m}^3\text{)} \qquad (40)$$

$$c_{\mathrm{KHCO3}} = \frac{35.09 \times V_{\mathrm{A}} \times M_{\mathrm{A}}}{V_{\mathrm{S}}} c_{\mathrm{KHCO3}} \quad \text{(in lb/bbl)} \qquad (41)$$

where

c_{NaHCO3} is the concentration of titratable basic species, expressed as kg/m^3 or lb/bbl of sodium bicarbonate;

c_{KHCO3} is the concentration of titratable basic species, expressed as kg/m^3 or lb/bbl of potassium bicarbonate;

V_{A} is the volume of hydrochloric acid used to the first endpoint or target pH, expressed in milliliters;

V_{B} is the volume of hydrochloric acid used to reach the second endpoint or target pH, expressed in milliliters;

M_{A} is the molarity of the hydrochloric acid, expressed in moles per liter;

V_{S} is the volume of undiluted brine, expressed in milliliters.

NOTE 1 The molecular weight of $NaHCO_3$ is 84.01, and the molecular weight of $KHCO_3$ is 100.12.

NOTE 2 The above equations do not apply to formate brines due to the titration of and interference from formate to formic acid equilibrium when acid is added (see 13.1.4.1).

Annex A

(informative)

Completion Fluids Report Form

ANY BRINE COMPANY **DAILY COMPLETION FLUIDS REPORT**

WELL IDENTIFICATION, GEOMETRY, AND ZONE DATA

Report date.	Contractor and rig name.	Name of current zone.
Report number.	Well name and location.	BHT of current zone.
Operator name.	Country, region/state, county/ parish, block.	BHP of current zone.
Supervisor name(s).	Casing and DP/tub dimensions and lengths.	TVD of current zone.
	Well volume expressed as capacity, annular, pipe, and pipe in hole.	

SYSTEM PROPERTIES

Properties include but are not limited to:

- actual specific gravity at actual temperature,
- actual measured specific gravity or density at measured temperature,
- density at 20 °C or 70 °F,
- pH at temperature,
- nephelometric turbidity unit,
- % solids,
- iron content.

Additional 3 to 6 blank lines for optional data.

FLUIDS ACCOUNTING

Fluids are identified by fluid type, density, and volume in barrels;

Fluids accounting consists of four (4) main elements:

- fluid volume brought to or created on location,
- physical inventory,
- fluid loss,
- fluid volume balance.

DAILY COMMENTARY

Textual section; summary of daily operations as related to fluids, additives, waste, loss, and filter operations.

Document sample dates/type; orders made and received; certain instructions by operator.

COST ACCOUNTING

Tabulation of all material and service costs for the day and as a cumulative total for the project.

The values may be given as a:

- simple total of day and cumulative cost,
- grouping by primary cost category by day and cumulative, or
- detailed account of each product/service that reports quantities used by day and cumulative.

Figure A.1—Daily Brine Report

Annex B
(informative)

Gas Hydrates

B.1 The intent of this annex is to make the user aware of the consequences of potential hydrate formation during completion and workover operations. More information about natural gas hydrates is available in the documents and website listed in Bibliography References [6], [7], [10] to [12], [14], [17] to [22], and [24]. Consult a brine service company about the potential for hydrate formation for any situation where high pressure and low temperature exist.

B.2 Clathrate hydrates are ice-like compounds formed by a hydrogen-bonded network of water molecules stabilized by a hydrocarbon guest molecule, such as methane, ethane, or propane.

B.3 Inorganic gases such as hydrogen sulfide and carbon dioxide can also stabilize and promote hydrate formation. Since several hydrate formers are components of natural gas, clathrate hydrates are commonly referred to as “gas hydrates.” Gas hydrates are typically about 85 % water and 15 % guest molecules.

B.4 Four elements are required for hydrate formation:

a) low temperature,

b) high pressure,

c) a hydrate-forming compound,

d) water.

B.5 Depending upon the pressure and the gas composition, hydrates can form at temperatures significantly above the freezing point of water. Since low temperature and high hydrostatic pressure exist at the sea floor, hydrates can form in sea floor equipment and in the wellbore whenever and wherever water or water-based fluid comes into contact with natural gas. The gas can be the result of the thermal decomposition of hydrocarbons, gas production zones, or the bacterial decay of organic matter.

B.6 Gas hydrates can plug subsea wellheads, choke and kill lines, other subsea equipment, and pipelines. Although deepwater mudline temperatures and pressures are conducive to hydrate formation and are the primary focus of hydrate inhibition, cold ambient temperatures at the surface can facilitate hydrate formation in pressurized equipment. Increasing the pressure in all of these situations to “clear the plug” simply makes the situation worse.

B.7 The most common method used for hydrate mitigation is to add an inhibitor to the water. There are two classes of hydrate inhibitors, called thermodynamic and kinetic. Thermodynamic inhibitors reduce the equilibrium temperature of hydrate formation at a given pressure. Kinetic inhibitors delay (or retard) hydrate formation at a defined temperature and pressure.

B.8 Common thermodynamic inhibitors include sodium chloride, calcium chloride, and formate salts. Some organic inhibitors are methanol, ethylene glycol, and propylene glycol.

B.9 Kinetic inhibitors consist of two classes, anti-agglomerates and threshold inhibitors. Hydrates will form if kinetic inhibitors are added, but the mass of hydrates can be more manageable.

B.10 Anti-agglomerates prevent the accumulation of hydrate crystals into masses that can cause plugs. Threshold inhibitors increase the time that hydrates take to form at a given temperature and pressure.

Threshold inhibitors produce an effect that is very similar to super-cooling in brine fluids, where the temperature of the fluid can be taken below the crystallization temperature of the brine, but crystallization of the fluid will not occur. As with a brine fluid, super-cooling is not a stable state and catastrophic nucleation can occur at any time.

Annex C
(informative)

Pressure Crystallization of Brines

C.1 Principle

C.1.1 Brine solutions have thermodynamic or true crystallization temperatures (TCT) that have been thoroughly studied and used to properly formulate brine for specific applications. TCT values for brine formulations have been well documented for brine formulation at atmospheric pressures. However, pressure can influence the temperature at which a given brine crystallizes and the pressure effect can be very significant. Therefore, both pressure and temperature must be factored into the formulation of brine for specific applications. The potential for pressure crystallization of brine is magnified for scenarios that induce high pressure at low temperature.

C.1.2 Several high-pressure low-temperature scenarios occur during routine field operations and include the hydrostatic pressure applied to brine at the mudline in deepwater operations, the pump pressure applied to brine during cold weather pumping operations especially when first circulating fluid into the hole after being stagnant at low temperature or during displacement operations, and pressure testing of blowout preventers in deepwater operations. If the effect of maximum pressure and lowest temperature for the brine environment has not been properly incorporated into the brine formulation, adverse crystallization might occur and subsequently cause extreme difficulties and safety hazards.

C.1.3 Single salt brines with salt content lower than the eutectic mixture crystallize under pressure at a temperature equal to or lower than the brine TCT and form ice crystals.

C.1.4 Brines with salt content higher than the eutectic mixture exhibit a solubility of one or more dissolved salts, which can decrease under applied pressure. For these brines, a threshold pressure exists above which salt crystals will form in the brine at a temperature higher than the TCT.

C.1.5 The resulting TCT at a specified pressure above ambient is termed pressure crystallization temperature (PCT). PCT is recorded as x C-PCT at y kPa or as x F-PCT at y psi. For example, a PCT of −2 °C at 69,000 kPa (30 °F at 10,000 psi) indicates that the brine fluid will crystallize at 69,000 kPa (10,000 psi) when the fluid temperature is lowered to –2 °C (30 °F).

C.1.6 PCT measurements are routinely conducted to 103 MPa (15,000 psi) at temperatures from 21 °C (70 °F) to −40 °C (−40 °F), and more recently, pressures to 138 MPa (20,000 psi) are conducted.

C.2 Measuring PCT

C.2.1 Conventional methods for measuring TCT are difficult to modify for the measurement of PCT, predominantly because massive cells are required to contain the high pressure required to measure PCT values. Controlled agitation of the fluid and direct observation (visualization) of the crystallization process are recognized requirements for accurate measurement of TCT and routinely performed, but they are also difficult to implement for the measurement of PCT.

C.2.2 Nonetheless, equipment that incorporates controlled agitation of the fluid and direct observation (viewing) of the crystallization process have been constructed, and necessary techniques and procedures to determine PCT were developed. By necessity, these devices measure temperature and pressure changes that occur during the crystallization process and accurately record the crystal formation and crystal dissolving process, which enables accurate cycling of the process and excellent repeatability. By directly observing (viewing) the crystallization process, these devices adequately control the super-cooling process, which is critical to accurate TCT and PCT measurements.

C.2.3 Other devices have been constructed that measure changes in pressure, temperature, and/or volume without direct observation. These techniques require the application of safeguards to ensure that artificially low values due to “super-cooling” are avoided, otherwise artificially low PCT values would be obtained.

C.2.4 If a brine is tested at the anticipated low-temperature high-pressure environment and its crystallization temperature found to be equal to or higher than the anticipated pressure and temperature conditions, the brine formulation is modified to prevent brine crystallization.

Annex D
(informative)

Brine Viscosity

D.1 Principle

The viscosity of brine solutions can have a significant impact on completion operations. This is true for neat brines, viscosified brines, and mixtures of brines with other fluids, especially at interfaces such as with certain crude oils.

Viscosity, especially high viscosity, can significantly increase the friction pressure in work strings and coil tubing during pumping operations, negatively impact the capacity to clean pipe and casing surfaces, and potentially cause formation damage. If a completion brine exhibits a viscosity that is too high, it should be reformulated to provide a lower desired viscosity.

Conversely, viscosity, especially high viscosity, can significantly improve the separation and minimize the interaction between spacers in a displacement train, increase the capacity of the fluid to lift drilled cuttings and solids out of the wellbore, and create effective fluid loss control pills. Effective viscosifying agents are available for each of the brine systems.

D.2 Measuring the Viscosity

Viscosity is measured using several different instruments and procedures, with each method tailored to the type of fluid being evaluated, the purpose for which the fluid was formulated, and the limitations of the measurement device. Standard drilling and fracturing fluid viscometers are suitable to measure the viscosity of brine or viscosified brine at ambient and elevated temperatures and pressures. For specific procedures to measure or adjust the viscosity of completion brine, consult a completion fluid supplier.

Annex E
(informative)

Principle of Corrosion Testing

E.1 Principle

E.1.1 Common practice in the upstream oil and gas industry includes the use of well service fluids made from solids-free brines primarily due to their minimal damage to formations. This clause deals with all aqueous solutions of inorganic and organic salts used in oilfield drilling, completion, and/or packer fluid operations.

E.1.2 Solids-free brines must be properly formulated to address corrosion issues that could lead to failure of the well tubulars. These fluids vary in corrosivity to the tubing, casing, and downhole equipment metallurgy depending on salt type, additives, possible contaminants, and well conditions such as temperature, acidic gases, and pressure.

E.1.3 The following will address the topics of metallurgy, brine types, corrosion types, test methods, and control of corrosion.

NOTE This document is meant to provide only the necessary basic background. This information is given for the convenience of users and does not constitute any warranty, either written or implied, by API of this information. References are provided for further and more detailed information.

E.2 Metallurgy

E.2.1 The metallic alloys most commonly used in oilfield tubing and casing, downhole, and surface equipment include the following.

a) Carbon steels, e.g. AISI 1020, AISI 1040.

b) Low-alloy steel, e.g. AISI 4130, AISI 4140.

c) Stainless steels:

   1) austenitic, e.g. AISI 316;

   2) martensitic, e.g. AISI 410, 13Cr/420Mod, S13Cr;

   3) duplex, e.g. 22Cr/2205, 25Cr/2507;

   4) precipitation hardened, e.g. 17-4 PH, 450.

d) Nickel-based alloys:

   1) solid solution, e.g. 825, G3, C-276;

   2) precipitation hardened, e.g. 925, 718, 725.

E.2.2 Alloys are selected based on mechanical properties, corrosion and cracking resistance, cost availability, etc. Alloys that are not carbon steel or low-alloy steel are referred to as corrosion-resistant alloys (CRAs). This designation includes iron-based, nickel-based, cobalt-based, and titanium-based alloys.

E.2.3 In well construction, casing is most always a low-alloy carbon steel, while tubing may be either low-alloy carbon steel or CRA. Surface or facility equipment may also be either type.

E.2.4 A brief description of these common oilfield alloys is contained in E.2.4.1 through E.2.4.5, but a more detailed understanding can be gained through available courses and textbooks. [28]

E.2.4.1 Carbon and Low-alloy Steels

E.2.4.1.1 Steel is an alloy of iron and carbon with iron as its principal element. The material is considered to be carbon steel when no minimum content is specified or required for any other element typically added to obtain a desired alloying effect. Mild steel is the most common form of steel because it is low cost and malleable. Low-carbon steel contains approximately 0.05 % to 0.15 % carbon and mild steel contains 0.16 % to 0.29 % carbon. Higher carbon steels have carbon content in the range of 0.30 % to 1.70 % by weight. Generally, carbon is less than 2 % and more commonly less than 0.8 %. Carbon and low-alloy steels are commonly used for well casing, production tubing, and well completion equipment. AISI 4130 and AISI 4140 are low-alloy steels with the first two letters (or numbers), 41XX, designating “chrome-moly” steel. The last two letters (or numbers) designate average carbon content, e.g. 0.30 % carbon for 4130. N-80 and L-80 are designations for casing and tubing material per API 5CT, and the last two digits refer to the minimum yield strength, expressed in one thousand pounds per square inch, ksi. [30] [31]

NOTE 1 ksi = 1000 psi = 6895 kPa = 6.90 N/mm^2.

E.2.4.1.2 Carbon and low-alloy steels are the most commonly used downhole materials since they are lower in cost than CRAs and can be easily heat treated to various strength levels. These steels can be heat treated to soften (annealing) or harden (quenching). In the as-quenched state, steels are brittle and are usually tempered to a desired strength level. Tempering greatly improves the toughness. Heat treatments can be specified to produce the desired mechanical properties for a given steel chemistry. Similarly, chemical compositions can be tailored to achieve desired mechanical properties. Alloying elements, like carbon, manganese, nickel, copper, chromium, molybdenum, and others are added to impart particular properties and hardenability of steels.

E.2.4.1.3 Carbon steel and low-alloy steels have limited corrosion resistance in aqueous environments containing CO_2 that are found downhole in both oil and gas wells. Additionally, these CO_2 environments may also contain H_2S. If the CO_2 content is low, and there is enough H_2S present to form a protective FeS scale on the tubulars, general corrosion may not be a problem. However, if the H_2S partial pressure is greater than 0.05 psia, then stress corrosion cracking (SCC) may occur even if the general corrosion rate is low. In these cases, steel processing and its mechanical properties are governed by NACE MR0175 that place limits on hardness, strength, and steel processing. [31]

E.2.4.1.4 In environments containing little or no CO_2 but significant levels of H_2S [32] [33] [34] [35], steels may have tolerably low corrosion rates but be susceptible to environmental cracking if the steels are not processed properly. This processing requires limits on strength, hardness, cold work and other properties.

E.2.4.2 Stainless Steels (SS)

E.2.4.2.1 SS’s are alloys of primarily iron and chromium. Other elements may be added for strength, corrosion resistance, or for other reasons. In the presence of oxygen and water, these steels form a chromium oxide layer that does not easily corrode or stain, hence the stainless steel name. Chromium oxide forms a thin, tightly-packed film on the surface of the SS. This layer or passive film quickly "heals" if scratched or mechanically disturbed in the presence of oxygen. Chloride ions are known to disrupt the passive film, particularly at higher temperatures. While a minimum of 10.5 % chromium is required to be classified as stainless steel, typical chromium concentration is at least 11.5 %. However, 9Cr-1Mo has been used successfully in corrosive (wet CO_2), low temperature wells for many years. SS’s are classified according to their microstructure, e.g. ferritic, austenitic, martensitic. Ferritic steels are not commonly used in oilfield applications.

E.2.4.2.2 Austenitic stainless steel contains 16 % to 22 % chromium, 6 % to 12 % nickel, and a maximum of 0.15 % carbon. These steels are nonmagnetic and are not hardenable by heat treatment. The austenitic steels are strengthened through cold-working. These steels are used in oilfield applications either in the annealed or cold-worked (CW) condition. The annealed condition is low strength, hence used where high strength is not required such as in piping, vessels, or valves. CW austenitic SS are used where strength is required, usually in well components such as production tubing or equipment placed in wells.

CW austenitic SS may be susceptible to SCC; therefore, environmental limits of the steel are required before it is used. Annealed austenitic SS may also be susceptible to SCC, but it is usually used in low stress applications.

The most common types of austenitic steel are the AISI 304 and AISI 316 stainless steels. Their use in sour service is governed by NACE MR0175.

E.2.4.2.3 Martensitic stainless steel (MSS) contains 10.5 % to 18 % chromium, 0.2 % to 1 % molybdenum, 0 % to less than 2 % nickel, and 0.1 % to 1 % carbon. MSS are the most common oilfield stainless steels and all are magnetic. The alloy L80-13Cr or AISI 420 is the most common. MSS offer good resistance to CO_2 corrosion but have limited cracking resistance in sour environments. L80-13Cr is usually supplied at 80 ksi minimum yield strength. There are several modified martensitic grades with higher nickel and molybdenum to improve localized corrosion resistance, increase strength (minimum yield strength of 95 ksi and higher), and improve toughness. These modified or super 13Cr SS are also susceptible to SCC in certain environments. Their use in sour service is governed by NACE MR0175.

E.2.4.2.4 Duplex stainless steels (DSS) contain 23 % to 26 % chromium, 4 % to 8 % nickel, molybdenum, manganese, and less than 0.3 % carbon. DSS have both ferritic and austenitic microstructures present in roughly the same percentage, e.g. 50:50. In the annealed condition, these steels offer higher strength and slightly better corrosion resistance than austenitic stainless steels. Example of DSS include 22Cr, 25Cr, and S25Cr. These are used in both the annealed and CW condition. The annealed condition is low strength, hence used where high strength is not required as in piping, vessels, or valves. CW DSS are used where strength is required, usually in well components such as production tubing or equipment placed in wells. Their use in sour service is governed by NACE MR0175.

E.2.4.3 Nickel-based Alloys

E.2.4.3.1 Nickel-based alloys have nickel as the major element. The most common oilfield nickel alloys also contain chromium and molybdenum. The solid solution condition alloys, e.g. 825, G3, and C-276, are cold worked to high strength for tubing used in highly corrosive environments.

E.2.4.3.2 The precipitation hardened alloys, e.g. 925 and 718, are heat treatable to high strength. Higher molybdenum alloys, e.g. 725, 625+, and G3, are used in hotter and more severely corrosive environments. Their use in sour service is governed by NACE MR0175.

E.2.4.4 Strength and Hardness

E.2.4.4.1 The mechanical properties of oilfield alloys are derived from their chemistry and thermo-mechanical processing, e.g. hot or cold work, heat treat.

E.2.4.4.2 In general, higher strength and hardness results in a decrease in resistance to both SCC and sulfide stress cracking (SSC).

E.2.4.5 Oil Country Tubular Goods

E.2.4.5.1 The most common metallurgy for wellbore construction equipment is carbon or low-alloy steels. API 5CT for casing and tubing does not specify a chemical composition beyond placing limits on the sulfur and phosphorous contents at 0.030 % for the most common grades. Rather, the standards specify mechanical properties, dimensions, nondestructive examination, manufacturing requirements, etc. Examples of carbon and low-alloy steel pipes are listed in Table E.1.

Table E.1—Mechanical Properties of Selected Oil Country Tubular Goods

Grade	Yield Strength				Tensile Strength		Hardness
	min MPa	max MPa	min ksi	max ksi	min MPa	min ksi	Rockwell C
H40	276	552	40	80	414	60	[b]
J55	379	552	55	80	517	75	[b]
K55	379	552	55	80	655	95	[b]
N80 1	552	758	80	110	689	100	[b]
N80 Q	552	758	80	110	689	100	[b]
M65	448	586	65	85	586	85	22 max
L80 1	552	655	80	95	655	95	23 max
L80 9Cr	552	655	80	95	655	95	23 max
L80 13Cr [a]	552	655	80	95	655	95	23 max
C90	621	724	90	105	689	100	25.4 max
C95	655	758	95	110	724	105	[b]
T95	655	758	95	110	724	105	25.4 max
P110	758	965	110	140	862	125	[b]
Q125	862	1034	125	150	931	135	[b]

[a] The above grades are all carbon and low-alloy steels except L-80 13Cr. Other proprietary, non–API 5CT grades are also available. For CRA oil country tubular goods, see also API 5CRA. [29]

[b] API 5CT does not specify maximum hardness for these grades. The maximum variation for Q125 is restricted as a manufacturing control in accordance with API 5CT, Sections 7.8 and 7.9.

E.3 Corrosion Types

E.3.1 Corrosion and Well Integrity

E.3.1.1 The corrosion resistance of the materials used in wells, when in contact with clear brine, is an important factor in preserving the integrity of the well.

E.3.1.2 Due to the increased use of alloys such as modified MSS or DSS, the assessment of corrosion resistance of materials in clear brine has been critical. This subclause addresses the different corrosion and environmental cracking problems that may take place in the presence of clear brine. Also included are the test methods commonly used to assess the corrosion resistance of materials and the methods used to control and mitigate corrosion. Corrosion engineers and other specialists should be involved in the assessment of the risk of corrosion damage to completion materials.

E.3.1.3 Corrosion is the deterioration of a metal by electrochemical/physical interaction with its environment. Electrochemical cells are formed by the metallic hardware as the anode and cathode electrodes and brine as the electrolyte. Any metal surface is a composite of electrodes electrically connected through the body of the metal itself, completing the electrical circuit through the metal and the electrolyte.

E.3.1.4 The area of the metal where the oxidation reaction takes place is the anode. In this area, metal loss in the form of generalized or localized corrosion takes place.

E.3.1.5 The area of the metal where the reduction reaction takes place is the cathode. No metal loss is associated with the cathodic reaction. The cathodic reactions may involve oxygen when present or ionic hydrogen in absence of oxygen and at low pH. The atomic hydrogen formed on the metallic surface may be absorbed in the metal structure which may cause cracking (hydrogen embrittlement).

E.3.1.6 The corrosion process depends strongly on the metal concerned and the environment in which it is exposed. The material and environment should always be considered together when assessing the corrosion resistance of a material or the aggressiveness of the environment. The discussions apply to clear brines and the normally used metallurgy.

E.3.2 Dissolved Gases

E.3.2.1 Dissolved gases such as oxygen (from the surface), carbon dioxide, and hydrogen sulfide (from the reservoir) may cause corrosion or cracking problems depending on the environment (type of brine, temperature, pH, additional chemical, etc.), the type of material, its characteristics, and the applied stress in service.

E.3.2.2 The presence of hydrogen sulfide accelerates the absorption of the hydrogen atoms in the metal structure causing SSC in susceptible materials. Cracking can happen also in the absence of H_2S, but the probability of cracking metallic alloys increases in the presence of H_2S. Additionally, H_2S may increase the probability of pitting corrosion.

E.3.2.3 Carbon dioxide, like hydrogen sulfide, may contaminate annular brines, e.g. tubing-to-annulus leaks. The severity of this type of corrosion depends on the concentration of the CO_2 in solution, composition of the brine, temperature, etc. CO_2 can cause general or localized corrosion.

E.3.2.4 Oxygen is a very corrosive agent for most of the metallic alloys used in well completion and can be deleterious even at concentrations as low as 50 µg/kg. Oxygen can come in contact with the brine by air entering the fluid at the surface during circulation or by air entering the well annulus at the surface. Dissolved oxygen in brine fluids is rarely greater than 8 mg/kg. It can be rapidly depleted by the corrosion process on carbon steel, e.g. casing. The time it is present may be sufficient to cause severe corrosion and/or cracking, e.g. an annular gas cap containing oxygen.

E.3.3 Brine Characteristics

E.3.3.1 The pH of brine is another very important factor. Generally, the corrosivity of the brine increases with the decrease in pH. An example of low pH brine is zinc bromide ($ZnBr_2$), with a specific gravity above 2.10 (17.5 lb/gal).

E.3.3.2 Halide ions, in particular chloride ions, can be detrimental to the corrosion resistance of CRA. The deleterious effect normally increases with concentration and temperature. The presence of chloride ions is known to cause pitting and SCC of the 300 series stainless steels and other CRAs with intermediate levels of nickel, e.g. super martensitic (S13Cr) and duplex (22Cr) stainless steels.

E.3.3.3 Other sources of corrosive species include formation fluids and contaminants left in the wellbore or introduced into the brine. Drilling fluid residues, acid gases, formation water, oxygen, inhibitors for corrosion, hydrate and/or scale, oxygen scavengers, biocides and stimulation fluids are some examples of the possible contaminants. These materials can be corrosive or degrade and produce corrosive by-products. Organic acids, such as naphthenic, acetic acids, etc., indigenous to formation fluids can also promote corrosion.

E.3.3.4 Temperature has a strong effect on the corrosion process. Generally, the increase in temperature increases the initial corrosion rate. There are cases where lower temperatures are more dangerous as in the case of hydrogen embrittlement or where there is a temperature of maximum susceptibility, as in DSS at above 90 °C (195 °F).

E.3.3.5 The corrosion process depends on many factors, some already mentioned and others that have to do with the transport phenomena, electrochemical reaction rates, protective films formed on the steel surface (like iron sulfide and iron carbonate films), etc. Corrosion engineers and other specialists should be involved in the assessment of the risk of corrosion damage to completion materials and adopt the necessary measures to control or mitigate corrosion and environmental cracking.

E.3.4 Corrosion Forms

E.3.4.1 Aqueous Systems

In aqueous systems such as brines, general and localized corrosion may take place.

E.3.4.2 General Corrosion

E.3.4.2.1 General corrosion is a form of corrosion that attacks large areas of the metal surface. An example is corrosion of carbon steel in low pH brines.

E.3.4.2.2 The risk and rate of general corrosion increases with increasing CO_2 concentration, decreasing pH, and increasing temperature.

E.3.4.3 Localized Corrosion

E.3.4.3.1 Localized corrosion can be in the form of pitting, crevice corrosion, selective attack, and cracking of the metal (SCC, SSC, hydrogen embrittlement, corrosion fatigue, etc.).

E.3.4.3.2 Localized corrosion occurs where there are actively corroding areas surrounded by passive, noncorroding areas.

E.3.4.4 Pitting Corrosion

E.3.4.3.1 Pitting corrosion is a form of localized corrosion that has the morphology of cavities that start at the metal surface.

E.3.4.4.2 Pitting may affect wide areas of the metal or be limited to a few locations. The penetration rate and the geometry of the caverns (pits) vary widely depending on the material and the environment in which it is exposed. Pitting corrosion is typical for materials that owe their corrosion resistance to the formation of passive films, e.g. CRA.

E.3.4.4.3 Chloride and other halides, high temperature, low pH, and deposits on the metal surface are factors that increase the risk of pitting corrosion. The pits initiate where the metallic surface is weaker, i.e. where inclusions or surface imperfections are present, where the protective film is physically or chemically damaged, or other factors. It is not possible to accurately predict the penetration rate of the pits, and for this reason, materials should be selected that are fully resistant to pitting corrosion in a given environment.

E.3.4.5 Crevice Corrosion

E.3.4.5.1 Crevice corrosion is a form of corrosion that takes place in crevices formed on the metal surface, like at the coupling of tubulars or downhole equipment.

E.3.4.5.2 The phenomenon has a similar mechanism to pitting corrosion but differs in the initiation process. The effect of the environmental parameters is the same as those mentioned above for pitting corrosion. The preferred mitigation method is to use sufficiently corrosion-resistant materials.

E.3.4.6 Galvanic (Bimetallic) Corrosion

E.3.4.6.1 Galvanic (bimetallic) corrosion occurs when two metals of different composition are in electrical contact in an electrolyte.

E.3.4.6.2 The more active (less noble) metal will corrode (anodic reaction), while the more noble (passive) metal will be the site of cathodic reaction.

E.3.4.6.3 When there is substantial potential difference between the two coupled materials, the effect can be deleterious not only to the less noble material where corrosion will be accelerated but also to the more noble material where the formation of atomic hydrogen (cathodic reaction) may cause hydrogen damage.

E.3.4.6.4 Galvanic corrosion is not common in oxygen-free brine, and failures in completion brines have not been reported.

E.3.4.7 Erosion and Erosion-corrosion

E.3.4.7.1 Erosion and erosion-corrosion forms of damage are an issue during drilling. Erosion and erosion-corrosion are caused by fluid movement over a metal surface such as high velocity conditions, turbulence, and impingement with sand and/or other suspended solids.

E.3.4.7.2 Erosion-corrosion is characterized by smooth-bottomed shallow pits. As it progresses, a directional pattern related to the path taken by the erodent as it moves over the metal surface may be exhibited. Erosion and erosion-corrosion damage is not normally an issue in packer fluids as the fluid is stagnant.

E.3.4.8 Stress Corrosion Cracking (SCC)

E.3.4.8.1 SCC is a form of corrosion that takes place when the following three factors are present concurrently:

a) a corrosion environment,

b) tensile stresses (applied or residual),

c) a susceptible material.

E.3.4.8.2 The presence of high chloride concentration, or other halide ions, hydrogen sulfide, high temperatures, or low pH increase the risk of this form of corrosion.

E.3.4.8.3 The methods of preventing SCC include reducing tensile stresses, mitigating the corrosive environment, or selecting more resistant materials. Generally, high-strength alloys are more susceptible to SCC than low-strength alloys.

E.3.4.9 Hydrogen Embrittlement

E.3.4.9.1 Hydrogen embrittlement occurs when free hydrogen atoms are generated on a metal surface. Individual hydrogen atoms (H^+) can be absorbed into the metal microstructure, or they can combine to form gaseous molecular hydrogen (H_2), which does not enter the metal.

E.3.4.9.2 In susceptible metals, the atoms that enter the metal crystalline structure can accumulate in high tensile stress zones and deteriorate fracture resistance. The result may be cracking of the material depending upon factors such as temperature, hydrogen concentration, and stress level.

E.3.4.9.3 Hydrogen embrittlement is normally worse at low temperature, that is 20 °C (70 °F) or below.

E.3.4.10 Sulfide Stress Corrosion (SSC)

E.3.4.10.1 SSC is a form of hydrogen embrittlement. In the presence of hydrogen sulfide, the sulfide ion reduces the rate at which the hydrogen atoms combine to form hydrogen gas.

E.3.4.10.2 This exposes the metal surface to atomic hydrogen for a longer time and a larger percentage of the hydrogen atoms enter the metal. This can result in SSC when the material is under tensile stress, either applied or residual.

E.3.4.10.3 The resistance of different alloys to this type of corrosion varies widely. Temperature has an important role in the resistance of the material.

E.3.4.11 Fatigue and Corrosion-fatigue

E.3.4.11.1 Fatigue and corrosion-fatigue cause damage due to the repetitive stresses over time that initiate and propagate cracks. The fatigue limit is the number of stress cycles to failure and is a function of stress, material, and operating environment.

E.3.4.11.2 The fatigue limit or the time to failure will be reduced if the material is exposed to an aggressive environment that promotes corrosion fatigue. Materials to be used under cyclic stress, e.g. drillstring, coil tubing, etc., should be tested for fatigue resistance in an environment that simulates the service conditions.

E.3.4.12 Microbiologically Induced Corrosion (MIC)

E.3.4.12.1 MIC may occur when bacteria grow on the metal surface forming a biofilm, see E.5.5.

E.3.4.12.2 The environment under the biofilm may become quite different from the bulk solution and become very corrosive to the material. MIC may happen in some brines and the use of biocides may become necessary to prevent the growth of bacteria and consequently the onset of MIC.

E.4 Corrosion Testing Methods

E.4.1 Weight-loss Test Method

E.4.1.1 The weight-loss test consists of corrosion coupons immersed in brine in conditions (temperature, pH, acid gases, etc.) that simulate the service conditions. An important variable that should match the actual well parameter is the brine volume to metal surface area ratio, and it is applicable to all corrosion test methods. The results are evaluated by visual examination normally with the help of a stereo microscope and by weighing the material before and after the exposure.

E.4.1.2 To calculate a corrosion rate, the surface area of the coupon must be measured before exposure. The difference between the original weight and the after-test weight is converted to a corrosion rate in terms of total thickness lost per year, millimeters per year (mm/y), or mils per year (mpy).

E.4.1.3 Weight-loss tests are conducted for at least 7 days, but most commonly for 30 days. Longer durations have been used as well. Tests should be conducted with duplicate or triplicate coupons per exposure.

E.4.1.4 The metal coupon is visually examined for surface conditions, especially for evidence of pitting corrosion and pit depth, etching, and other forms of localized corrosion. Microscopic, scanning electron microscope (SEM), and other surface monitoring techniques are often used to examine the test coupon. Pit distribution and dimensions are measured.

E.4.2 Galvanic (Bimetallic) Corrosion Method

E.4.2.1 Galvanic testing is conducted similarly to the weight-loss testing described in E.4.1. Before submersion in the test brine, dissimilar metals are electrically coupled together. The relative surface area of the two coupons can impact the corrosion rate of each coupon and is taken into account during the design of the test.

E.4.2.2 Surface area ratios generally reflect the localized ratios anticipated in the target well. Duration of the test is similar to a standard weight-loss test, and the individual coupons are treated and evaluated after the test as described in E.4.1.3 and E.4.1.4.

E.4.2.3 The corrosion and/or penetration rate of the more active metal can be significantly greater than that obtained from standard weight-loss testing.

E.4.3 Crevice Corrosion Method

E.4.3.1 Crevice corrosion tests are similar to the galvanic corrosion test in E.4.2. However, the crevice is formed using the same metal or a nonconducting washer attached to the coupon with a nonconducting or insulated metal fastener.

E.4.3.2 Typically, the washer has eight or more fingers radiating outward from the center. The corrosion pattern that results under the fingers can be used to quantitatively evaluate the crevice corrosion attack.

E.4.3.3 Tests are typically conducted for 30 days. Results are often reported as the depth of attack and the number of fingers that resulted in crevice corrosion over the total number of fingers. For example, if crevice corrosion was evident under three out of eight fingers, then it would be reported as 3/8.

E.4.4 SCC Methods

E.4.4.1 The procedures used to assess the resistance of a material to SCC, SSC, and hydrogen embrittlement are similar. There are different methods to stress the specimens. This is achieved by the application of:

a) constant load;

b) constant strain, e.g. smooth tensile, three or four point bent-beam, C-ring U-bend specimens, and double cantilever beam;

c) slowly increasing strain, e.g. slow strain rate technique.

E.4.4.2 Bent-beam and C-ring specimens are commonly used to assess the resistance of various alloys in completion brines at high temperatures due to their compact dimensions that make it easy to place them in autoclaves. The slow strain rate technique is often used for quality control, screening, and/or ranking materials with respect to their corrosion resistance.

E.4.4.3 Stress tests are typically conducted with an applied stress equal to some percent of its yield stress, up to and including 100 %. The system is pressurized with the appropriate gas or gases and heated to the target temperature. This temperature is maintained throughout the test duration, which is usually 30 days.

E.4.4.4 The specimens are visually examined for cracks and surface defects. Stereoscopes, metallographs, and SEMs are frequently used to examine the test coupon for subtle indications of "cracking" and to view freshly cut surfaces. Any crack by any of the above methods is considered a failure.

E.4.4.5 SCC testing can also be conducted with galvanic coupling or a crevice that is usually affixed to the point of maximum stress or to some other area.

E.4.5 Electrochemical Corrosion Testing Method

E.4.5.1 Short-term electrochemical test methods are available to evaluate the effectiveness of corrosion control. These short-term methods are generally run in addition to long-term corrosion test methods conducted with oilfield metal for 7 to 30 days or more.

E.4.5.2 These short-term methods usually take less than a day, and they provide useful information for the corrosion specialist. Test methods include linear polarization, potentiodynamic, and impedance measurement methods. Electrochemical data is more widely accepted when validated by long-term corrosion tests or field history.

E.4.6 Corrosion Testing of Brine Fluids

E.4.6.1 Various standards and methods are available to conduct corrosion tests for brine fluids. Listed in E.4.6.2 through E.4.6.4 are several references to standard test methods by NACE, ASTM, and ISO.

E.4.6.2 ISO Test Methods

ISO 7539-1, *Corrosion of metals and alloys—Stress corrosion testing—Part 1: General guidance on testing procedures*

ISO 7539-2, *Corrosion of metals and alloys—Stress corrosion testing—Part 2: Preparation and use of bent-beam specimens*

ISO 7539-5, *Corrosion of metals and alloys—Stress corrosion testing—Part 5: Preparation and use of C-ring specimens*

ISO 7539-7, *Corrosion of metals and alloys—Stress corrosion testing—Part 7: Method for slow strain rate testing*

E.4.6.3 NACE Test Methods

TM0169, *Laboratory corrosion testing of metals*

TM0171, *Autoclave corrosion testing of metals in high temperature* (withdrawn)

TM0177, *Laboratory testing of metals for resistance to sulfide stress cracking and stress corrosion cracking in* H_2S *environments*

TM0270, *Method of conducting controlled velocity laboratory corrosion tests (withdrawn)*

TM0274, *Dynamic corrosion testing of metals in high temperature (withdrawn)*

E.4.6.4 ASTM Test Methods

a) Pitting corrosion:

- G46, *Standard guide for examination of evaluation of pitting corrosion*;

- G48, *Standard test methods for pitting and crevice corrosion resistance of stainless steels and related alloys by use of ferric chloride solution.*

b) Crevice corrosion:

- G48, *Standard test methods for pitting and crevice corrosion resistance of stainless steels and related alloys by use of ferric chloride solution*;

- G78, *Standard guide for crevice corrosion testing of iron-base and nickel-base stainless alloys in seawater and other chloride containing aqueous environments.*

c) Stress corrosion:

- G30, *Standard practice for making and using U-bend stress-corrosion test specimens*;

- G38*, Standard practice for making and using C-ring stress-corrosion test specimens*;

- G39*, Standard practice for preparation and use of bent-beam stress-corrosion test specimens*;

- G123, *Standard test method for evaluating stress-corrosion cracking of stainless alloys with different nickel content in boiling acidified sodium chloride solution.*

d) Galvanic corrosion:

- G83, *Standard test method for wear testing with a cross-cylinder apparatus.*

e) Erosion corrosion:

- G73*, Standard practice for liquid impingement erosion testing.*

f) Electrochemical test measurements:

- G3*, Standard practice for conventions applicable to electrochemical measurements in corrosion testing*;

- G96*, Standard guide for on-line monitoring of corrosion in plant equipment (electrical and electrochemical methods)*;

- G102*, Standard practice for calculation of corrosion rates and related information from electrochemical measurements.*

g) Potentiodynamic polarization resistance:

- G5*, Standard reference test method for making potentiostatic and potentiodynamic anodic polarization measurements*;

- G59, *Standard method for conducting potentiodynamic polarization resistance measurements*;

- G61, *Standard test method for conducting cyclic potentiodynamic measurements for localized corrosion susceptibility of iron-, nickel-, or cobalt-based alloys.*

E.5 Control of Corrosion

E.5.1 Control of corrosion is accomplished through the selection of materials and fluids, the use of inhibitors, scavengers, and biocides, and the elimination of contaminants.

E.5.2 Materials Selection

E.5.2.1 Proper materials, i.e. metallurgy, selection is essential. The use of compatible tubulars and fluids can greatly reduce the risk of corrosion.

E.5.2.2 CRA have been developed for use in corrosive and sour environments.

E.5.2.3 Strength requirements, relevant temperature, and well environment, including the formation water composition and the partial pressures of acid gases, are some of the factors that influence the choice of materials.

E.5.3 Fluids Selection

E.5.3.1 A proper fluid that will reduce the likelihood of corrosion can be selected for use according to the requirements of the operation.

E.5.3.2 The choice of a proper fluid is driven by operational requirements and material compatibility.

E.5.4 Corrosion Inhibitors

E.5.4.1 Corrosion inhibitors are used for controlling general corrosion. Inhibitors can be protective by either physically filming the metal surface or by chemically passivating the surface.

E.5.4.2 In either case, the metal surface is protected or partially protected from the corrosive fluid environment thus lowering the corrosion.

E.5.4.3 Common inhibitors are often blends or derivatives of organic amines such as quaternary amines, imidazoline, morpholine, alkylpyridine, etc. It is essential to take care in the selection of the corrosion inhibitor to avoid introducing the risk of cracking, e.g. thiocyanate.

NOTE Careful formulation and dosing of treatment packages are essential to avoid increased risk of corrosion.

E.5.5 Scavengers

E.5.5.1 Additives that mitigate or remove corrosive constituents from the fluid are available to treat for small amounts of dissolved oxygen, carbon dioxide or hydrogen sulfide.

E.5.5.2 These additives include sulfites, bisulfites, erythorbates, phosphates/alkyl phosphates, salts, amine compounds, etc. The compatibility of the materials and chemicals is important. For instance, sulfite- and bisulfite-oxygen scavengers should be limited to use in monovalent brines as they will precipitate in divalent brines.

NOTE Careful formulation and dosing of treatment packages is essential for avoiding increased risk of corrosion.

E.5.6 Biocides

E.5.6.1 MIC may be treated with biocides that control bacteria (aerobic and anaerobic), fungi, algae, etc.

E.5.6.2 Microorganisms can produce biofilms that coat metal surfaces, and anaerobic bacteria can reduce sulfate to hydrogen sulfide. This not only increases the corrosivity of the fluid but also causes the formation of tubercles that accelerate corrosion through the formation of concentration cells.

E.5.6.3 Bacteria also produce organic acids that initiate or accelerate corrosion on the metal surface beneath the colonies.

E.5.6.4 Enzymes are produced that can increase the corrosion rate by direct participation in the electrochemical process.

NOTE Careful formulation and dosing of treatment packages is essential for avoiding increased risk of corrosion.

E.5.7 Elimination of Contaminants

E.5.7.1 Various contaminants can cause or accelerate corrosion. It has already been mentioned that dissolved or entrained oxygen can induce corrosion and contaminate brines and often needs to be eliminated or significantly reduced.

E.5.7.2 Other contaminants, which may need to be reduced or eliminated, include aqueous acids, thiocyanates, sulfur-containing reducing and oxidizing agents, and oxidants.

Bibliography

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