This is the ballot draft for API RP 13J, 6th Edition

Testing of Heavy Brines

1 Scope

This standard 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.

This standard 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 at which the brines make the transition between liquid and solid at atmospheric pressure (a discussion of crystallization temperature under pressure is provided Annex C), the pH, iron contamination, and buffering capacity. This standard also contains a discussion of gas hydrate formation and mitigation, brine viscosity, corrosion testing, crystallization temperature under pressure, and a daily completion fluids report with example (Annex A).

This standard 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 standard. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

API RP 13B-1, *Field Testing Water-based Drilling Fluids*

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

ASTM E617, *Standard Specification for Laboratory Weights and Precision Mass Standards*

NIST[2] SRM 185h, *Potassium Hydrogen Phthalate, pH Standard*

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

NIST SRM 191C, *pH Standard*

NIST SRM 3126a, *Iron Standard Solution*

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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   Terms, Definitions, Acronyms, Abbreviations, and Symbols

3.1   Terms and Definitions

For the purposes of this standard, 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).

3.1.2
calibration
The verification of an instrument or to the adjustments made to the instrument if it is out of calibration.

 NOTE   In this standard, the word "calibrate" refers to instruments that, if not calibrated, as shown by "verification" of instruments that can be adjusted to bring them back into calibration. The word "calibrate" also refers to instruments that cannot be adjusted if they are inaccurate and to determine their correction factors.

3.1.3
converted density
Density of the brine at the reporting temperature, 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
corrected relative density
Measured density or relative density 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
measured relative density
Density or relative 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 (SG) hydrometer
relative density hydrometer
Common hydrometer measuring the relative density (specific gravity) of a liquid: the density of the liquid at a reference temperature (60 °F) to the density of distilled water at a reference temperature (60 °F) (i.e., relative density 60 °F/60 °F).

NOTE 1   The standard reference temperature can be taken at 15.56 °C

NOTE 2   Density hydrometers provide a direct measurement of the density of a liquid at a reference temperature.

3.1.9
relative density
Dimensionless ratio of the mass of a volume of an object substance to the mass of the same volume of a reference substance, i.e., the ratio of their respective mass densities.

NOTE 1   Generally speaking, the reference substance is pure water.

NOTE 2   Relative density is commonly known as specific gravity.

3.1.10
user
Manufacturer, service company, end user, or operator applying the testing of this part of this standard.

3.2   Acronyms and Abbreviations

ACS   American Chemical Society

AISI   American Iron and Steel Institute

ANSI   American National Standards Institute

CAS   Chemical Abstracts Service

CRA   corrosion-resistant alloy

CW   cold-worked

DSS   duplex stainless steel

FCTA   first crystal to appear

ISO   International Organization for Standardization

LCTD   last crystal to dissolve

meq_{ACID} milliequivalents of hydrochloric acid

mL_{BRINE} milliliters of brine

MIC   microbiologically induced corrosion

MSS   martensitic stainless steel

MTALC   maximum temperature after last crystal

NACE   National Association of Corrosion Engineers

NTU	nephelometric turbidity unit
PCT	pressure crystallization temperature
psi	pound-force per square inch
SCC	stress corrosion cracking
SG	relative density (specific gravity)
SS	stainless steel
SSC	sulfide stress cracking
TCT	true crystallization temperature
TD	to deliver

3.3 Symbols

B_c	density-measuring device-correction curve intercept, expressed in measuring-device density unit
C	brine density conversion factor, expressed in grams per milliliter and per degrees Celsius
$C_{P,SI}$	pressure compensation factor, expressed in (kilograms per cubic meter and per megapascal [(kg/m^3)/MPa]
$C_{P,USC}$	pressure compensation factor, expressed in pounds per gallon and per 1000 pounds-force per square inch ([lb/gal]/kpsi)
C_{SI}	brine density conversion factor, expressed in kilograms per cubic meter and per degrees Celsius
C_{USC}	brine density conversion factor, expressed in pounds per gallons and per degrees Fahrenheit
C_g	glass expansion/contraction correction factor, expressed in grams per milliliter or dimensionless
$C_{\theta,SI}$	temperature compensation factor, expressed in (kilograms per cubic meter and per 100 degrees Celsius [(kg/m^3)/100°C]
$C_{\theta,USC}$	temperature compensation factor, expressed in pounds per gallon and per 100 degrees Fahrenheit [(lb/gal)/100°F]
c_{B1}	first buffer concentration, expressed in milliequivalents of acid per milliliter of brine (meq$_{ACID}$/mL$_{BRINE}$)
c_{B2}	second buffer concentration, expressed in milliequivalents of acid per milliliter of brine (meq$_{ACID}$/mL$_{BRINE}$)
c_{KHCO_3}	concentration of titratable basic species, expressed in kilograms per cubic meter or in pounds per barrel of potassium bicarbonate
$c_{K_2CO_3}$	concentration of titratable basic species, expressed in kilograms per cubic meter or in pounds per barrel of potassium carbonate

c_{Na2CO_3}	concentration of titratable basic species, expressed in kilograms per cubic meter or in pounds per barrel of sodium carbonate
c_{NaHCO_3}	concentration of titratable basic species, expressed in kilograms per cubic meter or in pounds per barrel of sodium bicarbonate
F_c	is the density-measuring device-correction factor, expressed in measuring-device density unit
$h_{TVD,SI}$	true vertical depth, expressed in meters
$h_{TVD,USC}$	true vertical depth, expressed in feet
M_{HCl}	molarity of the hydrochloric acid used, expressed in moles per liter
m_S	mass of total suspended solids, expressed in milligrams per liter
m_{S-nv}	mass of total non-volatile solids or residue, expressed in milligrams per liter
m_{S-v}	mass of total volatile solids, expressed in milligrams per liter
m_1	original mass of pan and glass-fiber filter, expressed in milligrams
m_2	final mass of pan, glass-fiber filter and residue, expressed in milligrams
m_3	mass of porcelain evaporating dish and filter medium, expressed in milligrams
m_4	mass of porcelain evaporating dish and filtered sample after drying at 105 °C (220 °F), expressed in milligrams
m_5	mass of porcelain evaporating dish and filtered sample after auto-ignition at 550 °C (1000 °F), expressed in milligrams
$P_{hyd-h_{TVD},SI}$	hydrostatic pressure in the wellbore, expressed in kilopascals
$P_{hyd-h_{TVD},USC}$	hydrostatic pressure, in the wellbore, expressed in pounds-force per square inch
R	density hydrometer corrected reading at measured temperature, expressed in grams per milliliter
R_{SG}	SG hydrometer corrected reading at measured temperature, dimensionless
R_1	average density reading at the lower bath temperature
R_2	average density reading at the higher bath temperature
V_{A-HCl}	volume of hydrochloric acid used to the first endpoint or target pH, expressed in milliliters
V_{B-HCl}	volume of hydrochloric acid used to reach the second endpoint or target pH, expressed in milliliters
V_{HCl}	volume of hydrochloric acid added, expressed in milliliters
V_s	volume of brine sample, expressed in milliliters

Z_c	density-measuring device-correction curve slope, expressed in measuring device unit per either degrees Celsius or per degrees Fahrenheit
$\Gamma_{DFG,SI}$	drilling fluid gradient expressed in kilopascals per meter
$\Gamma_{DFG,USC}$	drilling fluid gradient expressed in ponds-force per square inch and per foot (psi/ft) calculated from density expressed in pounds per gallon
$\Gamma_{DFG,USC-2}$	drilling fluid gradient, expressed in pounds per square foot, calculated from density in pounds per cubic foot
ΔpH	change in pH after addition of hydrochloric acid aliquot (dimensionless)
ΔV_{HCl}	volume of hydrochloric acid aliquot addition, expressed in milliliters
$\theta_{BH,SI}$	brine temperature measured at bottom hole, expressed in degrees Celsius
$\theta_{BH,USC}$	brine temperature, measured at bottom hole, expressed in degrees Fahrenheit
θ_{Ref}	sample reference temperature of hydrometer, expressed in degrees Celsius or Fahrenheit
$\theta_{Surf,SI}$	brine temperature measured at the surface or assumed to be 20 °C, expressed in degrees Celsius
$\theta_{Surf,USC}$	brine temperature measured at the surface or assumed to be 70 °F, expressed in degrees Fahrenheit
θ_m	measurement temperature, expressed in degrees Celsius or Fahrenheit
$\theta_{m,SI}$	measured temperature, expressed in degrees Celsius
$\theta_{m,USC}$	measured temperature, expressed in degrees Fahrenheit
θ_1	average temperature at the lower bath temperature, expressed in degrees Celsius or Fahrenheit
θ_2	average temperature at the higher bath temperature, expressed in degrees Celsius or Fahrenheit
θ_{1-SI}	lower temperature, expressed in degrees Celsius
θ_{2-SI}	higher temperature, expressed in degrees Celsius
ρ	corrected density, expressed in grams per milliliter
ρ_{SI}	density, expressed in kilograms per cubic meter
ρ_{USC}	density, expressed in pounds per gallon
ρ_{USC-2}	density, expressed in pounds per cubic foot
$\rho_{av,SI}$	average brine density in the wellbore, expressed in kilograms per cubic meter
$\rho_{av,USC}$	average brine density in the wellbore, expressed in pounds per gallon
$\rho_{Surf,SI}$	brine density at the surface, expressed in kilograms per cubic meter

$\rho_{\text{Surf,USC}}$	brine density at the surface, expressed in pounds per gallon
ρ_1	corrected density at lower temperature, expressed in grams per milliliter
ρ_2	corrected density at higher temperature, expressed in grams per milliliter
ρ_{20}	density at 20 °C, expressed in grams per milliliter
$\rho_{20,\text{SI}}$	converted density at 20 °C, expressed in kilograms per cubic meter
$\rho_{70,\text{USC}}$	converted density at 70 °F, expressed in pounds per gallon
ρ_{θ_m}	density at measurement temperature θ_m, expressed in grams per milliliter
$\rho_{\theta_\text{m},\text{SI}}$	density at measurement temperature θ_m, expressed in kilograms per cubic meter
$\rho_{\theta_\text{m},\text{USC}}$	density at measurement temperature θ_m, expressed in pounds per gallon

4   Requirements

4.1   Quality Control Instructions

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

4.2   Records Retention

Records specified in this standard 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 when deemed appropriate.

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

5.1.3   The user shall maintain and use laboratory equipment and reagents that prevent measurement uncertainty and meet the 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:

a)   document and maintain calibration records for laboratory equipment;.

b)   periodically review these records for trends, sudden shifts, or other signals of approaching malfunction, and;

c)   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, shall be used. Shelf life shall not exceed the manufacturer's recommendation., If no recommendation is stated, than shelf life shall not exceed 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.

5.2.2   Distilled or Deionized Water

The user shall develop, document, and implement a method to determine resistivity or conductivity of water. The water shall not be used if resistivity is less than 18.2 milliohms or conductivity is greater than 0.055 microsiemens.

5.3   General Requirements for Calibration of Particular Apparatus

5.3.1   Volumetric Glassware

Calibration of laboratory volumetric glassware used for testing, including flasks, graduated cylinders, and pipettes, is generally performed by the glassware manufacturer or supplier. Users of products in accordance with this standard shall document evidence of glassware calibration prior to use. Manufacturer or supplier certification of calibration shall be acceptable. In the absence of manufacturer or supplier certification, calibration shall be performed gravimetrically using a procedure based on API RP 13B-1 and meeting the product specification. Periodic recalibration shall not be 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, or international equivalent standard body or, certified master instrument in accordance with ASTM E77 or to equivalent national or international standard(s) 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 E617 Class 1, 4, or 6 or better weights, depending on the specifications for the balance accuracy. In accordance with good laboratory practices, good management practices, or ISO quality management standards, balances shall be serviced and adjusted whenever calibration indicates a problem.

If ASTM E617 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 or 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 national or international standard and according to the equipment manufacturer's recommendations.

5.3.5   Density Meter

The user shall calibrate each density meter to a known national or 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. After calibration, note and record each density meter 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 at least according to manufacturer recommendation and user specified.

5.5 Calibration/Verification—Temperature-measuring Device

Calibration verification of temperature-measuring devices shall be performed as per the following.

a) Place the temperature-measuring device 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.

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

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

d) 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 0.5 °C (1 °F), or the smallest scale division on the temperature-measuring device being calibrated.

e) If the manufacturer of the temperature-measuring device recommends test calibration at multiple temperatures, repeat item a) through item b) in water baths at multiple temperatures.

f) 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.

5.6 Calibration/Verification—Density-measuring Device

NOTE   Calibration/verification procedure is applicable to density as well as to relative density measuring devices.

5.6.1 Calibration Procedure

Each density-measuring device to be used shall be calibrated against a national or international traceable standard density-measuring device. Calibration shall be performed using the same test solution in the anticipated density range at temperatures spanning the anticipated test temperatures.

Each density-measuring device shall be calibrated using the following method.

a) Prepare 1 L of test solution of the relevant density.

b) 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 density-measuring device and wait at least 5 min for the device and solution to reach the bath temperature, as measured by equilibrium of the solution temperature.

c) Read and record the reading obtained by the density-measuring device. 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.

d) Repeat item b) through item c) using the density-measuring device to be calibrated.

e) Calculate the average density-measuring device reading and designate this as R_1. Calculate the average temperature reading and designate it as θ_1.

f) Repeat item b) through item c) with the bath temperature set to the highest expected test temperature. Calculate average density-measuring device and temperature readings and designate these readings as R_2 and θ_2.

5.6.2   Correction Curve

The density-measuring device-correction curve should be defined by the curve slope and its intercept.

a) The density-measuring device-correction curve slope, Z_c, shall be calculated using Equation (1).

$$Z_c = \frac{R_1 - R_2}{\theta_2 - \theta_1}$$

(1)

where:

Z_c is the density-measuring device-correction curve slope, expressed in measuring device density unit per either °C or °F;

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

R_2 is the average density 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 °C or °F and all measurements and calculations are consistent in units.

Density reading may be according to the measuring-device in calibration/verification a density expressed in g/mL (g/cm³) or any density units, or a relative density (dimensionless).

b) The density-measuring device-correction curve intercept, B_c, shall be calculated using Equation (2).

$$B_c = (Z_c \times \theta_1) + (R_1 - 1)$$

(2)

where:

B_c is the density-measuring device-correction curve intercept expressed in measuring-device density unit;

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

Z_c is the density-measuring device-correction curve slope, expressed in measuring device density unit per either °C or °F;

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

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

c) Record Z_c, B_c, and density-measuring device serial number in a permanent calibration record.

5.6.3 Calibration Correction Factor

Z_c and B_c can be used to calculate the appropriate correction factor at a specific measurement temperature using Equation (3).

$$F_c = \left(Z_c \times \theta_m\right) + B_c \tag{3}$$

where:

F_c is the density-measuring device-correction factor, expressed in density-measuring device unit

Z_c is the density-measuring device-correction curve slope, expressed in measuring-device density unit per either °C or °F;

θ_m is the specific measurement temperature, expressed in either °C or °F;

B_c is the density-measuring device-correction curve intercept, expressed in measuring-device density unit.

Correction factor F_c should be subtracted from density or relative density readings obtained at that specific measurement temperature.

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 relative density (specific gravity) or pressure gradient. Relative density 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 relative density 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 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 kilopascals per meter (kPa/m). In USC units, it is expressed in pounds-force per square inch, per foot [(lbf/in.²)/ft or commonly 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, the procedures outlined in API RP 13B-1 should 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.

6.1.5   The pressurized and atmospheric 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 meters shall be used instead of a mud balance. The procedures specified in API RP 13B-1 shall use mud balances.

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 meters 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).

6.2   Apparatus

6.2.1   Set of calibrated glass hydrometers, which cover the density or relative density 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 relative density unit (dimensionless). Refer to section 5.5.2 for hydrometer calibration verification method.

NOTE   Hydrometers graduated in kg/m^3 or lb/gal are not common oilfield apparatuses.

The hydrometer is a weighted bulb with a graduated stem. Two types of hydrometers can be used: density hydrometers (density meter) and relative density hydrometers [specific gravity (SG) hydrometer]. 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 the temperature correction and/or conversion factors if required.

Each type of hydrometer is identified with:

— the reference temperature at which the measurement is made, called the sample reference temperature;

and, in addition for SG hydrometers:

— the reference temperature at which the reference material is 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 SG hydrometer reference temperatures are 20 °C/4 °C and 20 °C/20 °C (often with one temperature written directly above the other).

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

NOTE 2   Most SG 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 SG 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. Most density hydrometers are graduated with a reference temperature of 20 °C.

Freshly filtered samples should be used.

NOTE   Any oil present in the sample will interfere with the measurement.

The following information shall be permanently and legibly marked on the hydrometer.

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

2) The sample reference temperature for the SG hydrometer measurement (e.g., 20 °C, 60 °F) and the reference temperature for the reference standard (e.g., 15.56 °C, 60 °F). For 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.

   N0TE   M50 hydrometers are providing an accuracy of ±0.001, at least series M100 and S50 are required.

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 shall be applied first to the measurement whenever the measurement is made at a temperature different from the sample reference temperature (see 6.4).

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 Relative density hydrometer (SG hydrometer)

The sample reference temperature and the reference material reference temperature when using a SG hydrometer, are typically 15.56 °C (60 °F). SG hydrometers are like density hydrometers and have a graduated stem with dimensionless graduations in relative density units not greater than 0.002. Brine temperature shall be recorded to apply temperature correction and/or conversion factors if needed.

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

The measurement is the 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.

NOTE   The density of the reference material deaerated distilled water, for the most popular SG hydrometer (60 °F/60 °F) used for oilfield brine measurements is 0.999 g/mL (8.337 lb/gal) (see 6.4).

When converting the measured relative density 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, qualitative hardened lint-free cotton linter filter paper designed for laboratory filtration.

6.3   Measurement of Relative Density or Density using a Hydrometer

This procedure is applicable for both density and SG hydrometers. Measurement shall be done as per the following procedure.

a)   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.

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

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

d)   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 1.
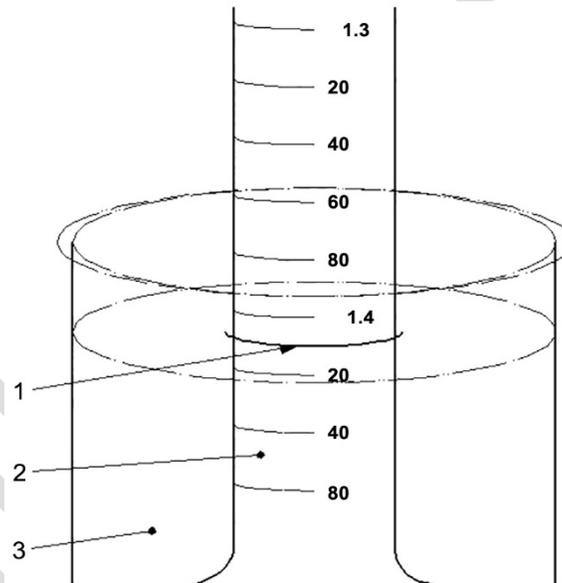
Key

1   reading at bottom of meniscus
2   hydrometer
3   sample

Figure 1—Hydrometer Reading at Bottom of Meniscus

e)   Determine the temperature of the sample fluid immediately following reading the hydrometer.

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

   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 relative density of the brine at some other temperature.

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 relative density of the brine at the measured temperature, if significant (see 6.4).

    The brine thermal expansion/contraction factor (conversion factor) can then be used to obtain the density or relative density of the brine at other temperatures.

6.4 Density Corrections for Hydrometers and Brines

6.4.1 Temperature Corrections for Hydrometer Readings

6.4.1.1 Density hydrometer

If the hydrometer density 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.

As generally density hydrometers are graduated in g/mL, corrected density of a brine, ρ_{θ_m}, at measurement temperature, θ_m, is given by the density hydrometer corrected reading, R, at measured temperature θ_m and can be calculated using Equations 4 to 6 according to the desired unit.

a) ρ_{θ_m}, expressed in g/mL is given as follows:

$$\rho_{\theta_m} = R \tag{4}$$

b) $\rho_{\theta_m,SI}$, expressed in kg/m^3, is given as follows:

$$\rho_{\theta_m,SI} = 1000 \times R \tag{5}$$

c) $\rho_{\theta_m,USC}$, expressed in lb/gal, is given as follows:

$$\rho_{\theta_m,USC} = \rho_{\theta_m} \times 62.43 = \rho_{\theta_m,SI} \times 0.06243 \tag{6}$$

where:

R is the density hydrometer corrected reading for thermal glass expansion/contraction at measured temperature (see Table 1)

6.4.1.2 Relative density and density by SG hydrometer

If the SG 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		Relative Density Reading (R_{SG}) or Density Reading (R)						
		Dimensionless or expressed in g/mL (10^{-3} kg/m³)						
°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 relative density or or density (g/mL) at the measured temperature. They are based on the equation:

$C_g = 25 \times 10^{-6} \times R_{SG} \times (\theta_{Ref} - \theta_m)$

where:

C_g is the correction for glass expansion/contraction dimensionless for relative density or in g/mL for density

R_{SG} is the relative density hydrometer reading dimensionless or R density reading in g/mL;

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

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

NOTE 2 Cubical volume expansion factor for glass is 25×10^{-6} per °C, shall be replaced by (13.9×10^{-6} per °F when temperature are expressed in °F.

Corrected density of a brine, ρ_{θ_m}, at measurement temperature, θ_m, based on the SG hydrometer corrected relative density reading, R_{SG}, at measured temperature θ_m can be calculated using equations 7 to 9 according to the desired unit:

a) ρ_{θ_m}, expressed in g/mL, using Equation (7), 0.999 is the density of deaerated distilled water at 15.56 °C (60 °F) expressed in g/mL:

$$\rho_{\theta_m} = 0.999 \times R_{SG} \tag{7}$$

b) $\rho_{\theta_m,SI}$, expressed in kg/m³, using Equation (8), 999 is the density of deaerated water at 15.56 °C (60 °F) expressed in kg/m³:

$$\rho_{\theta_m,SI} = 999 \times R_{SG} \tag{8}$$

c) $\rho_{\theta_m,USC}$, expressed in lb/gal, using Equation (9), 8.337 is the density of deaerated water at 15.56 °C (60 °F) expressed in lb/gal:

$$\rho_{\theta_m,USC} = 8.337 \times R_{SG} \tag{9}$$

where:

R_{SG} is the SG hydrometer corrected reading for thermal glass expansion/contraction at measured temperature (see Table 1)

6.4.2 Temperature Corrections for Brine Density

The reported density of a brine sample shall be corrected to 20 °C for SI units reporting and to 70 °F for USC units reporting if the hydrometer measurement was taken at any other measurement temperature. This brine volume expansion/contraction factor is due to the change in volume of brine as the temperature of the brine changes. Therefore, brine density shall be corrected for brine volume changes when converting from one temperature to another using conversion factor, C (C_{SI} or C_{USC}), either an estimated factor read from Table 2, , or calculated from equations 10 through 14 according to the desired unit.

a) For SI derived units expressed in g/mL, C shall be calculated using Equation (10):

$$C = 10^{-3} \times \left[(-0.12868) + \left(1.4999 \times \rho_{\theta_m}\right) - \left(1.036 \times \rho_{\theta_m}^2\right) + \left(0.2727 \times \rho_{\theta_m}^3\right) \right] \tag{10}$$

where:

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

ρ_{θ_m} is the hydrometer corrected density reading at measured temperature expressed in g/mL;

b) For SI units expressed in kg/m³, C_{SI} shall be calculated using Equation (11):

$$C_{SI} = (-0.12868) + \left(1.4999 \times \rho_{\theta_m}\right) - \left(1.036 \times \rho_{\theta_m}^2\right) + \left(0.2727 \times \rho_{\theta_m}^3\right) \tag{11}$$

where:

C_{SI} is the brine density conversion factor in kg/m³ per °C;

ρ_{θ_m} is the hydrometer corrected density reading at measured temperature expressed in g/mL;

or using Equation (12):

$$C_{SI} = \left[\begin{array}{l} \left(-0.12868\right) + \left(1.4999 \times 10^{-3} \times \rho_{\theta_m,SI}\right) - \left(1.036 \times 10^{-6} \times \rho_{\theta_m,SI}^2\right) \\ + \left(0.2727 \times 10^{-9} \times \rho_{\theta_m,SI}^3\right) \end{array} \right] \tag{12}$$

where:

$\rho_{\theta_m,SI}$ 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} shall be calculated using Equation (13):

$$C_{USC} = 10^{-3} \times \left[\begin{array}{l} \left(-0.59659\right) + \left(0.83411 \times \rho_{\theta_m,USC}\right) - \left(0.06904 \times \rho_{\theta_m,USC}^2\right) \\ + \left(0.00218 \times \rho_{\theta_m,USC}^3\right) \end{array} \right] \tag{13}$$

where:

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

$\rho_{\theta_m,USC}$ is the hydrometer corrected density reading at measured temperature expressed in lb/gal;

or directly from corrected SG hydrometer relative density reading using Equation (14):

$$C_{USC} = 10^{-3} \times \left[\left(-0.59659\right) + \left(6.954 \times R_{SG}\right) - \left(4.799 \times R_{SG}^2\right) + \left(1.263 \times R_{SG}^3\right) \right] \tag{14}$$

where:

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

R_{SG} is the relative density corrected reading for a 60 °F/60 °F SG hydrometer (dimensionless)

Using the conversion factor from either Equations (10) to (14) or Table 2, the converted density shall be calculated at 20 °C for SI units or at 70 °F for USC units.

a) If temperature measurement is given in degrees Celsius, use Equation (15) to find the converted density in g/mL:

$$\rho_{20} = \rho_{\theta_m} + \left[\left(\theta_{m,SI} - 20\right) \times C \right] \tag{15}$$

where:

ρ_{20} is the converted density at 20 °C, expressed in g/mL;

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

   NOTE $\rho_{\theta_{m}}$ can be calculated using Equation (4) or (7) and a corrected hydrometer reading.

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

C is the brine thermal expansion/contraction factor from Table 2 or Equation (10).

b) If temperature measurement is given in degrees Celsius, use Equation (16) to find the converted density in kg/m^3:

$$\rho_{20,SI} = \rho_{\theta_{m},SI} + \left[\left(\theta_{m,SI} - 20 \right) \times C_{SI} \right]$$ (16)

where:

$\rho_{20,SI}$ is the converted density at 20 °C, expressed in kg/m^3;

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

NOTE $\rho_{\theta_{m},SI}$ can be calculated using Equation (5) or (8) and a corrected hydrometer reading.

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

C_{SI} is the brine thermal expansion/contraction factor from Table 2 or Equation (11) or (12)

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

Hydrometer Corrected Density Reading ρ_{θ_m} g/mL	SG Hydrometer 60 °F/60 °F Corrected Relative Density Reading R dimensionless	Brine Density at Measured Temperature		Brine Thermal Expansion/Contraction Factors		
		$\rho_{\theta_m,SI}$ kg/m^3	$\rho_{\theta_m,USC}$ lb/gal	C (g/mL)/°C	C_{SI} (kg/m^3)/°C	C_{USC} (lb/gal)/°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.

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c) If the temperature measurement is given in degrees Fahrenheit, use Equation (17) or Equation (18) to find the converted density in lb/gal. The coefficient of 8.337 is the deaerated distilled water density at 15.56 °C (60 °F) in lb/gal:

$$\rho_{70,\text{USC}} = (8.337 \times R_{\text{SG}}) + C_{\text{USC}} \times \left[(8.337 \times R_{\text{SG}}) - 70 \right] \tag{17}$$

or, using $\rho_{\theta_m,\text{USC}}$ from Equation (6) or (9) to calculate the converted density :

$$\rho_{70,\text{USC}} = \rho_{\theta_m,\text{USC}} + \left[(\theta_{m,\text{USC}} - 70) \times C_{\text{USC}} \right] \tag{18}$$

where:

$\rho_{70,\text{USC}}$ is the converted density at 70 °F, expressed in lb/gal;

R_{SG} is the SG hydrometer corrected reading, dimensionless;

$\rho_{\theta_m,\text{USC}}$ is the SG hydrometer corrected density reading at measured temperature expressed in lb/gal;

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

C_{USC} is the brine thermal expansion/contraction factor from Table 2 or Equation (13) or (14).

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 SG hydrometer. In both cases, the measured densities should be corrected using the method described in 6.4.1. The conversion factor should be then calculated using Equation (19), illustrated for C expressed in g/mL per °C:

$$C = \frac{\rho_1 - \rho_2}{\theta_{2,\text{SI}} - \theta_{1,\text{SI}}} \tag{19}$$

where:

C is the brine thermal expansion/contraction factor, expressed in g/mL per °C;

ρ_1 is the corrected density at lower temperature, expressed in g/mL;

ρ_2 is the corrected density at higher temperature, expressed in g/mL;

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

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

NOTE   Conversion factor, C_{SI} or C_{USC}, should be calculated by an identical equation with densities and temperatures expressed in SI units (kg/m3 and °C) or USC units (lb/gal and °F).

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 should? be used for density conversion to 20 °C for SI units or 70 °F for USC units. This curve will be specific for the 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, the density and the temperature of the brine shall be accurately measured.

NOTE   Minor variations in either of these measurements lead to errors in the density correction from the calculations and the graphs.

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 g/mL or kg/m³

6.5.1   Calculate the density in g/mL and kg/m³ to other common units by the following Equations (20) through (22).

As

$$\rho_{SI} = \rho \times 1000 \tag{20}$$

where:

ρ is the density, expressed in g/mL;

ρ_{SI} is the density in SI units, expressed in kg/m³.

and

$$\rho_{USC} = \rho \times 8.345 = \rho_{SI} \times 0.008345 \tag{21}$$

where:

ρ_{USC} is the density in USC units, expressed in lb/gal;

ρ is the density, expressed in g/mL;

ρ_{SI} is the density in SI units, expressed in kg/m³;

or

$$\rho_{USC\text{-}2} = \rho \times 62.43 = \rho_{SI} \times 0.06243 \tag{22}$$

where:

$\rho_{\text{USC-2}}$ is the density in USC units, expressed in lb/ft^3;

ρ is the density, expressed in g/mL;

ρ_{SI} is the calculated density in SI units, expressed in kg/m^3;

6.5.2 The fluid gradient from the density shall be calculated as Equations (23) through (26):

$$\Gamma_{\text{DFG,SI}} = \frac{\rho}{0.10197} \tag{23}$$

where:

$\Gamma_{\text{DFG,SI}}$ is the SI fluid gradient, expressed in kPa/m;

ρ is the density, expressed in g/mL;

or

$$\Gamma_{\text{DFG,USC}} = \frac{\rho_{\text{USC}}}{19.24} \tag{24}$$

$$\Gamma_{\text{DFG,USC}} = \frac{\rho}{2.3056} \tag{25}$$

where:

$\Gamma_{\text{DFG,USC}}$ is the fluid gradient, expressed in pounds per square inch per foot (psi/ft), calculated from density expressed in lb/gal;

ρ_{USC} is the density, expressed in lb/gal;

ρ is the density, expressed in g/mL;

or

$$\Gamma_{\text{DFG,USC-2}} = \frac{\rho_{\text{USC-2}}}{144} \tag{26}$$

where:

$\Gamma_{\text{DFG,USC-2}}$ is the fluid gradient, expressed in lb/ft^2 calculated from density expressed in lb/ft^3;

$\rho_{\text{USC-2}}$ is the density expressed in lb/ft^3.

NOTE   The results from Equation (24), Equation (25) and Equation (26) are equivalent.

6.6 Calculations 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 The average brine density in the wellbore, in SI units of kg/m^3 shall be calculated using Equation (27):

$$\rho_{\text{av,SI}} = \frac{\left\{\rho_{\text{Surf,SI}} \times \left[2000 - \left(0.0098 \times C_{\text{P,SI}} \times h_{\text{TVD,SI}}\right)\right]\right\} + \left[10 \times C_{\theta,\text{SI}} \times \left(\theta_{\text{Surf,SI}} - \theta_{\text{BH,SI}}\right)\right]}{\left[2000 - \left(0.01962 \times C_{\text{P,SI}} \times h_{\text{TVD,SI}}\right)\right]} \tag{27}$$

where:

$\rho_{\text{av,SI}}$ is the average brine density in the wellbore, expressed in kg/m^3

$\rho_{\text{Surf,SI}}$ is the brine density at the surface, expressed in kg/m^3;

$C_{\text{P,SI}}$ is the pressure compensation factor, see Table 3, expressed in (kg/m^3)/MPa

$h_{\text{TVD,SI}}$ is the true vertical depth, expressed in m;

$C_{\theta,\text{SI}}$ is the temperature compensation factor, see Table 4, expressed in (kg/m^3)/100 °C;

$\theta_{\text{Surf,SI}}$ is the brine temperature, measured at the surface expressed in °C or assumed to be 20 °C;

$\theta_{\text{BH-SI}}$ is the brine temperature, measured at bottom hole, expressed in °C.

Table 3—Pressure Compensation Factor in SI Units

Brine Typ)e	Density ρ_{SI} kg/m^3	Isobaric Coefficient of Volumetric Expansion [(Vol/Vol)/kPa] 10^{-6}	Pressure Compensation Factor $C_{P,SI}$ (kg/m^3)/MPa [a]
NaCl	1137	0.287	0.327
CaCl$_2$	1373	0.218	0.299
NaBr	1496	0.242	0.362
CaBr$_2$	1714	0.222	0.380
ZnBr$_2$/CaBr$_2$/CaCl$_2$	1919	0.202	0.387
ZnBr$_2$/CaBr$_2$	2309	0.238	0.549
NOTE Compressibility of heavy brine was measured at 198 °F from 6895 kPa (1000 lbf/in.²) to 68,950 kPa (10,000 lbf/in.²) (Bibliography Reference [5]).			
[a] 1 MPa = 1000 kPa			

Table 4—Temperature Compensation Factor in SI Units

Brine Type	Density ρ_{SI} kg/m^3	Isothermal Coefficient of Compressibility [(Vol/Vol)/°C] 10^{-4}	Temperature Compensation Factor $C_{\theta,SI}$ kg/m^3/100 °C
NaCl	1137	4.57	52.0
CaCl$_2$	1373	4.30	59.1
NaBr	1495	4.81	71.9
CaBr$_2$	1714	4.19	71.9
ZnBr$_2$/CaBr$_2$/CaCl$_2$	1918	4.09	78.4
ZnBr$_2$/CaBr$_2$	2309	4.57	105.6
NOTE Expansibility of heavy brine was measured at 82,740 kPa (12,000 lbf/in.²) from 22.44 °C to 92.22 °C (76 °F to 198 °F) (Bibliography Reference [5]).			

6.6.3   The average brine density in the wellbore in SI units (kg/m^3) is calculated using Equation (28) from a value in USC units (lb/gal).

$$\rho_{av,SI} = 119.83 \times \rho_{av,USC} \tag{28}$$

where:

$\rho_{av,SI}$ is the average brine density in the wellbore, expressed in kg/m^3;

$\rho_{\text{av,USC}}$ is the average brine density in the wellbore, expressed in lb/gal.

6.6.4 The average brine density in the wellbore, in USC units of lb/gal shall be calculated using Equation (29):

$$\rho_{\text{av,USC}} = \frac{\left\{ \rho_{\text{Surf,USC}} \times \left[2000 - \left(0.0052 \times C_{\text{P,USC}} \times h_{\text{TVD,USC}} \right) \right] \right\} + \left[10 \times C_{\theta,\text{USC}} \times \left(\theta_{\text{Surf,USC}} - \theta_{\text{BH,USC}} \right) \right]}{\left[2000 - \left(0.104 \times C_{\text{P,USC}} \times h_{\text{TVD,USC}} \right) \right]} \tag{29}$$

where:

$\rho_{\text{av,USC}}$ is the average brine density in the wellbore, expressed in lb/gal;

$\rho_{\text{Surf,USC}}$ is the density at the surface, expressed in lb/gal;

$C_{\text{P,USC}}$ is the pressure compensation factor, see Table 5, expressed in (lb/gal)/kpsi ;

    NOTE 1 kpsi = 1000 lbf/in.²

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

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

$C_{\theta,\text{USC}}$ is the temperature compensation factor, see Table 6, expressed in (lb/gal)/100 °F;

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

6.6.5 The hydrostatic pressure in the wellbore in SI units of kilopascal using the temperature and pressure average brine density shall be calculated using Equation (30):

$$P_{\text{hyd-}h_{\text{TVD}},\text{SI}} = 0.009807 \times \rho_{\text{av,SI}} \times h_{\text{TVD,SI}} \tag{30}$$

where:

$P_{\text{hyd-}h_{\text{TVD}},\text{SI}}$ is the hydrostatic pressure in the wellbore , expressed in kPa;

$\rho_{\text{av,SI}}$ is the average brine density in the wellbore, expressed in kg/m³;

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

Table 5—Pressure Compensation Factors in USC Units

Brine Type	Density ρ_{USC} lb/gal	Isobaric Coefficient of Volumetric Expansion [(Vol/Vol)/psi] $\times 10^{-6}$	Pressure Compensation Factor $C_{P,USC}$ (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 relative density)	16.01	1.39	0.022
ZnBr$_2$/CaBr$_2$ (greater than 2.1 relative density)	19.27	1.64	0.031
NOTE Compressibility of heavy brine was measured at 198 °F from 6894.8 kPa (1000 lbf/in.²) to 68,948 kPa (10,000 lbf/in.²) (Bibliography Reference [5]).			
[a] 1 kpsi = 1000 psi = 1000 lbf/in.²			

Table 6—Temperature Compensation Factors in USC Units

Brine Type	Density ρ_{USC} lb/gal	Isothermal Coefficient of Compressibility [(Vol/Vol)/°F] $\times 10^{-4}$	Temperature Compensation Factor $C_{\theta,USC}$ (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 lbf/in.²) from 22.44 °C to 92.22 °C (76 °F to 198 °F) (Bibliography Reference [5]).			

6.6.7   The hydrostatic pressure in the wellbore in USC unit of lbf/in.² using the temperature and pressure average brine density shall be calculated using Equation (31):

:

$$P_{\text{hyd-}h_{\text{TVD}},\text{USC}} = 0.052 \times \rho_{\text{av,USC}} \times h_{\text{TVD,USC}} \tag{31}$$

where:

$P_{\text{hyd-}h_{\text{TVD}},\text{USC}}$ is the hydrostatic pressure in the wellbore, expressed in lbf/in.²;

$\rho_{\text{av-USC}}$ is the average brine density in the wellbore, expressed in lb/gal;

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

6.6.5 The hydrostatic pressure in the wellbore in SI unit (kPa) is calculated Equation (32) from a value in USC unit (lbf/in.²)

$$P_{\text{hyd-}h_{\text{TVD}},\text{SI}} = 6.8948 \times P_{\text{hyd-}h_{\text{TVD}},\text{USC}} \tag{32}$$

where:

$P_{\text{hyd-}h_{\text{TVD}},\text{SI}}$ is the hydrostatic pressure in the wellbore, expressed in kPa;

$P_{\text{hyd-}h_{\text{TVD}},\text{USC}}$ is the hydrostatic pressure in the wellbore, expressed in lbf/in.².

7 Crystallization Temperature

7.1 Principle

7.1.1 This section describes methods for the measurement of crystallization temperatures of brines (non-formate and formate) used in completion, workover, fracturing, and drilling operations.

7.1.2 Four different temperature values are often distinguished for the same brine because of the nature of the brine cooling curve. The following defines the four temperature values, discusses the practical significance of each temperature value, and explains the difference between crystallization of salt crystals from a brine and the freezing of water from a brine.

7.1.3 The 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 of its components. 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 shall have a crystallization temperature below the lowest anticipated operating temperature 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 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-salts 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-salts 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 2 and Table 7 show the crystallization temperature of calcium chloride solution as a function of density, relative density, and salt concentration. Table 8 shows the concentration of sodium chloride solution as a function of density, relative density, and salt concentration. The Tables and Figure are given as examples.
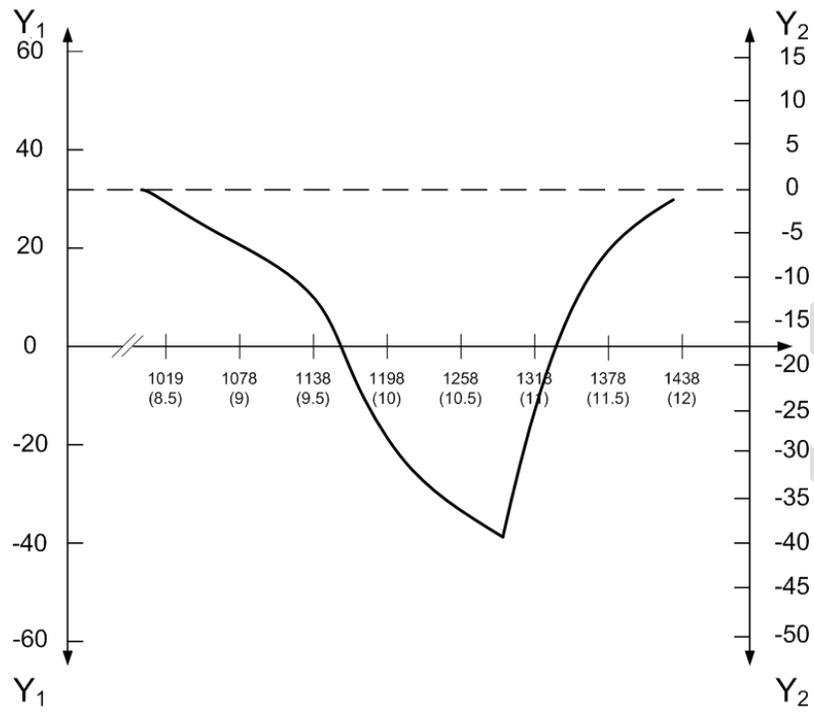
Key

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

Y$_1$ temperature, °F

Y$_2$ temperature, °C

Figure 2—Calcium Chloride Crystallization Temperature

Table 7—Calcium Chloride Solutions—Crystallization Temperature [6]

Density 15.56 °C (60 °F) lb/gal	Relative Density 15.56 °C (60 °F)	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 temperatures are given as an approximation as they 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 relative density (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 a lower crystallization temperature.

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

Table 8—Sodium Chloride Solutions—Crystallization Temperature [6]

Density 15.56 °C (60 °F)	Relative Density	NaCl	Sodium Ion [a]	Chloride Ion [a]	Crystallization Temperature [b]	
lb/gal	15.56 °C (60 °F)	%	mg/L	mg/L	°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 temperatures are given as an approximation as they 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 values.

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 3 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 shall 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 such as existence of metastable salt crystals. This is the super-cooling effect. Super-cooling can be minimized with agitation and the use of selected solid surfaces to initiate the nucleation of crystals. Barium oxide, barium hydroxide, calcium carbonate, and bentonite have been found to be effective nucleates for halide brines while formate brines, especially potassium formate, need to be seeded with formate salt crystals. 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 TCT of the brine.

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 temperature (PCT) has determined that the most accurate crystallization measurements were obtained when the maximum temperature after the last crystals (MTALC) 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.

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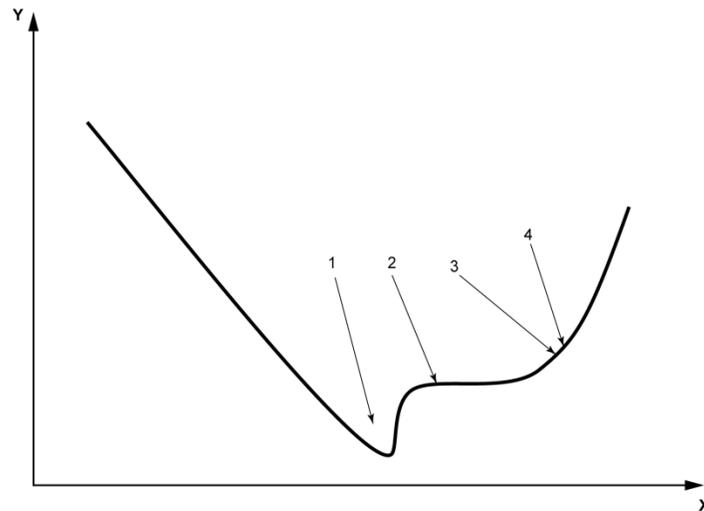
Key

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 3—Typical Crystallization Curve for Brine**

7.1.15   When measuring the crystallization temperature of brine, 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; then if it is considered, a 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), the measurements shall be repeated 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). Temperature during crystallization determination procedure shall be recorded.

A typical crystallization temperature-measuring system is shown in Figure 4.
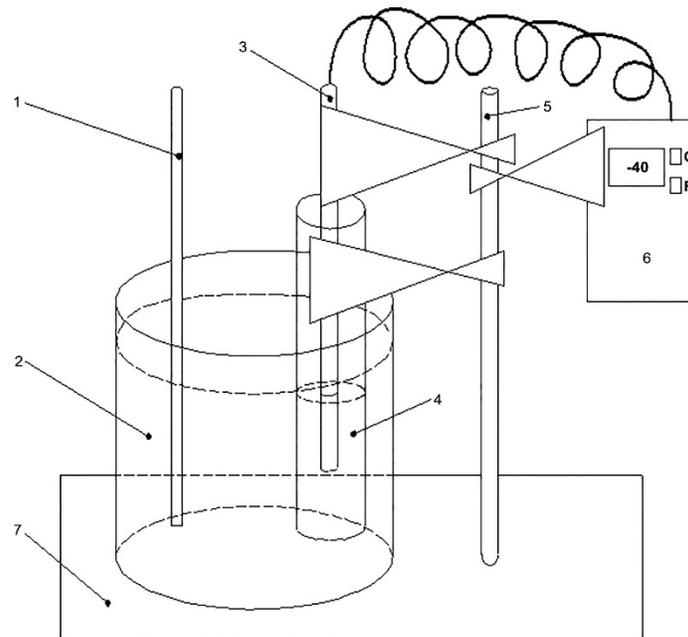
Key

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

Figure 4—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. An electronic cooling system or one or more of the following should (shall) be used:

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, the manufacturer's recommended test procedure shall be followed.

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

See 7.1.12. 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 Temperature of Non-Formate Brines

For non-formate brines, crystallization temperature shall be determined as per the following procedure:

a) Measure approximately 25 mL of the brine to be tested into the sample container. Add the seeding material to the sample unless using crystals precipitated in situ from the brine. Crystal seeding material should be added about 1 °C (2 °F) below the expected crystallization temperature. 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.

b) 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.

c) 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 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. For the repeat test, the sample should be warmed above the LCTD point, but the MTALC shall be no more than 1.0 °C (2.0 °F) higher than the LCTD point.

d) 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.

e) Repeat item b) through item c) 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.

f) Calculate average readings of the three or more tests from item e). 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.

7.4 Determination of Crystallization Temperature of Formate Brines

7.4.1 General

The crystallization temperature should be measured in the following formate single-salt and blended brines:

— sodium formate brine;

— potassium formate brine;

— cesium formate brine;

— sodium/potassium formate brine blends;

— potassium/cesium formate brine blends.

The procedural steps for measurement of the crystallization temperature of formate brines shall be followed:

a) prepare seeding material (see 7.4.2);

b) select seeding material (see 7.4.3);

c) determine approximate crystallization temperature (see 7.4.4);

d) determine accurate crystallization temperature (see 7.4.5).

7.4.2 Preparation of formate seeding material

7.4.2.1 General

Formate single-salt and blended brines' crystallization temperature shall be measured with one or more of the following seeding materials:

— sodium formate crystals;

— potassium formate stable crystals;

— cesium formate crystals.

Formate brine seeding crystals may be stored in plastic containers in the freezer. Formate brines or crystals should never be stored in glass containers.

7.4.2.2 Sodium and cesium formate brine seeding crystals

The following steps shall be executed.

a) Prepare a sample with density in the range:

— sodium formate brine: 1.25 g/mL to 1.33 g/mL (10.43 lb/gal to 11.10 lb/gal);

— cesium formate brine: 2.15 g/mL to 2.35 g/mL (17.94 lb/gal to 19.61 lb/gal).

b) Cool the sample to a temperature of approximately -40°C (-40 °F) and let it stay for minimum 1 hour.

c) Verify visually that crystallization has occurred in the sample; these are the seeding crystals that shall be stored at a temperature lower than -10°C (14 °F).

d) If crystallization is not observed, shake the sample by hand to attempt initiating crystallization.

e) If shaking by hand does not initiate crystallization, transfer the cold sample to a glass container.

f) If the sample still has not crystallized, increase the brine concentration by either evaporation or by adding more salt in powder form to the sample without exceeding the limits stated in the first step, and return to item b).

7.4.2.3 Potassium formate brine seeding crystals

The following steps shall be executed.

a) Prepare potassium formate brine sample with density in the range 1.50 g/mL to 1.59 g/mL (12.50 lb/gal to 13.27 lb/gal).

b) Cool the sample to a temperature of approximately -40°C (-40 °F) and let it stay for minimum 1 hour

c) Observe visually whether crystallization occurs in the sample; if crystals are observed, proceed to item g).

d) If crystallization is not observed, shake the sample by hand to attempt initiating crystallization.

e) If shaking by hand does not initiate crystallization, transfer the cold sample to a glass container.

f) If the sample still has not crystallized, increase the brine concentration by either evaporation or by adding more salt in powder form to the sample without exceeding the limits stated in the first item a), and return to item b).

g) Produce stable potassium formate crystals by stirring a new sample of the potassium formate (first item a) with the metastable crystals formed in item c) at the approximate metastable crystallization temperature.

The transition is observed by a significant and rapid increase in temperature and increase in the amount of visual crystals. If the transition does not take place after one hour, the stirring rate should be increased. Patience is often required, as transformation does not always take place easily. Stable potassium formate crystals cannot convert back to metastable crystals and can safely be stored at a temperature below -10°C.

7.4.3 Selection of formate seeding material

7.4.3.1 General

Seeding material shall be selected based on brine composition. Figures 5 and 6 can be used as guidance.
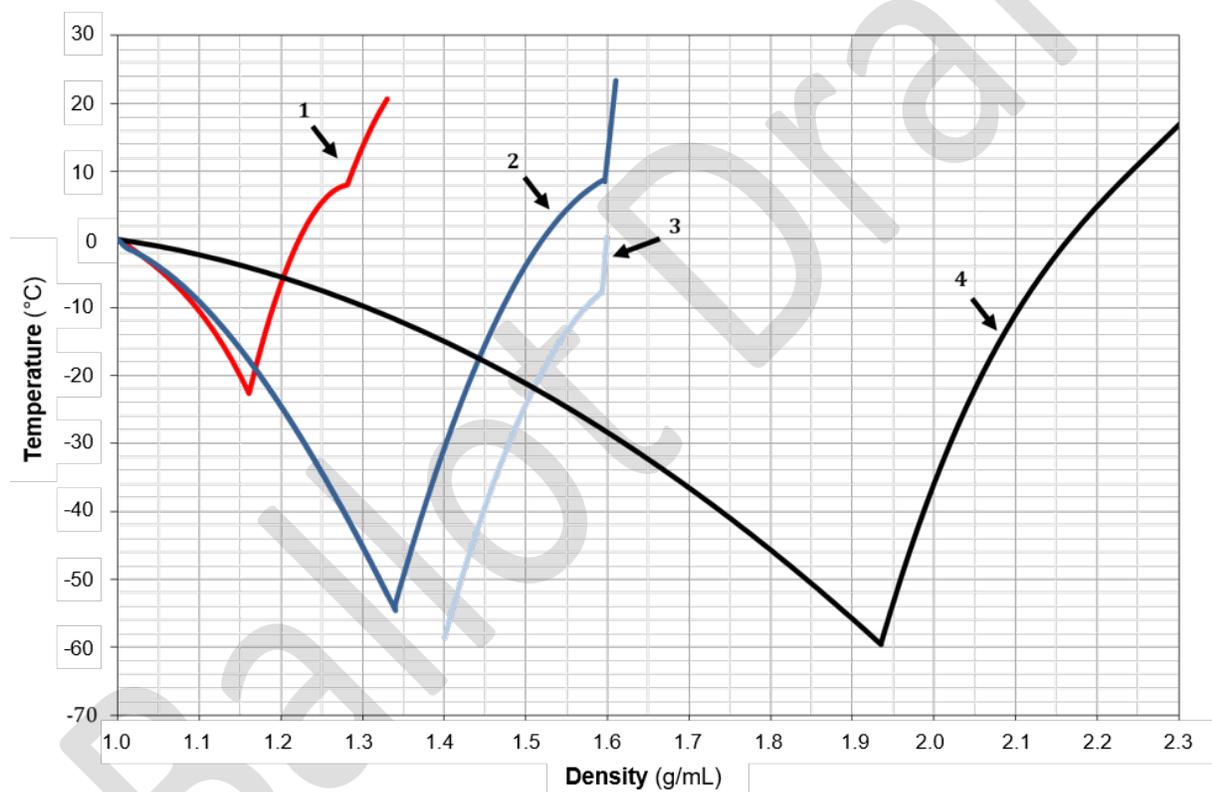
Key

1 sodium formate

2 potassium formate – stable phase

3 potassium formate – metastable phase

4 cesium formate

NOTE 1   Temperature °F = (1.8 x °C) + 32

NOTE 2   Density lb/gal = 8.345 x (g/mL)

Figure 5 — Crystallization Temperature of Sodium, Potassium, and Cesium Formate Single-salt Brines as Function of Brine Density
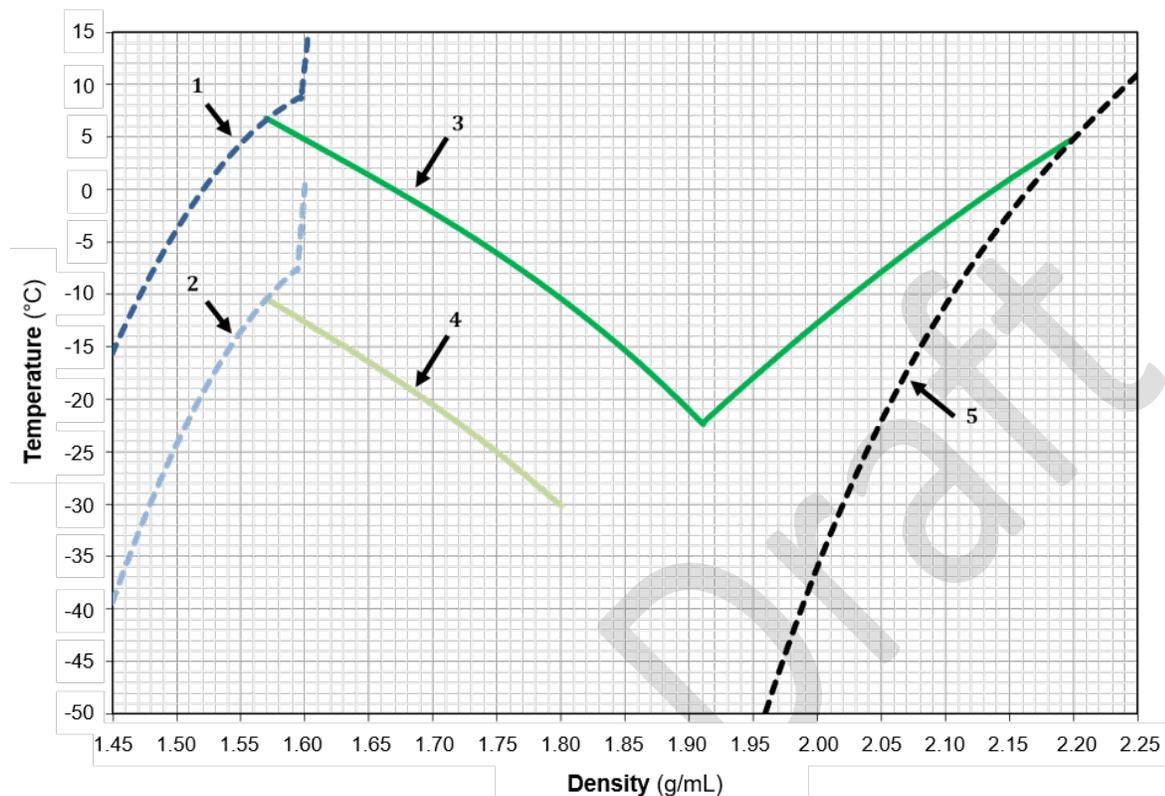
Key

1	potassium formate – stable phase	**4**	cesium/potassium formate – metastable phase
2	potassium formate – metastable phase	**5**	cesium formate
3	cesium/potassium formate –stable phase		

NOTE 1   Temperature °F = (1.8 x °C) + 32

NOTE 2   Density lb/ gal = 8.345 x (g/mL)

Figure 6 — Crystallization Temperature of Blends of 1.57 g/mL Potassium Formate and 2.20 g/mL Cesium Formate Brine as Function of Brine Density

7.4.3.2 Single salt formate brines

If the brine's density is on the left side of the eutectic point (minimum in Figure 5), seeding is not required.

If the brine's density is on the right side of the eutectic point (minimum in Figure 5), a crystal of the same brine, produced as per 7.4.2 shall be used. If measuring crystallization temperature of potassium formate brine, a stable crystal should be used, produced as per 7.4.2.3 item g).

7.4.3.3 Blended formate brines

If measuring crystallization temperature of a blended brine (cesium/potassium formate and sodium/potassium formate), the salt that crystallizes first when the brine is cooled down shall be used as

seeding material. If it is not known which salt crystallizes first, it can be determined in the following way, using Figure 6 as guidance.

a) If the brine dilution causes water crystallization (freezing) before salt crystallization, seeding is not required.

b) For cesium/potassium formate blends not covered in item a):

1) If the density is higher than 1.95 g/mL (16.27 lb/gal), cesium is the dominant cation and cesium formate crystals shall be used.

2) If the density of the blend is in the range from 1.85 g/mL to 1.95 g/mL (15.44 lb/gal to 16.27 lb/gal), shall be used cesium formate crystals and stable potassium formate crystals.

3) If the density is lower than 1.85 g/mL (15.44 lb/gal) in a brine that has not been diluted with water, potassium is the dominant cation and stable potassium formate crystals shall be used.

4) If the density of the brine is lower than 1.85 g/mL (15.44 lb/gal) and the brine could have been diluted with a significant amount of water, shall be used cesium formate crystals and stable potassium formate crystals.

c) For sodium/potassium formate blends not covered in item a):

1) If it is known that sodium is the dominant cation, sodium formate crystals shall be used.

2) If it is known that potassium is the dominant cation, stable potassium formate crystals shall be used.

3) If the composition is unknown or sodium and potassium concentrations are similar, shall be used sodium formate crystals and stable potassium formate crystals.

7.4.4 Determination of approximate formate crystallization temperature

7.4.4.1 General

An approximate crystallization temperature is needed for programming the temperature controller described in 7.4.5 and to determine when the seeding crystals are to be added.

7.4.4.2 Single salt formate brines

Figure 5 shall be used to read the approximate crystallization temperature for the relevant brine.

7.4.4.3 Blended cesium and potassium formate brines

The following provisions shall apply for blended cesium and potassium formate brines.

a) If it is a straight blend of concentrated cesium formate [density ~2.20 g/mL (~18.36 lb/gal)] and potassium formate [density ~1.57 g/mL (~13.10 lb/gal)] brines with no water added or removed, the approximate crystallization temperature can be read from Figure 6.

b) If it is known that the brine could contain some extra water, 5 °C to 10 °C (9 °F to 18 °F) should be subtracted from the value read from Figure 6.

c) If it is known that water can have been removed from the blend, for example by evaporation or addition of dry salt, a 5 °C to 10 °C (9 °F to 18 °F) should be added to the value read from Figure 6.

7.4.5 Accurate determination of formate crystallization temperature

7.4.5.1 General

The sample should be seeded once. For the subsequent cycles, no seeding is required. Figure 7 shows the sequence of three such cycles, indicating the various steps required for measurement.

If appropriate seeding crystals have been used, the three values FCTA, TCT, and LCTD should be very close. If no seeding material was used, the first TCT is likely to be much too low because of supercooling, assuming the temperature of the cooling bath is low enough to overcome the supercooling. For potassium formate, if metastable potassium formate crystals, or no seeding material at all, or seeding material other than what is specified in 7.4.3 are used, the recorded TCT value can drift upwards with time as precipitated potassium formate crystals transform from the metastable phase to the stable phase.

When measuring crystallization temperature at or around the eutectic or critical points, it shall be recommended to measure on both sides of these points and extrapolate the measured crystallization temperature curves.

7.4.5.2 Experimental set up

A temperature-controlled circulating bath with an attached circulation sample holder should be used. The test brine shall be placed directly in the sample holder. The sample holder with stir bar shall be placed on a magnetic stirrer. The sample holder should be covered with a plastic film to eliminate water absorption from the air.

7.4.5.3 Measurement procedure

For formate brines, accurate crystallization temperature shall be determined as per the following procedure. Figure 7 is providing an example of temperature recording when measuring crystallization temperature.

a) The temperature controller shall be programmed to set the first target temperature to approximately 8°C (14 °F) below the approximate crystallization temperature determined by the method described in 7.4.3. Cooling rate is not critical when the brine is seeded with the recommended seeding crystals as described in 7.4.3.

b) The seeding crystals shall be added approximately 1°C (2 °F) below the approximate crystallization temperature. A needle or spatula shall be inserted into the seed crystal sample (from the freezer) and then inserted in the test sample. Even if the crystals cannot be seen, they will be present. It is neither necessary nor desirable to add a large amount of seeding crystals.

c) Watch carefully for crystallization. If crystallization does not occur within a few minutes, lower the approximate crystallization temperature by 5 °C (9 °F) and repeat item b).

d) As soon as crystals are observed, the temperature shall be recorded. This temperature is referred to as FCTA. Shortly after the first crystals have formed, the temperature will increase and then decrease again.

e) The highest temperature observed shall be recorded as TCT.

f) Once the temperature starts decreasing, the cooling should be turned off.

g) The target temperature shall be adjusted 3 °C (5 °F) above the recorded TCT. The heating rate is not critical.

h) As soon as there are no crystals visibly present, LCTD temperature shall be recorded. The stirring shall be turned off. The cooling shall be turned on. The set point shall be adjusted to 8 °C (14 °F) below the previously recorded TCT [item d)].

i) Once the sample temperature reaches the previously recorded TCT, the stirring shall be turned on.

j) Steps 4 to 9 shall be repeated until three consistent at ±1 °C (±2 °F) TCT values are recorded.

k) Crystallization temperature shall be calculated as the average of the three consistent TCT values.
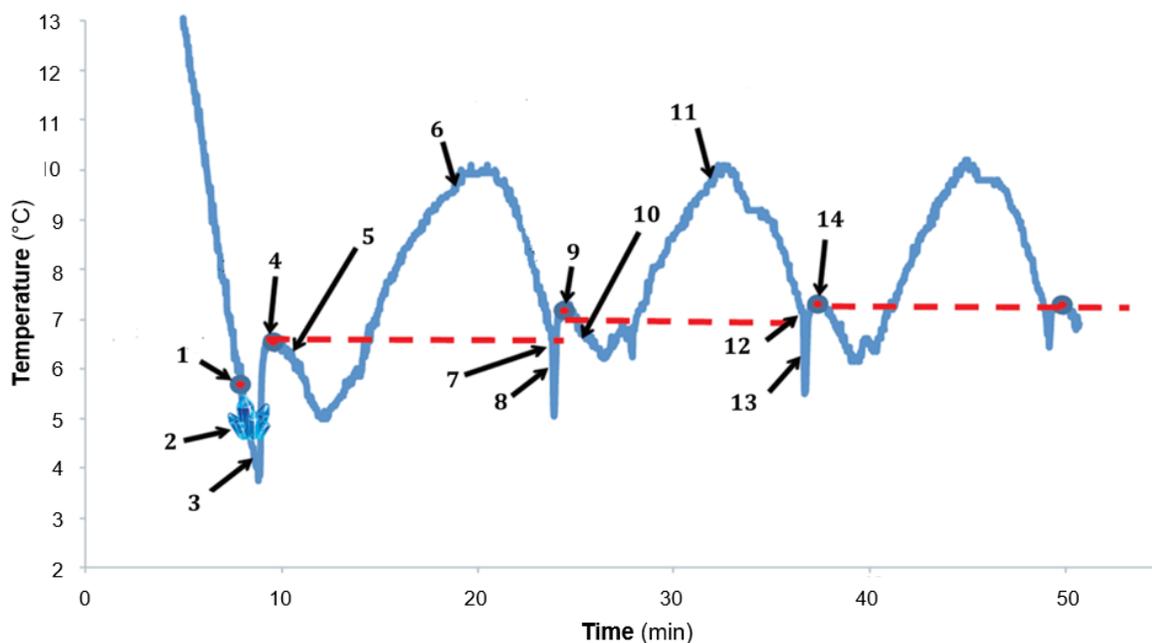
Key

1	approximate CT	**8**	FCTA
2	seeding (~1,0 °C below approximate CT)	**9**	TCT (second recording)
3	FCTA	**10**	start heating
4	TCT (first recording)	**11**	LCTD (stop stirring, start cooling)
5	start heating	**12**	restart stirring
6	LCTD (stop stirring, start cooling)	**13**	FCTA
7	restart stirring	**14**	TCT (third recording)

NOTE Temperature °F = (1.8 x °C) + 32

Figure 7 — Typical Plot of Temperature versus Time during Cooling/Heating Cycles when Measuring Crystallization Temperature of Formate Brines

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. Total suspended solids in brine shall be quantified.

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   **NTU calibration standards.**

Two types of turbidity calibration standards shall be available – primary and secondary standards. A primary standard shall be used to calibrate a meter directly, or to calibrate a secondary standard. A secondary standard should be used as a daily calibration check and shall be monitored periodically for deterioration using a primary standard. All calibrations must eventually be traceable to a primary standard. Turbidity calibration standards should not be used past their expiration date.

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   Deionized or **Distilled 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

Brine clarity shall be determined by the following procedure.

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

b)   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.

c)   Clean the exterior of the standard and sample cuvettes with mild cleaning solution, then rinse with distilled or deionized water. Dry with a lint-free cloth.

d)   Switch on the NTU meter**.**

e)   Insert an appropriate standard cuvette to verify calibration. If calibration verification is not within manufacturer specification, calibrate the turbidity meter according to the manufacturer's recommendations.

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

g)   Record the reading for the sample cuvette, and report brine clarity 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 non-volatile, 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 non-volatile (typically indicating organic or inorganic species, respectively). This differentiation is accomplished by measuring loss on ignition, which can be performed

on the total sample, the soluble portion, or the filtered residue from drying. Impurities are reported as total volatile solids and total non-volatile 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, bromide, and/or formate can be hygroscopic and should 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 $\pm$1 °C (220 °F $\pm$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.

NOTE   A Gooch crucible should be an adequate filter support

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   **Deionized** or **Distilled 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

Glass-fiber filter disk shall be prepared as per the following procedure.

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

b)   Apply a vacuum to the filtration device and wash the disk three times using 20 mL deionized or distilled water for each wash.

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

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

e)   Dry in the oven for 1 h.

f)   Remove to the desiccator and cool to room temperature. Store glass-fiber filter disk in desiccator until needed.

9.4   Selection of Sample Volume

Sample volume shall be selected by application of the following procedure.

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

b)   Wet the filter with a small amount of distilled or deionized water to seat it against the fritted support.

c)   Using vacuum, filter 100 mL of brine through the glass-fiber filter. Wash the graduated cylinder, filter, nonfilterable residue, and filter funnel wall with three portions of distilled or deionized water. Allow complete drainage between washings.

d)   Remove the glass-fiber filter, dry, and reweigh.

e)   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.

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

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

2. 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.

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

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

5. Plot the observed time versus volume filtered.

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

9.5 Determination of Total Suspended Solids

Procedure to determine total suspended solids shall be as per the following.

a) 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.

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

c) Mark three aluminum pans with individual identifying numbers or letters. Weigh the pans with the glass-fiber filter or crucible/filter disk and record the mass to 0.1 mg as m_1.

d) Assemble the filter apparatus and place the filter on the frit. Wet the glass-fiber filter with a small volume of distilled or deionized water to seat it against the fritted support.

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

f) 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 deionized or distilled 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 would be 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 deionized or distilled water to between 4 to 5 with HCl 0.1N solution to prevent precipitation of zinc during washing.

g) Carefully remove the filter disk from the filter support and place in a pre-weighed aluminum pan. Repeat item e) through item f) two additional times.

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

i) 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.

j)   Record the mass of pan with glass-fiber filter and residue for each sample as m_2.

9.6   Calculation of Total Suspended Solids

Total suspended solids shall be calculated using Equation (33):

$$m_S = \frac{m_2 - m_1}{V_s} \times 1000 \tag{33}$$

where:

m_S is the total suspended solids, expressed in mg/L.

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

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

V_s is the volume of the original brine sample, expressed in mL;

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 Non-volatile Solids

Following procedure shall allow to determine volatile and non-volatile solids.

a)   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.

b)   Remove from desiccator and weigh. Record mass as m_3.

c)   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.

d)   Reweigh following the drying procedure and record the mass of dish with fiber filter as m_4.

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

f) Reweigh the porcelain evaporating dishes and record the masses as m_5.

9.9 Calculation of Non-volatile and Volatile Solids

Use Equation (34) and Equation (35) to calculate the total non-volatile and volatile solids, respectively:

$$m_{\text{S-nv}} = \frac{m_5 - m_3}{V_s} \times 1000 \tag{34}$$

$$m_{\text{S-v}} = \frac{m_4 - m_5}{V_s} \times 1000 \tag{35}$$

where:

$m_{\text{S-nv}}$ is the total non-volatile solids or residue, expressed in mg/L;

$m_{\text{S-v}}$ is the total volatile solids, expressed in mg/L

m_3 is the mass of the porcelain evaporating dish and filter medium, expressed in mg;

m_4 is the mass of the porcelain evaporating dish and filtered sample after drying at 105 °C (220 °F), expressed in mg;

m_5 is the mass of the porcelain evaporating dish and filtered sample after auto-ignition at 550 °C (1000 °F), expressed in mg;

V_s is the volume of the original sample, expressed in mL;

10 pH

10.1 Principle

10.1.1   Field measurement of brine fluid pH and adjustments to the pH are fundamental to fluid control. The primary pH-related concerns are formation damage, scale precipitation, corrosion of oilfield tubulars and rig equipment, rig-site filtration efficiency and brine quality. Mismanaged completion brine pH can also promote deleterious chemical reactions with connate water or formation solids and may promote oil emulsification. Solubility of completion fluid components and contaminants and effectiveness of additives can also be affected by pH, as can the control of acidic and sulfide corrosion processes.

10.1.2   pH is a thermodynamic value defined as the negative logarithm (base 10) of the hydrogen ion activity, a_{H^+}, in aqueous solutions:

$$pH = -\log_{10}\left(a_{H^+}\right)$$

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 a_{OH^-} is also 10^{-7} mol/L in aqueous systems at 24 °C (75 °F), the ion product, [H$^+$] [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 precise 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.

Color-matching pH paper and sticks are not recommended for non-formate brines. Both glass-electrode and pH paper can be used, when measuring pH of formate brines. The preferred method to measure pH of formate brines is with a glass-electrode pH meter due to its higher accuracy. If the purpose of the pH measurement is to determine carbonate and bicarbonate concentrations in formate brines, a glass-electrode shall be used.

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, or an equivalent national or international standard, as appropriate (see Section 2). The shelf life shall not exceed the manufacturer's recommendation If no recommendation is stated, then shelf life shall not exceed 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.

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 Deionized or **Distilled water**, preferably in a wash or spray bottle.

NOTE   Demineralizer wash bottles are available which are partially filled with mixed-bed ion exchange resin that exhibits a color change as it nears exhaustion.

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 should be as follows:

a)   pH range: 0 to 14;

b)   electronics type: solid state;

c)   power source: batteries;

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

e)   readout: digital;

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;

    2)   slope of electrode system;

    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. The connection to the meter shall be waterproof.

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 Preparation of the brine sample to be tested

10.4.1.1 Non-formate brines

Non-formate brine sample shall be prepared by 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 brine and mix thoroughly. Allow dilution to reach 24 °C ± 3 °C (75 °F ± 5 °F).

10.4.1.2 Formate brines

Formate brine sample shall be prepared by 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 brine and mix thoroughly. Allow dilution to reach 24 °C ± 3 °C (75 °F ± 5 °F).

c) Method 3—1:10 dilution. Prepare a 1:10 dilution by placing 18.0 mL of distilled/deionized water into a clean, dry 50-mL beaker or equivalent container. Add 2.0 mL of the formate brine and mix thoroughly. Allow dilution to reach 24 °C ± 3 °C (75 °F ± 5 °F).

NOTE 1:10 dilutions of halide brines in distilled/deionized water can lead to imprecise results.

10.4.2 Measurement of pH

The following procedure shall be applied to measure pH.

a) Obtain and prepare a sample of the brine to be tested, using one of the methods for preparation described in 10.4.1

When reporting pH values, specify whether neat (undiluted), 1:1 or 1:10 dilution was used.

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

Calibration procedure shall be as per the following.

   a) Allow the buffer solutions to reach the same temperature as the fluid to be tested (see 10.4.1).

   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 indicated temperature. 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.

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

   c) Follow the equipment manufacturer's recommended calibration procedure.

   d) Dispense 20 mL of the pH 7.0 buffer in a suitable container and immerse the probe. Calibrate the equipment to pH 7.0.

   e) Repeat steps 2 through step 4 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.

   f) 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.

c) When the pH 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.

d) Record the sample temperature and pH to the nearest 0.1 pH unit.

e) 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, the inter-laboratory reproducibility (standard deviation) of these pH assays ranged from 0.2 to 0.6 pH units for halide brines and 0.1 to 0.2 pH units for formate brines.

For 1:1 diluted brines, it ranged from 0.2 to 0.5 pH units for halide brines and 0.1 to 0.2 pH units for formate brines.

For 1:10 diluted brines, it ranged from 0.3 to 1.7 pH units for halide brines and 0.1 to 0.3 pH units for formate brines. It is speculated that the observed deviations may be due to the use of different brands of pH probes and/or pH variances of dilution water used in the round-robin testing (ranged from 5.3 to 8.2 with an average of 6.7 and standard deviation of 1.1).

10.6   Care of the Electrode

10.6.1   Cleaning the electrode shall be necessary, especially if oil or clay particles coat the face of the glass-electrode The owner's manual of the electrode should be referenced to determine the best procedure for cleaning it.

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

10.6.3   General care of the electrode shall involve the following steps.

a)   Clean the electrode with a blotting tissue or soft-bristle brush and a mild detergent.

b)   Recondition the electrode 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.

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. Total iron in brine shall be quantified   to mitigate its effects.

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 ferric thiocyanate chemistry, and shall be used. In an acidic solution, hydrogen peroxide oxidizes ferrous iron. The resulting ferric iron reacts with ammonium thiocyanate to form ferric thiocyanate, a red-orange colored complex, in direct proportion to the iron concentration. The iron content is quantified by comparing the intensity of the resultant colored complexes to standards. Commonly used brine additives at typical concentrations minimally impact the method.

This method for measuring iron content shall not be used on formate brines.

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

NOTE   Demineralization wash bottles are available which are partially filled with mixed-bed ion exchange resin that exhibits a color change as it nears exhaustion.

11.2.2   Acid solution (CAS No. 7647-01-0), 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 or an equivalent national or international standard as appropriate.

The shelf life shall not exceed the manufacturer's recommendation. If no recommendation is stated, then shelf life shall not exceed 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

Colorimetric standards shall be prepared for comparison of the test sample of brine. Standards shall be prepared as per the following.

a)   Using iron-free water, prepare dilutions of a traceable Iron Standard Reference Material (see 11.2.5). The iron concentrations of these standards shall bracket the iron concentration of the test brine. Prepare iron concentrations in 10 mg/L increments in the range 0 mg/L to 100 mg/L. Above 100 mg/L, prepare iron concentrations in 100 mg/L increments.

b)   Transfer 0.5 mL of the brine reference sample into a 50 mL volumetric flask via the 1.0 mL syringe.

c)   Transfer 1.0 mL of the acid solution via a 3.0 mL syringe.

d)   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.

e)   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.

f)   Transfer 1.0 mL of the solution from 11.4.6 into the test tube via a 3.0 mL syringe.

g)   Transfer 0.5 mL of the aqueous ammonium thiocyanate solution into the test tube via a 3.0 mL syringe. Swirl the contents 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

Following procedure shall be applied to measure iron contamination.

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

b)   Transfer 0.5 mL of the brine sample into a 50 mL volumetric flask via the 1.0 mL syringe.

c)   Transfer 1.0 mL of the acid solution via a 3.0 mL syringe.

d) 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 item d).

e) 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.

f) Transfer 1.0 mL of the solution from item e), into the test tube via a 3.0 mL syringe.

g) Transfer 0.5 mL of the aqueous ammonium thiocyanate solution into the test tube via a 3.0 mL syringe. Swirl the contents to ensure mixing. Wait 1 min.

h) 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. Report iron concentration.

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 should depend 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 8.9 mg/L. The variance (accuracy) compared to single atomic spectroscopy analyses was −12.7 %. The average repeatability was 2 mg/L.

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 +2.9 %.

11.6.4 The inter-laboratory reproducibility and variance have not been determined for brines containing greater than 700 mg/L iron contamination.

12 Buffering Capacity of Brines

12.1 Principle

12.1.1 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.

12.1.2 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 monovalent 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 brines have pH values about 7.5. The influx of CO_2 lowers the pH of all brine systems.

12.1.3 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.

12.1.3.1 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.

12.1.3.2 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.

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

12.1.4.1 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.

12.1.4.2 A second endpoint may be detected at a pH lower than pH 4.0, which includes the bicarbonate ion concentration.

12.1.5 For halide brines, the recommended measurements shall be 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 halide brines [7].

NOTE   This method for measuring buffer capacity shall not be used on formate brines.

12.2 Equipment

12.2.1 **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 should be as follows:

a) pH range: 0 to 14;

b) electronics type: solid state;

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;

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;

   2) slope of electrode system;

   3) calibration setting of readout.

12.2.2 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.

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

12.2.5 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.

12.2.6 Beaker, glass, 50 mL, 100 mL, or appropriate size.

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

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

12.2.9 Filter paper, qualitative.

12.2.10 Burettes, 25 mL ± 0.01 mL, 50 mL ± 0.01 mL, or appropriate size with accuracy ± 0.01 mL, for titrations.

12.2.11 Magnetic stirrer and **stirring bars**

12.3 Reagents and Materials

12.3.1   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 (see 10.4.2). 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 or an equivalent national or international standard as appropriate. The shelf life shall not exceed the manufacturer's recommendation If no recommendation is stated, then shelf life shall not exceed 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.

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

12.3.2   Deionized or **Distilled water.**

12.3.3   Mild liquid detergent.

12.3.4   Sodium hydroxide (CAS number 1310-73-2), 0.1 mol/L (0.1 N), to recondition the electrode.

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

12.3.7   Hydrochloric acid (CAS number 7647-01-0), freshly standardized M_{HCl} = 0.5 mol/L (0.5N) to 1.0 mol/L (1 N), for titration.

12.4   Procedure—Determination of Buffer Concentrations

12.4.1 Principle

To determine brine buffer concentration the following procedure shall be applied.

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

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

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

   d)   Titrate two undiluted samples, see 12.4.2.

   e)   Titrate two 1:1 diluted samples, see 12.4.3.

12.4.2 Calibration of pH meter

12.4.2.1 Calibration

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

Calibration procedure shall be as per the following.

a) Allow the buffer solutions to reach the same temperature as the fluid to be tested (see 10.4.1).

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 indicated temperature. 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.

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

c) Follow the equipment manufacturer's recommended calibration procedure.

d) Dispense 20 mL of the pH 7.0 buffer in a suitable container and immerse the probe. Calibrate the equipment to pH 7.0.

e) Repeat steps 2 through step 4 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.

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

When the pH 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

12.2.4.2 Care of the electrode

Cleaning the electrode shall be necessary, especially if oil or clay particles coat the face of the glass-electrode. 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.

Owner's manual of the glass-electrode should be referenced to determine the best procedure for cleaning and reconditioning it.

Refer to 10.6.3 for general care of the electrode procedure.

12.4.3   Titration of undiluted samples

Following titration procedure shall be applied.

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

b) Record the starting pH.

c) Titrate each of the two samples using a freshly standardized HCl (see 12.3.7) solution.

Record pH versus mL acid added, V_{HCl}. If using a manual titration procedure, record the pH at every 0.5 mL acid aliquot added (ΔV_{HCl}) and monitor pH change ΔpH versus volume of HCl acid added,

V_{HCl}. When indicated by an increase in $\Delta pH/\Delta V_{HCl}$ versus V_{HCl}, start adding 0.1 mL to 0.2 mL hydrochloric acid until the first endpoint is passed.

Record the volume of HCl to reach the first endpoint as $V_{A\text{-}HCl}$.

NOTE   pH increased is observed at about pH 9 for 1:1 diluted brine.

d) Continue titrating to the desired target pH.

Record the volume of HCl to the second endpoint as $V_{B\text{-}HCl}$.

NOTE   pH increased is observed at about pH 6 for 1:1 diluted brine.

e) Plot the data, pH versus V_{HCl}, using a computer-based or manual method, as shown in Figure 8. For a more accurate determination of endpoints, the recommended procedure shall be to plot and monitor $\Delta pH/\Delta V_{HCl}$ versus pH. The endpoint is the maximum value for the plotted curve. See Figure 9 for an example.
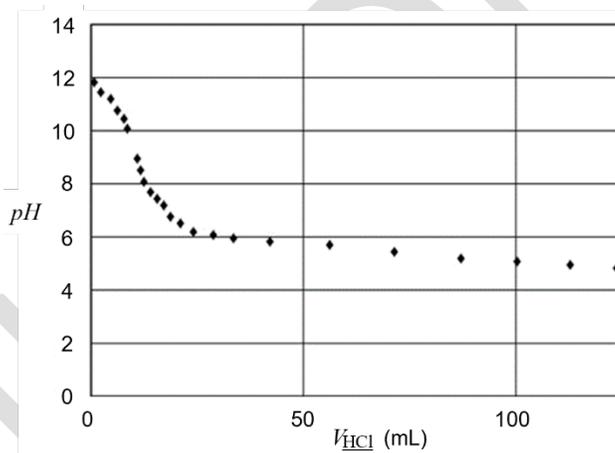

**Figure 8—Example of pH versus Volume of HCl Acid Added**
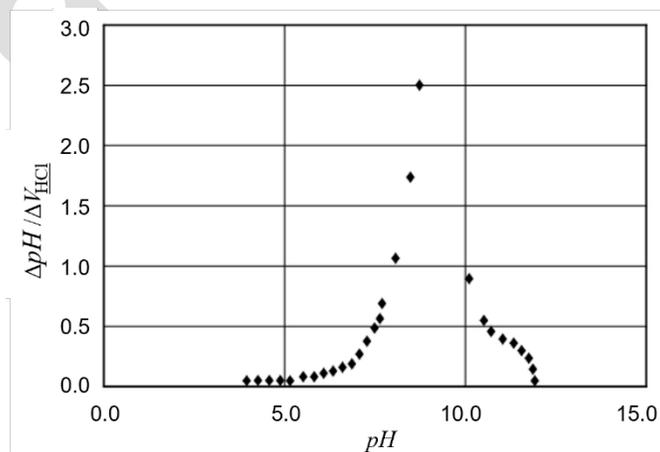
Figure 9—Example of $\Delta pH/\Delta V_{HCl}$ versus pH for more Accurate Determination of Titration Endpoint

f)   Report all endpoints observed as milliliters of hydrochloric acid used.

g)   Calculate the buffer concentration average milliequivalents of hydrochloric acid per milliliter of brine (meq_{ACID}/mL_{BRINE}) and report.

12.4.4   Titration of 1:1 Diluted Samples

Following titration procedure shall be applied.

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

b)   Measure and record the pH of the undiluted brine.

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

d)   Follow 12.4.3 item c) through item f). Report all endpoints observed as milliliters of hydrochloric acid used.

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

12.5   Calculation—First Endpoint or Target pH

12.5.1   For each brine samples, the buffer concentration (i. e., the first end point or target pH), expressed in milliequivalents of hydrochloric acid per milliliter of brine shall be calculated as given Equation (35).

$$c_{B1} = \frac{V_{A\text{-}HCl} \times M_{HCl}}{V_s} \tag{35}$$

where:

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

$V_{A\text{-}HCl}$ is the volume of hydrochloric acid used to the first endpoint or target pH, expressed in mL;

M_{HCl} is the molarity of the hydrochloric acid used, expressed in mol/L;

V_s is the volume of undiluted brine sample, expressed in mL.

12.5.2 The average of the duplicate titrations (for either c_{Na2CO_3} and c_{K2CO_3}) shall be calculated; rand c_{B1} the first endpoint in milliequivalents of acid per milliliter of brine (meq_{ACID}/mL_{BRINE}), or percentage reported. Titrations shall be repeated if duplicate results differ by 5 % or more.

12.5.3 Concentration of titratable basic species, sodium carbonate (c_{Na2CO_3}) and potassium carbonate (c_{K2CO_3}), shall be calculated as given respectively Equation (36) and Equation (37) when expressed in kilograms per cubic meter or, Equation (38) and Equation (39) when expressed in pounds per barrel.

NOTE   These calculations are of 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.

— Concentration expressed in SI units: kg/m^3

$$c_{Na_2CO_3} = 52.99 \times \frac{(V_{A\text{-}HCl} \times M_{HCl})}{V_s} \tag{36}$$

$$c_{K_2CO_3} = 69.10 \times \frac{(V_{A\text{-}HCl} \times M_{HCl})}{V_s} \tag{37}$$

— Concentration expressed in USC units: lb/bbl

$$c_{Na_2CO_3} = 18.57 \times \frac{(V_{A\text{-}HCl} \times M_{HCl})}{V_s} \tag{38}$$

$$c_{K_2CO_3} = 24.22 \times \frac{(V_{A\text{-}HCl} \times M_{HCl})}{V_s} \tag{39}$$

where:

c_{Na2CO_3} is the concentration of titratable basic species, expressed as kg/m^3 or lb/bbl of sodium carbonate;

c_{K2CO_3} is the concentration of titratable basic species, expressed as kg/m^3 or lb/bbl of potassium carbonate;

$V_{A\text{-}HCl}$ is the volume of hydrochloric acid used to reach the first endpoint, expressed in mL;

M_{HCl} is the molarity of hydrochloric acid, expressed in moles/L;

V_s is the volume of undiluted brine sample, expressed in mL.

NOTE   The molecular weight of Na_2CO_3 is 105.99, and the molecular weight of K_2CO_3 is 138.20.

12.6 Calculation—Second Endpoint or Target pH

12.6.1 For each brine sample, the second buffer concentration (i.e., the second endpoint or target pH) in milliequivalents of hydrochloric acid per milliliter of brine shall be calculated as given Equation (40):

$$c_{B2} = \frac{(V_{B\text{-HCl}} - V_{A\text{-HCl}}) \times M_{HCl}}{V_s} \qquad (40)$$

where:

c_{B2} is the second buffer concentration, expressed in milliequivalents of acid per milliliter of brine (meq_{ACID}/mL_{BRINE});

$V_{A\text{-HCl}}$ is the volume of hydrochloric acid used to the first endpoint or target pH, expressed in mL;

$V_{B\text{-HCl}}$ is the volume of hydrochloric acid used to reach the second endpoint or target pH, expressed in mL;

M_{HCl} is the molarity of the hydrochloric acid, expressed in mol/L;

V_s is the volume of undiluted brine sample, expressed in mL.

12.6.2 The average of the duplicate titrations (for either c_{NaHCO_3} and c_{KHCO_3}), shall be calculated and c_{B2}, the second endpoint in milliequivalents of acid per milliliter of brine (meq_{ACID}/mL_{BRINE}), or percentage. Titrations shall be repeated if duplicate results differ by 5 % or more.

12.6.3 The concentration of titratable basic species, sodium bicarbonate (c_{NaHCO_3}) and potassium bicarbonate (c_{KHCO_3}), between the two endpoints shall be calculated as given respectively Equation (41) and Equation (42) when expressed in kilograms per cubic meter or, Equation (43) and Equation (44) when expressed in pounds per barrel.

NOTE   These calculations are of the assumption that only NaHCO$_3$ or KHCO$_3$ contributed to acid consumption and totally ignores other buffering materials, inhibitors, etc.

— Concentration expressed in SI units: kg/m^3

$$c_{NaHCO_3} = 84.01 \times \frac{\left[(V_{B\text{-HCl}} - V_{A\text{-HCl}}) \times M_{HCL}\right]}{V_s} \qquad (41)$$

$$c_{KHCO_3} = 100.11 \times \frac{\left[(V_{B\text{-HCl}} - V_{A\text{-HCl}}) \times M_{HCl}\right]}{V_s} \qquad (42)$$

— Concentration expressed in USC units: lb/bbl

$$c_{\text{NaHCO}_3} = 29.44 \times \frac{\left[\left(V_{\text{B-HCl}} - V_{\text{A-HCl}}\right) \times M_{\text{HCl}}\right]}{V_{\text{s}}} \tag{43}$$

$$c_{\text{KHCO}_3} = 35.09 \times \frac{\left[\left(V_{\text{B-HCl}} - V_{\text{A-HCl}}\right) \times M_{\text{HCl}}\right]}{V_{\text{s}}} \tag{44}$$

where:

c_{NaHCO_3} is the concentration of titratable basic species, expressed as kg/m^3 or lb/bbl of sodium bicarbonate;

c_{KHCO_3} is the concentration of titratable basic species, expressed as kg/m^3 or lb/bbl of potassium bicarbonate;

$V_{\text{A-HCl}}$ is the volume of hydrochloric acid used to the first endpoint or target pH, expressed in mL;

$V_{\text{B-HCl}}$ is the volume of hydrochloric acid used to reach the second endpoint or target pH, expressed in mL;

M_{HCl} is the molarity of the hydrochloric acid, expressed in mol/L;

V_{s} is the volume of undiluted brine sample, expressed in mL.

NOTE   The molecular weight of NaHCO$_3$ is 84.01, and the molecular weight of KHCO$_3$ is 100.11.

13 Daily Completion Fluid Report

13.1 Principle

13.1.1 The daily completion fluid report shall document key completion fluid information and related completion operations for ongoing activities and end of well records.

13.1.2 Primary impact areas are:

a) well control,

b) formation damage potential,

c) materials accountability.

13.1.3 The daily completion fluid report should be similar in nature to the daily drilling fluid report but shall be configured for the unique conditions and measurements that completion fluids and completion operations impose.

13.1.4   The daily completion fluid report is often comprised of seven (7) primary elements, each containing specific information. The elements should be not exclusive; operators and vendors may add additional information, as desired. These seven elements are:

a)   Report header containing operator, rig/equipment, supervisor, date/report and well identification information

b)   wellbore geometry, casing and tubing details, work string, pumps, and zone data

c)   completion fluid properties

d)   fluids and products accounting

e)   cost accounting

f)   daily operations commentary

g)   vendor representative identification

h)   environmental and safety Information

13.1.5   Additional sections may be appropriate depending on the complexity of the operation. For example, during filtration operations it should be common to also have a separate daily filtration report, or a section devoted to filtration operations. Page size and number of pages should be at the discretion of the operator and supplier.

13.1.6   Annex A gives an example daily completions report. The content and arrangement of the sections are discretionary and should be agreed upon between operator and supplier.

13.2   Daily Report Header

13.2.1   Operator, Contractor, Rig Description, Legal Description, and other well identification information

The daily report header includes the following type of information:

a)   report date

b)   report number

c)   operator name

d)   operator representative name

e)   contractor

f)   contractor representative name

g)   rig name and number

h)   well name and number

i)   API well number (if applicable)

j)   field or development name

k)   geographic location

l)   country, region/state, county/parish, block

m)   current depths and activities

13.3   Wellbore geometry, pumps, and zone data

Wellbore geometry includes the following information:

a)   casing and liner weights, grades, dimensions, displacements, and depths/lengths

b)   drill pipe, tubing, work string, weights, grades, dimensions, displacements, and depths/lengths

c)   downhole tools, packers, description, dimensions, displacements, and depth/lengths

d)   well volume, expressed as capacity, annular or pipe volumes, and work string displacement

13.3.1   Pumps

a)   Model, liner/plunger sizes, pump rates, pump displacement, and circulation times

13.3.2   Zone Data

Well zone data includes the following information,

a)   name of current zone or zone of treatment,

b)   perforation depths,

c)   bottomhole temperature of zone,

d)   bottomhole pressure of zone,

e)   true vertical depth of zone.

13.4   Completion Fluid Properties

13.4.1   The system properties to be included in the daily completion fluid report shall be those tested in accordance with this standard:

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

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

c)   funnel viscosity

d)   pH at actual temperature, noting °C or °F

e)   TCT, noting °C or °F

f)   clarity, NTU

g)   percent solids (volume fraction)

h)   iron content, expressed in mg/L

i)   buffer capacity expressed in concentration of titratable basic species of sodium bicarbonate and potassium bicarbonate.

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

13.5   Fluids and Products Accounting

13.5.1   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.

13.5.2   Fluids accounting consists of the following 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 reported stated in 12.5.2 item a). Fluids 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 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.

e)   Fluids such as produced fluids and solids, contaminated fluids, spacers and flushes, and acid/pickle should also be documented in this section.

f)   Sacked and liquid additive products should be inventoried and accounted for in this section.

13.6   Usage and/or Cost Accounting

Usage and/or cost accounting is a tabulation of all material and service usage and/or costs done daily and cumulatively for the well. Typical values which should be reported are:

a)   total daily and cumulative cost

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

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

NOTE   For some operations, cost information is considered confidential and is not reported.

13.7   Daily Operational Commentary

The daily commentary is a textual section summarizing daily operations at the well. It includes a description of system performance and problems encountered. Often details for anticipated upcoming operations is also provides as well as information about fluid and product movements such as deliveries or returns.

13.8   Vendor Representative Identification

This portion of the daily completion fluids report should include

a)   Vendor representative names with contact information

b)   location of plant or stock point with contact information

c)   location of office with contact information.

13.9   Environmental and Safety Information

Often environmental related information and safety information is shown on the daily completion fluid report. Environmental related items that are often included are description and volumes of fluids discharged or disposed of, testing such as sheen, oil and grease, toxicity, flow rate and location of discharge. Safety information often documents attendance to safety meetings, job-safety-assessments, recommended PPE, safety observations, and incidents.

Annex A
(informative)

Example of Daily Completion Fluid Report

Daily Completion Fluid Report

Operator		Rig Name & No.		Report Date	
Operator Rep.		Well Name & No.		Report Number	
Contractor		Field Name		Vendor / Supplier	
Contractor Rep.		Block/County/Pad		Measured Depth	
Present Activity		Country		TVD	

Casing / Liner			String			Interval Length	Volumes				Pumps			Circ Rate	
OD	ID	Weight	OD	ID	Weight		Tubing	Annulus	Pits	Hole	#	Liner Size	Vol/stk	SPM	Vol/min
											1				
											2				
											Circulation				
														stks	min
											Bottoms-up				
											Surf to Zone				

Product Inventory							Treatment Zone	
Product	Unit Size	Start	Received	Used	Ending	Cumulative	Name	
							Depth MD/TVD	
							BHP	
							BHT	
							Deviation	

Fluid Properties		Fluid Volume Inventory				Fluid Volume Losses		
Description		Location	Fluid Type	Density	Volume	Location	Daily	Cumulative
		Well				Downhole		
Time		Active Pit #1				Rig Floor		
Temperature		Active Pit #2				BOP Stack		
Density		Active Pit #3				Shaker		
Corrected Density @		Active Pit #4				Pits		
Funnel Viscosity		Slug Pit				Filter Unit		
pH		Sand Trap				Transfers		
TCT		Trip Tank				Environmental		Safety Information
Clarity		Reserve #1				Testing		Meetings
Solids		Reserve #2				Discharges		JSA's
Iron		Other						PPE

Daily Operational Commentary	Usage and Cost Accounting		
	Fluids or Product	Daily Usage	Daily Cost
	Fluid		
	Spike		
	Products		
	Service Charge		
	Equipment / Rentals		

		Total Cost:	
Vendor Representative Name & Contact Information	Vendor Office	Stock Point	Phone

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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 [8] to [19]. 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 solid 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 often present in winter or in the arctic 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, as well as low molecular weight alcohols such as 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 TCT that have been thoroughly studied and used to properly formulate brine for specific applications. TCT values for brine formulations have been well documented 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 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 lbf/in.²) indicates that the brine fluid will crystallize at 69,000 kPa (10,000 lbf/in.²) when the fluid temperature is lowered to −2 °C (30 °F).

C.1.6   PCT measurements are routinely conducted to 103 MPa (15,000 lbf/in.²) at temperatures from 21 °C (70 °F) to −40 °C (−40 °F), and more recently, pressures to 138 MPa (20,000 lbf/in.²) are conducted.

C.2 Measuring Pressure Crystallization Temperature (PCT)

C.2.1   Conventional methods for measuring TCT should be difficult to modify for the measurement of PCT, predominantly because of the need to contain the high pressure required to measure PCT values. Controlled agitation of the fluid and direct or indirect monitoring of the crystallization process (such as visual observation, exotherm and/or turbidity measurements) are recognized requirements for accurate measurement of TCT and routinely performed, but they should be also difficult to implement for the measurement of PCT.

C.2.2   Nonetheless, equipment that incorporates controlled agitation of the fluid and direct or indirect monitoring 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. These devices adequately control super-cooling through controlled agitation and slow cooling rates (less than 1°F per minute), which is critical to accurate TCT and PCT measurements.

C.2.3   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 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 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 should be 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 should be 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, a completion fluid supplier should be consulted.

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 annex E 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 [3] 1020, AISI 1040.

b) Low-alloy steels, 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.

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[3]   American Iron and Steel Institute, 1140 Connecticut Avenue NW, Washington, DC 20036, USA, www.steel.org

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. [20]

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-force per square inch, (kpsi).[21] [22]

NOTE   1 kpsi = 1000 psi = 1000 lb/in.² = 6895 kPa = 6.90 N/mm^2 (kpsi are commonly also called ksi)

E.2.4.1.2 Carbon and low-alloy steels are 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 specific 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 (pound-force per square inch absolute), 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 ANSI/NACE MR0175/ISO 15156 that places limits on hardness, strength, and steel processing. [22]

E.2.4.1.4 In environments containing little or no CO_2 but significant levels of H_2S [23] [24] [25] [26], 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 SS, 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 SS 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 SSs 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 SSs. Their use in sour service is governed by ANSI/NACE MR0175/ISO 15156.

E.2.4.2.3 Martensitic stainless steels (MSS) contain 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 SS,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 ANSI/NACE MR0175/ISO 15156.

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 SSs. Examples of DSSs 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 DSSs 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 ANSI/NACE MR0175/ISO 15156.

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 C276, 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 ANSI/NACE MR0175/ISO 15156.

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 should be carbon or low-alloy steels. API SPEC 5CT [21] 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 kpsi [c]	max kpsi [c]	min MPa	min kpsi [c]	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 L80 13Cr. Other proprietary, non–API SPEC 5CT grades are also available. For CRA oil country tubular goods, see also API SPEC 5CRA. [27]

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

[c] 1 kpsi = 1000 psi = 1000 lbf/in.²

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 (O_2) from the surface, carbon dioxide (CO_2), and hydrogen sulfide (H_2S) 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 H_2S 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 CO_2, like H_2S, 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 O_2 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. O_2 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 O_2 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 O_2.

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 SSsand other CRAs with intermediate levels of nickel, e.g., super martensitic (S13Cr) and DSS (22Cr).

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, O_2, inhibitors for corrosion, hydrate and/or scale, O_2 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 O_2-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, H_2S, 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 a low temperature effect: most metals are relatively immune to hydrogen embrittlement above approximately 150°C (302°F).

E.3.4.10 Sulfide Stress Corrosion (SSC)

E.3.4.10.1 SSC is a form of hydrogen embrittlement. In the presence of H_2S, 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., drill string, 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 should be 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 should be 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 should be 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 should be 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 should be measured.

E.4.2   Galvanic (Bimetallic) Corrosion Method

E.4.2.1   Galvanic testing should be conducted similarly to the weight-loss testing described in E.4.1. Before submersion in the test brine, dissimilar metals should be electrically coupled together. The relative surface area of the two coupons can impact the corrosion rate of each coupon and should be considered 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 should be similar to a standard weight-loss test, and the individual coupons should be 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 should be 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 should be 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 should be pressurized with the appropriate gas or gases and heated to the target temperature. This temperature should be maintained throughout the test duration, which should be usually 30 days.

E.4.4.4   The specimens should be 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 polarization resistance, 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[4] 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[5] Test Methods

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[4]   International Organization for Standardization, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland; www.iso.org

[5]   NACE International Institute, 15835 Park Ten Place, Houston, Tx 7704, USA; www.ampp.org

NACE/ASTM TM0169 G0031 12A-2012-SG, *Standard Guide for Laboratory Immersion Corrosion Testing of Metals*

TM0171-HD1995-SG, *Autoclave Corrosion Testing of Metals in High-Temperature Water-HD1995*TM0177, *Laboratory testing of metals for resistance to sulfide stress cracking and stress corrosion cracking in H_2S environments*

TM0270-HD1972-SG, *Method of Conduction Controlled Velocity Laboratory Corrosion Tests-HD1972*

TM0274-HD1995-SG, *Dynamic Corrosion Testing of Metals in High-Temperature Water-HD1995*

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 Crossed-Cylinder Apparatus (Withdrawn 2005).*

e) Erosion corrosion:

— G73*, Standard Test Method for Liquid Impingement Erosion Using Rotating Apparatus.*

f) Electrochemical test measurements:

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

— G96, *Standard Guide for Online 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 Potentiodynamic Anodic Polarization Measurements*;

— G59, *Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements*;

— G61, *Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys.*

E.5 Control of Corrosion

E.5.1   Control of corrosion should be 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 should be 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 should be driven by operational requirements and material compatibility.

E.5.3.3   A joint industry project formed under the auspices of the American Petroleum Institute (API) evaluated the SCC risks of a range of CRAs in various halide brine compositions for the case of exposure to acidic production gas (CO_2+H_2S). Results of the project are summarized in API 13TR1 [28].

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 O_2, CO_2 or H_2S.

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- O_2 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 H_2S. 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 O_2 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.

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