
**Petroleum and natural gas industries —
Completion fluids and materials —**

**Part 3:
Testing of heavy brines**

*Industries du pétrole et du gaz naturel — Fluides et matériaux de
complétion —*

Partie 3: Essais de saumures denses



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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 13503-3 was prepared by Technical Committee ISO/TC 67, *Materials, equipment and offshore structures for petroleum, petrochemical and natural gas industries*, Subcommittee SC 3, *Drilling and completion fluids, and well cements*.

ISO 13503 consists of the following parts, under the general title *Petroleum and natural gas industries — Completion fluids and materials*:

- *Part 1: Measurement of viscous properties of completion fluids*
- *Part 3: Testing of heavy brines*

The following parts are under preparation:

- *Part 2: Measurement of properties of proppants used in hydraulic fracturing and gravel packing operations*
- *Part 4: Procedure for measuring stimulation and gravel-pack fluid leakoff under static conditions*
- *Part 5: Procedure for measuring the long-term conductivity of proppants*

Introduction

This part of ISO 13503 covers heavy brines commonly used in petroleum and natural gas completion, workover and drill-in fluids. These brines can be purchased or rented from multiple sources, and are available worldwide. No single source or limited source of supply is included, either by inference or reference.

Annexes A to F are given for information.

Petroleum and natural gas industries — Completion fluids and materials —

Part 3: Testing of heavy brines

1 Scope

This part of ISO 13503 covers the physical properties, potential contaminants and test procedures for heavy brine fluids manufactured for use in oil and gas well drilling, completion and workover fluids.

This part of ISO 13503 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 brine, the crystallization point or the temperature (both ambient and under pressure) at which the brines make the transition between liquid and solid, the pH, and iron contamination.

It also contains a discussion of gas hydrate formation and mitigation, brine viscosity, corrosion testing, buffering capacity and a standardised reporting form.

This part of ISO 13503 is intended for the use of manufacturers, service companies and end-users of heavy brines.

2 Normative references

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

ISO 10414-1:2001, *Petroleum and natural gas industries — Field testing of drilling fluids — Part 1: Water-based fluids*

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

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

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

NIST SRM 191C, *pH Standards*

NBS (NIST) Circular 555, *Testing of Hydrometers*, 22 Oct 1954

1) ASTM, American Society for Testing and Materials, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. <http://www.astm.org>.

2) NIST, National Institute of Standards and Technology, 100 Bureau Drive, Stop 3460, Gaithersburg, MD 20899-3460, USA. <http://www.nist.gov>.

3 Terms, definitions and abbreviated terms

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

3.1 Terms and definitions

3.1.1

ACS reagent grade

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

3.1.2

user

manufacturer, service company, end user or operator applying the testing of this part of ISO 13503

3.2 Symbols and abbreviated terms

ACS	American Chemical Society
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
CAS	Chemical Abstracts Service
FCTA	first crystal to appear
LCTD	last crystal to dissolve
NIST	National Institute of Standards and Technology
NTU	nephelometric turbidity unit
psi	pounds per square inch
TCT	true crystallization temperature
TD	to deliver
USC	United States Customary
V	volts
ρ	density, in g/cm ³
ρ_1	density at lower temperature
ρ_2	density at upper temperature
ρ_{70}	density at 70 °F (21 °C), in lb/gal
ρ_{21}	density at 21 °C (70 °F), in g/cm ³
ρ_{A-SI}	average wellbore density, in g/cm ³
ρ_{A-USC}	average wellbore density, in lb/gal
ρ_m	measured density

ρ_{cf}	density, in lb/ft ³
ρ_{SI}	density, in kg/m ³
ρ_{SI-21}	density at 21°C, in kg/m ³
ρ_{USC}	density, in lb/gal
ρ_W	density of water
θ	temperature, in °C (°F)
θ_1	temperature at lower reading, in °C (°F)
θ_2	temperature at upper reading, in °C (°F)
θ_m	measured temperature, in °C (°F)
∇_{cf}	mud gradient, in psi/foot calculated from density expressed in pounds per cubic foot
∇_{SI}	mud gradient, in kPa/m
∇_{USC}	mud gradient, in psi/foot calculated from density expressed in pounds per gallon
B_c	intercept of hydrometer-correction curve
C	density correction factor for temperature, in g/cm ³ per °C
C_θ	temperature correction factor, in lb/gal per 100 °F
C_p	pressure correction factor, in lb/gal per 1 000 psi
C_{SI}	density correction factor for temperature, in kg/m ³ per °C
C_{USC}	density correction factor for temperature, in lb/gal per °F
h	depth (height) of well, in feet
h_2	depth (height) of well at true vertical depth, in feet
R	hydrometer reading, specific gravity
R_1	hydrometer reading at lower temperature
R_2	hydrometer reading at higher temperature
V	volume, in cm ³
V_1	volume of the original sample, in cm ³
Z_c	slope of hydrometer-correction curve

4 Requirements

4.1 Quality control instructions

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

4.2 Records retention

All records specified in this part of ISO 13503 shall be maintained for a minimum of one year from the date of preparation.

5 Calibration of equipment

5.1 General requirements

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

5.1.2 The user shall control, calibrate, verify and maintain the laboratory equipment and reagents used in this part of ISO 13503 for measuring product conformance.

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

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

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

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

5.2 Reagents and materials for calibration

5.2.1 Chemicals and solutions

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

5.2.2 Distilled or de-ionized water

The user shall develop, document and implement a method to determine hardness of water, such as ASTM D1126 or equivalent. The water shall not be used if hardness is greater than $5 \mu\text{g}/\text{cm}^3$ calcium ion concentration.

5.3 General requirements for calibration of particular apparatus

5.3.1 Volumetric glassware

Laboratory volumetric glassware used for testing, including flasks and pipettes, are usually calibrated by the supplier. Users of products in accordance with this part of ISO 13503 shall document evidence of glassware calibration prior to use. Supplier certification is acceptable. Calibration may be checked gravimetrically. Periodic recalibration is not required.

5.3.2 Laboratory temperature-measuring devices

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

5.3.3 Laboratory balances

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

5.3.4 Hydrometers

The user shall check the calibration of each hydrometer with fluids of known density referenced to a standard.

5.3.5 Densitometer

The user shall calibrate each densitometer to a NIST standard 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.

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.

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.

5.5 Calibration verification

5.5.1 Temperature-measuring devices

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

5.5.1.2 Read and record the temperature of all temperature-measuring devices.

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

5.5.1.4 Calculate the average and the range of readings for each temperature-measuring device. The difference between the range of readings for each temperature-measuring device shall not exceed 0,1 °C (0,2 °F), or the smallest scale division on the temperature-measuring device being calibrated.

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

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

5.5.2 Hydrometers

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

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

5.5.2.3 Place the test solution into a sedimentation cylinder. Then place the cylinder in a constant-temperature bath. Set bath temperature to the lowest expected temperature for any actual test. Allow to reach equilibrium $\pm 0,2$ °C ($\pm 0,5$ °F). Insert the NIST standard hydrometer and wait at least 5 min for the hydrometers and solution to reach the bath temperature, as measured by equilibrium of the solution temperature.

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

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

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

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

5.5.2.8 Calculate the hydrometer-correction curve slope as follows.

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

where

Z_c is the hydrometer-correction curve slope;

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

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

θ_1 is the average temperature at the lower bath temperature;

θ_2 is the average temperature at the higher bath temperature.

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

5.5.2.9 Calculate the hydrometer-correction curve intercept as follows.

$$B_c = (Z_c \cdot \theta_1) [1000(R_1 - 1)] \quad (2)$$

where

B_c is the hydrometer-correction curve intercept;

Z_c is the hydrometer-correction curve slope;

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

θ_1 is the average temperature at the lower bath temperature;

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

6 Density

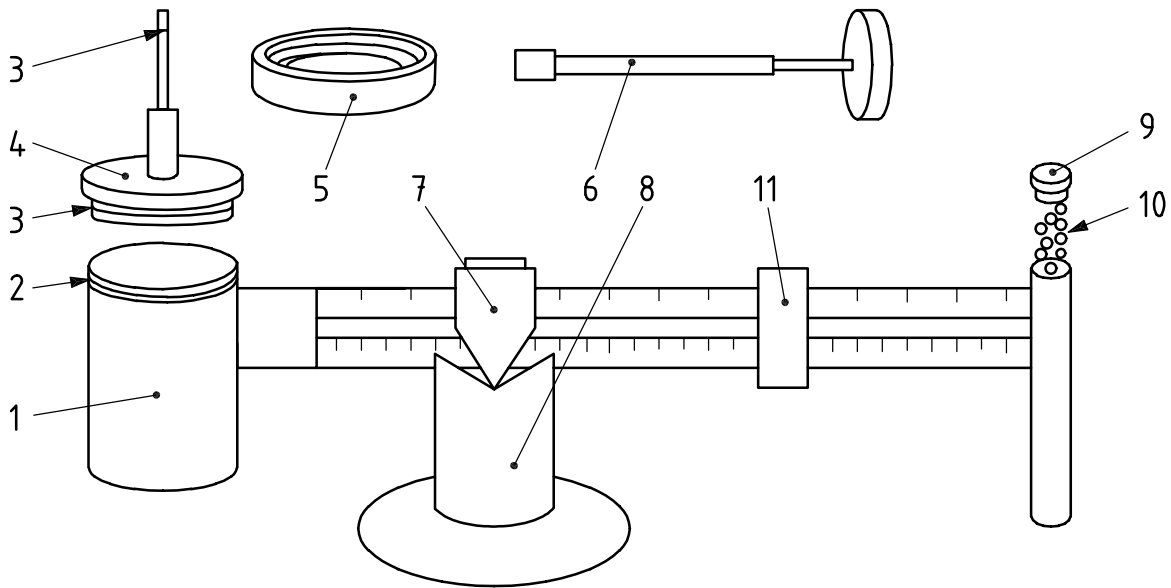
6.1 General

6.1.1 The density of a 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 a brine is the mass of brine per unit of volume. Density is generally reported as grams per cubic centimetre, kilograms per cubic metre, or pounds mass per gallon. Density may also be expressed in terms of specific gravity or pressure gradient. Specific gravity is the ratio of the mass of a specific volume of material at a specified temperature when compared to an equal volume of reference material at the same (or another) temperature. For brines, the reference material is water. Pressure gradient is the hydrostatic pressure exerted by the fluid per unit depth.

6.1.3 The reference temperature used to report density of heavy brines is 21 °C (70 °F). The corrected density is not used to determine hydrostatic pressure. Instead, the actual density at ambient temperature is used to calculate hydrostatic pressure.

6.1.4 The measurement of the density of brines is affected by entrapped gasses. If gas entrainment is a problem, it is recommended that the procedures outlined in ISO 10414-1 be used. These procedures use a pressurised fluid density (mud) balance and/or de-aerator to aid in the density measurement. See Figure 1 for an example of a mud balance.



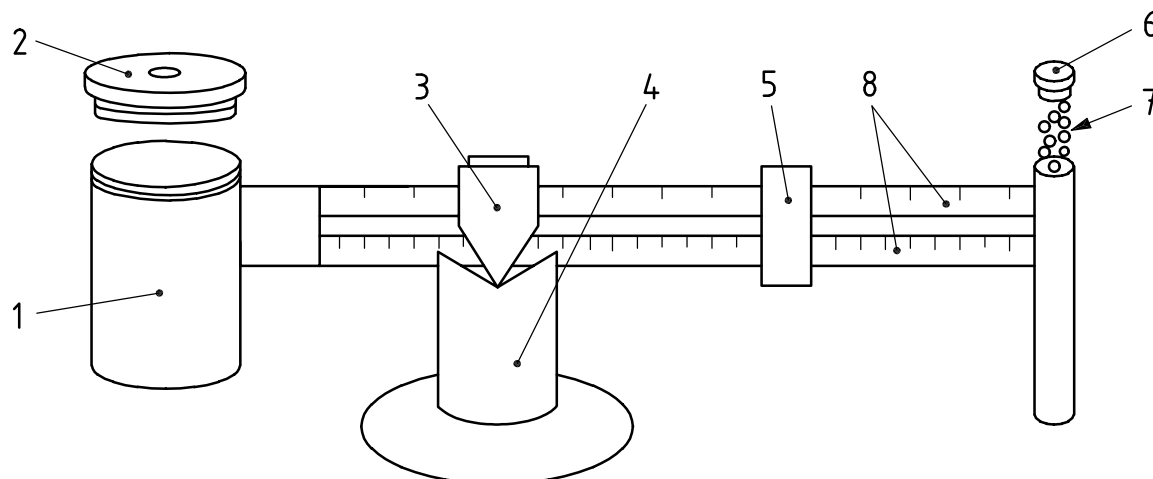
Key

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

Figure 1 — Pressurised mud balance

6.1.5 The atmospheric (see Figure 2) and pressurised 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 shall be used instead of a mud balance. For the use and calibration of mud balances, follow the procedures specified in ISO 10414-1.

6.1.6 Any instrument of sufficient precision to permit measurement to within $\pm 5 \text{ kg/m}^3$ ($\pm 0,005 \text{ g/cm}^3$; $\pm 0,05 \text{ lb/gal}$) and reportable to within $\pm 10 \text{ kg/m}^3$ ($\pm 0,01 \text{ g/cm}^3$; $\pm 0,1 \text{ lb/gal}$) may be used. Generally, this requires the use of hydrometers for fluid density measurements. An atmospheric or pressurised mud balance may be used, but lacks sufficient precision to meet the requirements of this clause for reporting brine density (see 6.2.1 through 6.2.3).

**Key**

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

Figure 2 — Atmospheric mud balance**6.2 Apparatus**

6.2.1 Set of glass hydrometers, covering the range of specific gravities encountered in heavy brine application with graduations in specific gravity units (dimensionless) not greater than 0,002.

The hydrometer is a weighted bulb with a graduated stem. The depth to which the hydrometer sinks in a fluid is determined by the density of the fluid and temperature. The specific gravity is read directly from the graduated stem^[5]. Any oil present in the sample will interfere with the measurement, and the use of freshly filtered samples is recommended.

If hydrometers with built-in thermometers are used, it is recommended that the sample be brought to 21 °C (70 °F) to avoid conversion errors.

Most hydrometers used in the oilfield are calibrated to water at 60 °F and sample at 60 °F. Therefore, the calculations reported herein are referenced to the specific gravity based on 60 °F/60 °F hydrometers.

6.2.2 Cylindrical sample container, plastic or glass.

For convenience in pouring, the cylinder may have a lip on the rim. The inside diameter of the cylinder shall be at least 2,54 cm (1,0 in) greater than the outside diameter of the hydrometer used. The height of the cylinder shall be such that the hydrometer floats in the sample fluid with at least 2,54 cm (1,0 in) clearance between the bottom of the hydrometer and the bottom of the cylinder.

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

6.2.4 Filter paper.

6.2.5 Constant temperature bath, regulated to 21 °C \pm 1 °C (70 °F \pm 2 °F).

6.3 Density measurement by hydrometer

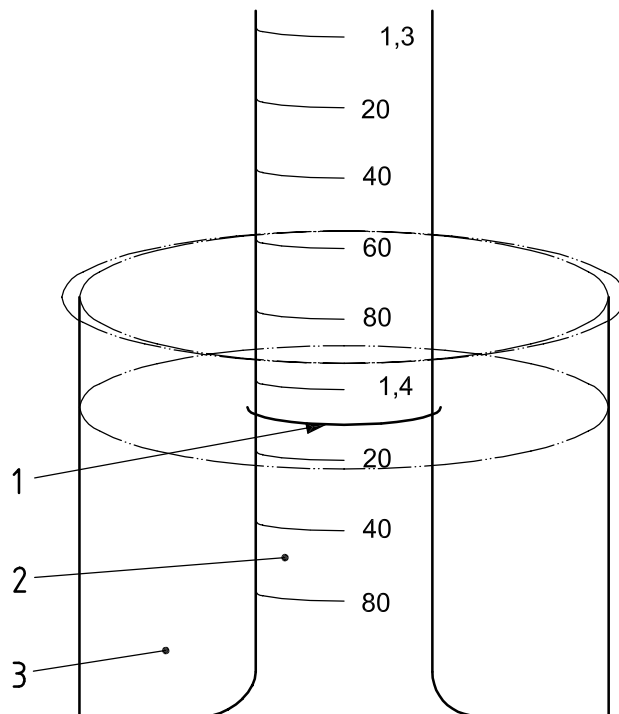
6.3.1 Pour the sample fluid into the clean, dry cylinder without splashing. Splashing can entrain air bubbles in the fluid. Remove any air bubbles adhering to the surface by touching them with a piece of clean filter paper.

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

6.3.3 Place the hydrometer vertically in the sample fluid and spin the cylinder to centre the device.

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

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



Key

- 1 reading at bottom of meniscus
- 2 hydrometer
- 3 sample

Figure 3 — Reading at bottom of meniscus

6.4 Density correction to 21 °C (70 °F)

6.4.1 The calculated density of the sample fluid shall be corrected to 21 °C (70 °F) if the measurement was taken at any other temperature. A correction factor for the brine shall be read from Table 1, which is an estimate of the correction factor or, for USC units, can be calculated using Equation (3).

$$C_{\text{USC}} = (-5,965\ 9 \times 10^{-4}) + (6,954 \times 10^{-3} R) - (4,799 \times 10^{-3} R^2) + (1,263 \times 10^{-3} R^3) \quad (3)$$

where

R is the hydrometer reading.

Table 1 — Estimated hydrometer correction factor

Density kg/m ³ at 21 °C ρ_{SI}	Density g/cm ³ at 21 °C ρ_{21}	Density lb/gal at 70 °F ρ_{70}	Correction factor kg/m ³ per °C C_{SI}	Correction factor g/cm ³ per °C C	Correction factor lb/gal per °F C_{USC}
1 019	1,019	8,5	0,60	0,000 61	0,002 84
1 078	1,078	9,0	0,63	0,000 63	0,002 91
1 138	1,138	9,5	0,64	0,000 64	0,002 97
1 198	1,198	10,0	0,65	0,000 65	0,003 02
1 258	1,258	10,5	0,66	0,000 66	0,003 07
1 318	1,318	11,0	0,67	0,000 67	0,003 13
1 378	1,378	11,5	0,69	0,000 69	0,003 18
1 438	1,438	12,0	0,70	0,000 70	0,003 24
1 498	1,498	12,5	0,71	0,000 71	0,003 30
1 558	1,558	13,0	0,73	0,000 73	0,003 37
1 618	1,618	13,5	0,74	0,000 74	0,003 44
1 678	1,678	14,0	0,76	0,000 76	0,003 53
1 738	1,738	14,5	0,78	0,000 78	0,003 63
1 797	1,797	15,0	0,81	0,000 81	0,003 74
1 857	1,857	15,5	0,83	0,000 83	0,003 86
1 917	1,917	16,0	0,86	0,000 86	0,004 00
1 977	1,977	16,5	0,90	0,000 90	0,004 16
2 037	2,037	17,0	0,94	0,000 94	0,004 34
2 097	2,097	17,5	0,98	0,000 98	0,004 54
2 157	2,157	18,0	1,03	0,001 03	0,004 76
2 217	2,217	18,5	1,08	0,001 08	0,005 01
2 277	2,277	19,0	1,14	0,001 14	0,005 28

Using the correction factor from either Equation (3) or Table 1, calculate the corrected density at 21 °C (70 °F).

- a) If temperature measurement is given in degrees Celsius, use Equation (4) to find the corrected density in kg/m³.

$$\rho_{\text{SI}-21} = 999R + [(\theta_m - 21)C_{\text{SI}}] \quad (4)$$

where

- ρ_{SI-21} is the density at 21 °C, in kg/m³;
- R is the hydrometer reading;
- θ_m is the measured temperature, in °C;
- C_{SI} is the correction factor from Table 1

- b) If temperature measurement is given in degrees Celsius, use Equation (5) to find the corrected density in g/cm³.

$$\rho_{21} = 0,999R + [(\theta_m - 21)C] \quad (5)$$

where

- ρ_{21} is the density at 21 °C, in g/cm³;
- R is the hydrometer reading;
- θ_m is the measured temperature, in °C;
- C is the correction factor from Table 1.

- c) If temperature measurement is given in degrees Fahrenheit, use Equation (6) to find the corrected density in lb/gal.

$$\rho_{70} = 8,337R + [(\theta_m - 70)C_{USC}] \quad (6)$$

where

- ρ_{70} is the density at 70 °F, in lb/gal;
- R is the hydrometer reading;
- θ_m is the measured temperature, in °F;
- C_{USC} is the correction factor from Table 1 or Equation (3).

6.4.2 The correction factor for a particular brine can also be calculated by measuring the density of the brine at two or more widely separated temperatures. The correction factor is then calculated using Equation (7), illustrated for C expressed in g/cm³ per °C:

$$C = \frac{\rho_1 - \rho_2}{\theta_2 - \theta_1} \quad (7)$$

where

- C is the correction factor, in g/cm³ per °C;
- ρ_1 is the density at lower temperature, in g/cm³;
- ρ_2 is the density at higher temperature, in g/cm³;
- θ_1 is the lower temperature, in °C;
- θ_2 is the higher temperature, in °C.

6.4.3 An additional field method for correction of brine density utilises a curve developed to compare the measured brine densities at various temperatures. The curve may then be used for density conversion to 21 °C (70 °F). This curve will be specific for the particular brine being tested and cannot be applied to any other fluid, nor can it be applied to the fluid after its composition has been altered (that is, dilution, increase in density, etc.).

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

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

6.5 Calculation of density in units other than kg/m³

6.5.1 Convert the density in kg/m³ to other common units by the following equations.

$$\rho_{\text{USC}} = \rho_{\text{SI}} \times 0,008\,345 \quad (8)$$

where

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

ρ_{SI} is the density calculated in kg/m³.

or

$$\rho_{\text{cf}} = \rho_{\text{SI}} \times 0,062\,43 \quad (9)$$

where

ρ_{cf} is the density in USC units of lb/ft³;

ρ_{SI} is the density calculated in kg/m³.

or

$$\rho = \rho_{\text{SI}} \times 0,001 \quad (10)$$

where

ρ is the density in g/cm³;

ρ_{SI} is the density calculated in kg/m³.

6.5.2 Calculate the mud gradient from the density.

$$\nabla_{\text{SI}} = \frac{\rho}{(0,102\,017)} \quad (11)$$

where

∇_{SI} is the mud gradient, in kPa/m;

ρ is the density, in g/cm³.

or

$$\nabla_{\text{USC}} = \frac{\rho_{\text{USC}}}{19,24} \quad (12)$$

where

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

ρ_{USC} is the density, in lb/gal.

or

$$\nabla_{\text{cf}} = \frac{\rho_{\text{cf}}}{144} \quad (13)$$

where

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

ρ_{cf} is the density, in lb/ft³.

Note that the results from Equation (12) and Equation (13) are equivalent.

6.6 Calculation for pressure and temperature compensation

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

NOTE Most completion brine service companies and fluid engineers have sophisticated computer models to calculate the average brine density in the wellbore. These models typically divide the wellbore into twenty or more slices and iterate the changes to the density caused by temperature and pressure at each wellbore interval. The calculations provided in this subclause 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 (mud line to true vertical depth).

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

6.6.2 Calculate the average brine density in the wellbore, in USC units of lb/gal.

$$\rho_{\text{A-USC}} = \frac{[(2\,000 - 0,052C_p \cdot h_2)\rho_1] - [10C_\theta(\theta_1 - \theta_2)]}{(2\,000 - 0,104C_p \cdot h_2)} \quad (14)$$

where

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

ρ_1 is the density at the surface, in lb/gal;

θ_1 is the brine temperature, in °F, measured at the surface or assumed to be 70 °F;

θ_2 is the brine temperature, in °F, measured at bottom hole;

C_θ is the temperature compensation factor, see Table 2;

C_p is the pressure compensation factor, see Table 3;

h_2 is the true vertical depth, in feet.

Table 2 — Temperature correction factor

Brine type	Density lb/gal ρ	Vol/Vol/°F $\times 10^{-4}$	Correction factor lb/gal/100 °F C_{θ}
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 82,74 MPa (12 000 psig) from 22,44 °C to 92,22 °C (76 °F to 198 °F) (see Bibliography [17]).

Table 3 — Pressure correction factor

Brine type	Density lb/gal ρ	Specific gravity at 60/60	Vol/Vol/°F $\times 10^{-6}$	Correction factor lb/gal/1 000 psi C_p
NaCl	9,49	1,138	1,98	0,019
CaCl ₂	11,46	1,374	1,50	0,017
NaBr	12,48	1,496	1,67	0,021
CaBr ₂	14,30	1,715	1,53	0,022
ZnBr ₂ /CaBr ₂ /CaCl ₂ (less than 2,1 specific gravity)	16,01	1,920	1,39	0,022
ZnBr ₂ /CaBr ₂ (greater than 2,1 specific gravity)	19,27	2,311	1,64	0,031

NOTE Compressibility of heavy brine was measured at 198°F from 6,90 MPa (1 000 psig) to 68,95 MPa (10 000 psig) (see Bibliography [17]).

6.6.3 Calculate the average brine density in the wellbore in SI units of g/cm³.

$$\rho_{A-SI} = \frac{\rho_{A-USC}}{8,345} \quad (15)$$

where

ρ_{A-USC} is the corrected average brine density in the wellbore, in lb/gal;

ρ_{A-SI} is the corrected average brine density in the wellbore, in g/cm³.

6.6.4 Calculate the average hydrostatic pressure in the wellbore in USC units of lb/in².

$$p_h = 0,052 \rho_{A-USC} h_2 \quad (16)$$

where

p_h is the hydrostatic pressure, in lb/in²;

ρ_{A-USC} is the corrected average brine density in the wellbore, in lb/gal;

h_2 is the true vertical depth, in feet.

6.6.5 Calculate the average hydrostatic pressure in the wellbore in SI units of kg/m³.

$$p_{h-SI} = 0,070\ 31\ p_h \quad (17)$$

where

p_{h-SI} is the hydrostatic pressure, in kg/m³;

p_h is the hydrostatic pressure, in lb/in².

7 Crystallization temperature

7.1 Principle

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

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

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

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

7.1.5 Precipitation of salt crystals in brine at or below the crystallization temperature can lead to a number of problems. Rapid plugging of filtration units can occur. If salt crystals settle in the tank, the density of the brine pumped downhole can be insufficient to control formation pressures. 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, low concentrations of salt solutions will expand and can lead to equipment failure.

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

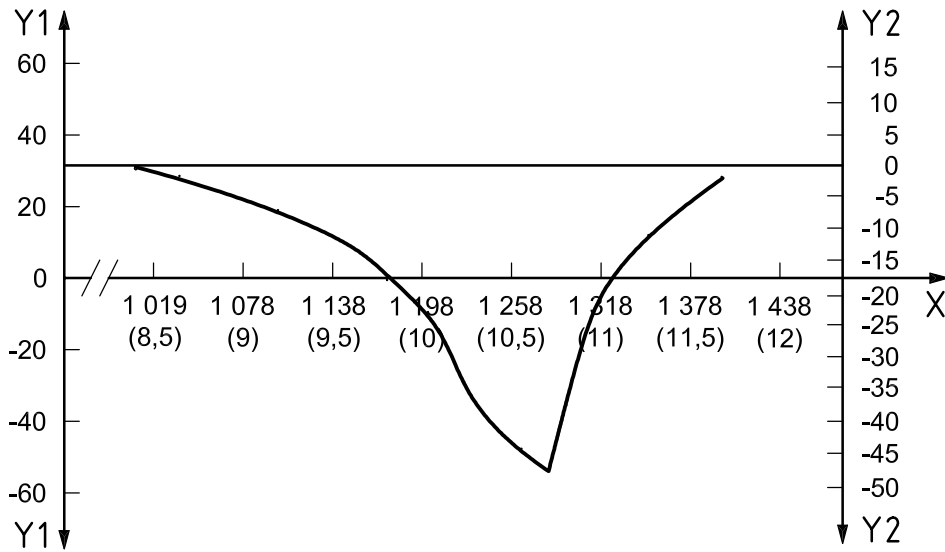
7.1.8 With dilute brine (for example, seawater), the salt in the water depresses the crystallization temperature or the freezing point of the brine. The salts reduce the temperature at which fresh-water ice will form.

7.1.9 Table 4 and Figure 4 show the crystallization temperature of calcium chloride solution as a function of concentration. The figure shows the true crystallization temperature, TCT.

Table 4 — Calcium chloride solutions — Crystallization temperature

Mass fraction %	Specific gravity at 60/60	Density kg/m ³ ρ_{SI}	Density lb/gal ρ_{USC}	Crystallization point °C (°F)
1	1,009	1 009	8,415	-0,5 (31,1)
2	1,017	1 017	8,482	-0,9 (30,4)
3	1,026	1 026	8,557	-1,4 (29,5)
4	1,034	1 034	8,624	-1,9 (28,6)
5	1,043	1 043	8,699	-2,4 (27,7)
6	1,051	1 051	8,765	-2,9 (26,8)
7	1,060	1 060	8,840	-3,4 (25,9)
8	1,068	1 068	8,907	-4,1 (24,6)
9	1,077	1 077	8,982	-4,7 (23,5)
10	1,085	1 085	9,049	-5,4 (22,3)
11	1,094	1 094	9,124	-6,2 (20,8)
12	1,103	1 103	9,199	-7,1 (19,3)
13	1,113	1 113	9,282	-8,0 (17,6)
14	1,122	1 122	9,357	-9,2 (15,5)
15	1,132	1 132	9,441	-10,3 (13,5)
16	1,141	1 141	9,516	-11,6 (11,2)
17	1,151	1 151	9,599	-13,0 (8,6)
18	1,160	1 160	9,674	-14,5 (5,9)
19	1,170	1 170	9,758	-16,2 (2,8)
20	1,180	1 180	9,841	-18,0 (-0,4)
21	1,190	1 190	9,925	-20,0 (-3,9)
22	1,200	1 200	10,008	-22,1 (-7,8)
23	1,210	1 210	10,091	-24,4 (-11,9)
24	1,220	1 220	10,175	-26,8 (-16,2)
25	1,231	1 231	10,267	-29,4 (-21,0)
26	1,241	1 241	10,350	-32,1 (-25,8)
27	1,252	1 252	10,442	-35,1 (-31,2)
28	1,262	1 262	10,525	-38,8 (-37,8)
29	1,273	1 273	10,617	-45,2 (-49,4)
30	1,284	1 284	10,709	-46,0 (-50,8)
31	1,295	1 295	10,800	-36,0 (-33,2)
32	1,306	1 306	10,892	-28,6 (-19,5)
33	1,317	1 317	10,984	-21,6 (-6,9)
34	1,328	1 328	11,076	-15,4 (+4,3)
35	1,340	1 340	11,176	-9,8 (+14,4)
36	1,351	1 351	11,267	-4,4 (+24,1)
37	1,363	1,363	11,367	+0,8 (+33,4)
38	1,375	1,375	11,468	+5,6 (+42,1)
39	1,387	1,387	11,568	+9,8 (+49,6)
40	1,398	1,398	11,659	+13,3 (+55,9)

NOTE See Bibliography reference [24].



Key

- X density, kg/m³ (lb/gal)
- Y₁ temperature, degrees Fahrenheit
- Y₂ temperature, degrees Celsius

Figure 4 — Calcium chloride crystallization temperature

The crystallization temperature of the brine decreases to as low as $-46,0\text{ °C}$ ($-50,8\text{ °F}$) at a mass fraction of 30 % CaCl_2 or $1\,280\text{ kg/m}^3$ (1,28 specific gravity, 10,7 lb/gal). In this portion of the curve, temperatures below the crystallization temperature result in the formation of fresh-water ice, producing brine with a higher salt concentration.

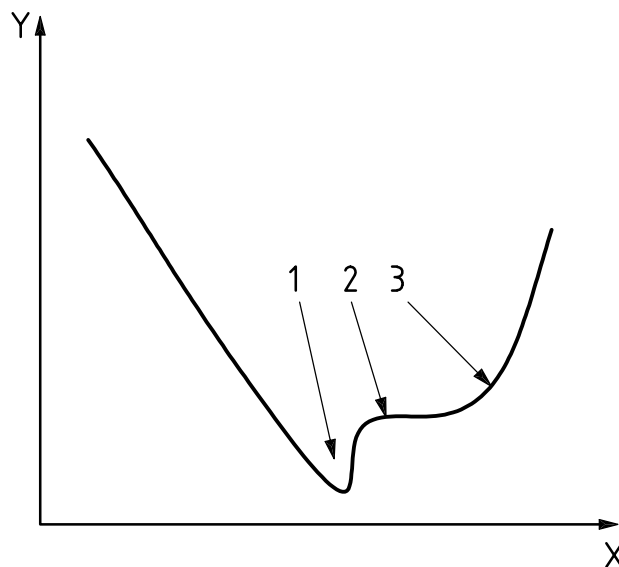
Brines with calcium chloride mass fractions above 30 % exhibit an increase in the crystallization temperature. This portion of the curve represents the solubility limit of calcium chloride in water. The crystallization temperature increases with increasing calcium chloride concentration.

As calcium chloride precipitates out of solution, the resulting brine will have a reduced salt concentration and density.

7.1.10 The crystallization profile of a brine is characterised by three temperature parameters:

- a) FCTA (First Crystal to Appear): 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);
- b) TCT (True Crystallization Temperature): 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 crystallise in pumps, lines, filtration units and tanks;
- c) LCTD (Last Crystal to Dissolve): 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.

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

**Key**

X time

Y temperature

1 first crystal to appear (FCTA)

2 true crystallization temperature (TCT)

3 last crystal to dissolve (LCTD)

Figure 5 — Typical crystallization curve for brine

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

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

7.1.14 The heat of dissolution is responsible for the inflection point at LCTD that can be observed as a crystallised 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 redissolved at LCTD, the brine will warm more rapidly.

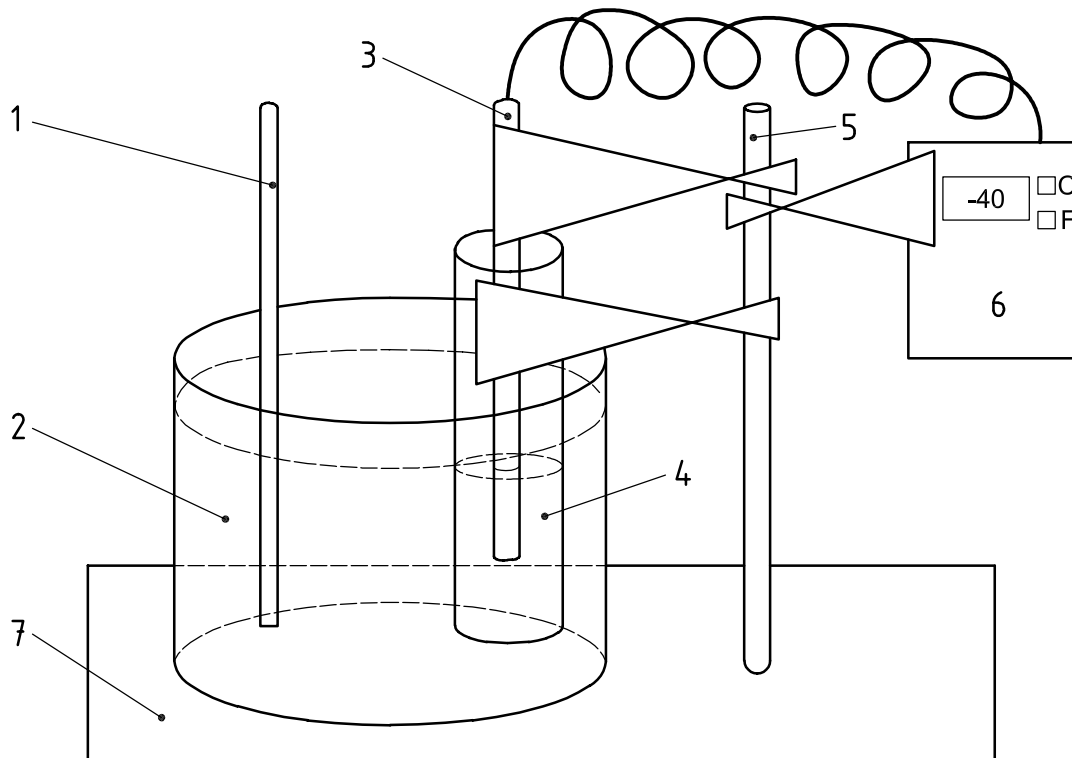
7.1.15 When measuring the crystallization temperature of brine, one should be aware that minor components can precipitate from solution before the TCT. For example, both sodium chloride and potassium chloride are less soluble than calcium chloride, calcium bromide or zinc bromide. If a brine is contaminated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

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

7.2 Apparatus

7.2.1 **Digital temperature-measuring device with thermistor or RTD probe**, having an indicating range of $-45\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$ ($-50\text{ }^{\circ}\text{F}$ to $100\text{ }^{\circ}\text{F}$) with a resolution of $0,05\text{ }^{\circ}\text{C}$ ($0,1\text{ }^{\circ}\text{F}$).

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



Key

- 1 thermometer
- 2 ice bath
- 3 thermistor
- 4 sample
- 5 laboratory stand
- 6 digital thermometer
- 7 laboratory base

Figure 6 — Typical crystallization temperature measurement setup

7.2.2 **Container**, minimum capacity 25 cm^3 .

A suitable container is a $2,0\text{ cm} \times 15,0\text{ cm}$ test tube that will fit inside a $2,5\text{ cm} \times 15,0\text{ cm}$ tube. 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 $11\text{ }^{\circ}\text{C}$ ($20\text{ }^{\circ}\text{F}$) below the FCTA temperature. Ideally, the cooling rate should be less than $0,5\text{ }^{\circ}\text{C}$ ($1\text{ }^{\circ}\text{F}$) per minute. This can be achieved through the use of an electronic cooling system or through the use of one or more of the following:

- a) ice/water slurry (1:1 volume ratio ice to water). The temperature of the bath will be 0 °C (32 °F). Use if FCTA temperature is above 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/CaCl₂ slurry (1:1 volume ratio crushed ice to CaCl₂ solution; CaCl₂ solution should contain 50 g CaCl₂ (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 11 °C (20 °F) less than the FCTA point.

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

7.2.4 Seeding material, 0,1 % mass fraction of an inert, insoluble nucleating agent.

See 7.1.12. Use approximately 0,03 g seeding material, equivalent to a few grains of salt, for 25 cm³ of brine.

7.2.5 Organic seeding marker.

7.3 Determination of crystallization point

7.3.1 Measure approximately 25 cm³ of the brine to be tested into the sample container. Add the nucleating agent to the sample. Place the sample container inside the outer container and place both in the cooling bath with the temperature-measuring device probe inserted in the brine.

7.3.2 Cool the sample slowly to minimise super-cooling. Stir the brine and record the temperature decrease of the sample. The temperature of the brine will decrease steadily until crystals begin to form. Record the minimum temperature reached before crystallization as the FCTA temperature.

7.3.3 Record the maximum temperature achieved immediately after crystallization has occurred. The temperature should stabilise briefly (10 s to 20 s). If the temperature does not stabilise, or if a large amount of super-cooling is evident [TCT minus FCTA is greater than 3 °C (5 °F)], repeat the test on the same sample. For the repeat test, the sample should be warmed above the LCTD point, but no more than 4 °C (8 °F) higher than the LCTD point.

7.3.4 Discontinue cooling the sample by removing the sample container from the bath or increasing the temperature setting of the cooling plate or bath. Allow the sample to warm, while observing for the dissolution of crystals. When all crystals have dissolved, record the temperature as the LCTD.

7.3.5 Repeat 7.3.2 through 7.3.4 at least three times using the same sample. The sample should be warmed above the LCTD but no more than 4 °C (8 °F) higher than the LCTD point.

7.4 Calculation of crystallization point

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

8 Brine clarity

8.1 Principle

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

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

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

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

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

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

8.1.6 NTU measurement of solids content provides a relative value that can be used to determine suitability of the brine for use. NTU values do not reflect a specific milligrams per litre (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 litre of solids in suspension.

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

8.2 Apparatus

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

Follow the manufacturer's recommendations for use and maintenance.

8.2.2 **Standard NTU reference cuvettes**.

8.2.3 **Sample cuvettes**.

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

8.2.4 **Mild cleaning solution**.

8.2.5 **Distilled or de-ionized water**.

8.2.6 **Lint-free cleaning cloth**.

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

8.3 Determination of brine clarity

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

8.3.2 Fill a sample cuvette to the appropriate level.

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

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

8.3.4 Switch on the NTU meter.

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

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

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

9 Solids evaluation by gravimetric procedures

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 categorisation 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 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 (TSS).

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

9.1.5 All non-representative 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 minimises this potential interference.

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

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

9.2 Apparatus

9.2.1 **Muffle furnace**, regulated to 550 °C (1022 °F).

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

9.2.3 **Glass-fibre filters**³⁾, without organic binder, 4,8 cm in diameter.

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

9.2.4 **Membrane filter support**, such as a glass or ceramic fritted disk⁴⁾, with coarse (40 µm to 60 µm) openings.

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

9.2.6 **Graduated cylinder**, (TD) 100 cm³.

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 drier⁵⁾.

9.2.10 **Distilled water**.

9.2.11 **Pipette**, 20 cm³, with large open tip.

9.2.12 **Aluminium weighing pans**.

9.2.13 **Porcelain evaporating dishes**.

9.3 Preparation of glass-fibre filter disk

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

9.3.2 Apply a vacuum to the filtration device, and wash the disk three times using 20 cm³ distilled water for each wash.

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

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

9.3.5 Dry in the oven for 1 h.

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

3) Many designs are available commercially, with some of the more common being Millipore® AP-40, Reeves® 934-AH and Gelman® Type A/E. This information is given for the convenience of users of this part of ISO 13503 and does not constitute an endorsement by ISO of this product.

4) Many designs are available commercially, with some of the more common being Hirsch, Buchner, or membrane filter holders. An alternative is the use of a Gooch crucible with equivalent coarse openings. This information is given for the convenience of the users of this part of ISO 13503 and does not constitute an endorsement by ISO of this product.

5) Drierite® is an example of a suitable product available commercially. This information is given for the convenience of the users of this part of ISO 13503 and does not constitute an endorsement by ISO of this product.

9.4 Selection of sample volume

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

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

9.4.3 Using vacuum, filter 100 cm³ of brine through the filter paper. Wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water. Allow complete drainage between washings.

9.4.4 Remove the filter paper, dry and reweigh.

9.4.5 The mass of residue remaining shall be no less than 1,0 mg. If the mass of residue remaining is less than 1,0 mg, increase the sample volume to provide at least 1,0 mg of residue.

If filters of other than 4,8 cm diameter are used, start with a sample volume equal to 7 cm³ per square centimetre of filter area. Collect at least a mass of residue proportional to the 1,0 mg stated.

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

- a) Use an unweighed glass-fibre filter of choice affixed in the filter assembly.
- b) Add a known volume of sample to the filter funnel and record the time elapsed after selected volumes have passed through the filter. These increments are suggested to be twenty, 5- cm³ aliquots with each aliquot timed for filtration rate.
- c) Continue to record the time and volume increments until filtration rate drops rapidly.
- d) Add additional sample if the filter funnel volume is inadequate to reach a reduced rate.
- e) Plot the observed time versus volume filtered.
- f) From the plot, select the proper filtration volume as that just before the time a significant change in filtration rate occurred.

9.5 Determination of total suspended solids

9.5.1 Repeat the drying cycle on a prepared glass-fibre filter disk, or Gooch crucible with disk, until constant mass is obtained, i.e. until the mass difference is less than 0,5 mg on successive measurements.

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

9.5.3 Mark three aluminium pans with individual identifying numbers or letters. Weigh the pans with the filter paper or crucible/filter paper and record the mass to four decimal places.

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

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

9.5.6 Using vacuum, wash the graduated cylinder, filter, residue and filter funnel wall with three portions of distilled water, allowing complete drainage between washings. Remove all traces of water by continuing to apply vacuum after water has passed through.

Total volume of wash-water used should equal approximately 30 cm³ for a 4,8 cm filter.

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

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

9.5.9 Remove the pans to a desiccator and cool. Reweigh and repeat the drying cycle until a constant mass is obtained, i.e. until the mass difference is less than 0,5 mg on successive measurements.

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

9.6 Calculation of total suspended solids

Calculate the total suspended solids using Equation (18).

$$m_3 = \frac{m_2 - m_1}{V_1} \times 1000 \quad (18)$$

where

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

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

V_1 is the volume of the original sample, in cm³;

m_3 is the total suspended solids, in mg/l.

NOTE Total suspended solids are also known as filterable residue.

9.7 Calculation of precision and bias

In studies by two analysts of four sets of ten 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

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

9.8.2 Remove from desiccator and weigh. Record mass.

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

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

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

9.8.6 Reweigh the porcelain evaporating dishes and record the masses.

9.9 Calculation of non-volatile and volatile solids

Use Equations (19) and (20) to calculate the total non-volatile and volatile solids, respectively.

$$m_7 = \frac{m_6 - m_4}{V_1} \times 1000 \quad (19)$$

$$m_8 = \frac{m_5 - m_6}{V_1} \times 1000 \quad (20)$$

where

m_4 is the mass of the porcelain evaporating dish and filter medium used in 9.5.1, in mg;

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

m_6 is the mass of the porcelain evaporating dish and filtered sample after auto-ignition at 550 °C (1 022 °F), in mg;

V_1 is the volume of the original sample, in cm³;

m_7 is the total non-volatile solids or residue, in mg/l;

m_8 is the total volatile solids, in mg/l.

10 pH

10.1 Principle

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

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

$$\text{pH} = -\log [\text{H}^+]$$

10.1.3 For pure water at 24 °C (75 °F), the hydrogen ion activity is 10⁻⁷ mol/l and pH = 7. This system is neutral because the hydroxyl ion activity [OH⁻] is also 10⁻⁷ mol/l. In aqueous systems at 24 °C (75 °F), the ion product, [H⁺] × [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 ten-fold change in both [H⁺] and [OH⁻]. Solutions with pH less than 7 are termed acidic, and those with pH greater than 7 are termed basic or alkaline.

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

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

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

10.2 Reagents and materials

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

Three solutions of pH = 4,0, pH = 7,0, and pH = 10,0 are standard pH buffer fluids. It is recommended that buffers be pre-made solutions or a dry powder package and obtained from chemical supply houses. These buffer solutions shall meet the requirements of NIST SRM 185h, NIST SRM 186g and NIST SRM 191C, as appropriate (see Clause 2). The shelf life shall not exceed the manufacturer's recommendation or six months after opening. 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 dihydrogen phosphate (CAS No. 7778-77-0) at 0,020 66 mol/l and disodium hydrogen phosphate (CAS No. 7558-79-4) at 0,029 34 mol/l in water gives a 7,0 pH at 24 °C (75 °F);
- c) **Buffer solution pH = 10,0:** Sodium carbonate (CAS No. 497-19-8) at 0,025 mol/l and sodium bicarbonate (CAS No. 144-55-8) at 0,025 mol/l in water gives a 10,01 pH at 24 °C (75 °F).

10.2.2 Distilled or de-ionized water, preferably in a wash or spray bottle.

NOTE De-ionization exchange resins are available.

10.2.3 Mild liquid detergent.

10.2.4 Sodium hydroxide solution, (CAS No. 1310-73-2), 0,1 mol/l, to recondition electrode.

10.2.5 Hydrochloric acid solution, (CAS No. 7647-01-0), 0,1 mol/l, to recondition electrode.

10.3 Apparatus

10.3.1 pH meter, millivolt (mV) range potentiometer calibrated to show pH units for measuring the potential between a glass-membrane electrode and a standard "reference" electrode.

The instrument should be water-, shock- and corrosion-resistant, and portable. Specifications are as follows:

- a) pH range: 0 to 14;
- b) electronics type: solid state, recommended;
- c) power source: batteries, recommended;
- d) operating temperature range: 0 °C to 66 °C (32 °F to 150 °F);
- e) readout: digital, recommended;
- f) resolution: 0,1 pH unit;
- g) accuracy: $\pm 0,1$ pH unit;
- h) repeatability: $\pm 0,1$ pH unit;
- i) meter adjustments:
 - 1) temperature compensation of electrode system, recommended;
 - 2) slope of electrode system, recommended;
 - 3) calibration setting of readout.

10.3.2 Electrode system.

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

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

10.3.3 Soft tissues, preferably lint-free, 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 cm³.

10.3.6 Beaker or equivalent container, 50 cm³.

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

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

10.4 Measurement of pH

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

a) Method 1: neat (undiluted) sample

Place 20 cm³ of the brine into a clean, dry 50 cm³ 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 cm³ of de-ionized water into a clean, dry 50 cm³ beaker or equivalent container. Add 10,0 cm³ of the sample, and mix thoroughly. Allow dilution to reach 24 °C ± 3 °C (75 °F ± 5 °F).

If the sample temperature deviates more than 11 °C (20 °F) from the calibration temperature, temperature calibration is required.

1:10 dilutions of inorganic brines in de-ionized water are neither suitable nor recommended. This leads to unacceptably imprecise results.

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

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

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

10.4.4 Follow the equipment manufacturer's recommended calibration procedure.

10.4.4.1 Dispense 20 cm³ of the pH 7,0 buffer in a suitable container and immerse the probe. Calibrate the equipment to pH 7,0.

10.4.4.2 Repeat 10.4.4.1, using a pH 4,0 buffer for an acidic sample or pH 10,0 buffer for an alkaline sample.

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

10.4.4.3 Check the meter with the pH 7,0 buffer again. Recalibrate if necessary. If the meter does not calibrate properly, recondition or replace the electrodes, see 10.6.

10.4.4.4 Calibrate the meter using two buffers daily or before each use of the meter. Check the meter with the pH 7,0 buffer every 3 h when in continuous use. Use fresh buffer solutions for calibration every day.

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

10.4.6 Record the sample temperature and pH to the nearest 0,1 pH unit.

10.4.7 Carefully clean the electrode in accordance with the manufacturers' procedures, in preparation for the next use. Store in a vial of pH 4 buffer or as recommended by the probe manufacturer. NEVER let the probe tip become dry, and do not leave the probe in the test brine. Avoid storing the instrument at extreme temperatures [below 0 °C (32 °F) or above 49 °C (120 °F)].

10.5 Precision statement

For neat brines and similarly for 1:1 diluted brines, the interlaboratory reproducibility (standard deviation) of these pH assays was in a range between 0,1 pH and 0,4 pH units, depending on the type of brine being evaluated. Many brands of pH probes were used in the round-robin testing, and this is most likely responsible for the observed deviations.

10.6 Care of the electrode

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

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

10.6.3 General care of the electrode involves the following steps.

- a) Clean the electrode with a blotting tissue or soft-bristle brush and a mild detergent.
- b) The electrode can be reconditioned by soaking it in 0,1 mol/l HCl (CAS No. 7647-01-1) for 10 min, rinsing in water, then soaking in 0,1 mol/l NaOH (CAS No. 1310-73-2) for 10 min, and rinsing it again in water.
- c) Check the electrode for response by performing a calibration, see 10.4.2 through 10.4.7.
- d) Replace the electrode system if the preceding steps a) through c) fail to recondition it.

11 Iron contamination

11.1 Principle

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

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

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

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

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

11.2 Reagents and materials

11.2.1 Distilled or de-ionized water, iron-free, preferably in a wash or spray bottle.

NOTE De-ionisation exchange resins are available.

11.2.2 Acid solution, 6,0 mol/l HCl.

11.2.3 Hydrogen peroxide (CAS No. 7722-84-1) solution, 3,0 % volume fraction.

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

11.2.5 Iron Standard Reference Material, matrix 5 % to 10 % HNO₃, 1 000 mg/l, traceable to NIST Standard Reference Material 3126a, Iron Standard Solution.

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

11.3 Apparatus

NOTE Self-filling ampoule and measured reagent test kits are commercially available⁶⁾.

11.3.1 Volumetric flasks or equivalent, 50 cm³.

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

11.3.3 Syringe, capacity 1,0 cm³.

11.3.4 Syringes, capacity 3,0 cm³.

11.3.5 Transfer pipettes, disposable.

11.3.6 Test tubes, capacity 5 cm³, clear, colourless 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.

6) CHEMetrics, Inc., www.chemetrics.com, "Iron in Brine", Kit K-6002 is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 13503 and does not constitute an endorsement by ISO of this product.

11.4 Preparation of colorimetric standards

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

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

11.4.3 Transfer 0,5 cm³ of the brine reference sample into a 50 cm³ volumetric flask via the 1,0 cm³ syringe.

11.4.4 Transfer 1,0 cm³ of the acid solution via a 3,0 cm³ syringe.

11.4.5 Add 0,25 cm³ (five drops) of the aqueous hydrogen peroxide solution via the transfer pipette. Swirl briefly to mix the contents. Wait 2,0 min, but not more than 3,0 min.

11.4.6 Fill the volumetric flask to the 50 cm³ mark with the iron-free water. Cap the flask and shake briefly to mix the contents. Remove the cap.

11.4.7 Transfer 1,0 cm³ of the solution from 11.4.6 into the test tube via a 3,0 cm³ syringe.

11.4.8 Transfer 0,5 cm³ of the aqueous ammonium thiocyanate solution into the test tube via a 3,0 cm³ syringe. Swirl the content to ensure mixing. Wait 1 min.

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

11.5 Measurement of iron contamination

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

11.5.2 Transfer 0,5 cm³ of the brine sample into a 50 cm³ volumetric flask via the 1,0 cm³ syringe.

11.5.3 Transfer 1,0 cm³ of the acid solution via a 3,0 cm³ syringe.

11.5.4 Add 0,25 cm³ (five drops) of the aqueous hydrogen peroxide solution via the transfer pipette. Swirl briefly to mix the contents. Wait 2,0 min, but not more than 3,0 min.

NOTE The presence of significant amount (greater than 0,5 volume %) of oxidizable organic additives can lead to inaccurate, low readings. This can be remedied by adding more of the oxidant hydrogen peroxide in 11.5.4.

11.5.5 Fill the volumetric flask to the 50 cm³ mark with the iron-free water. Cap the flask and shake briefly to mix the contents. Remove the cap.

11.5.6 Transfer 1,0 cm³ of the solution from 11.5.5, into the test tube via a 3,0 cm³ syringe.

11.5.7 Transfer 0,5 cm³ of the aqueous ammonium thiocyanate solution into the test tube via a 3,0 cm³ syringe. Swirl the content to ensure mixing. Wait 1 min.

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

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

11.6 Precision statement

11.6.1 The precision depends on the standards used to bracket the iron concentration of the test brine. The closer the incremental concentrations of the standards, 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 interlaboratory reproducibility (standard deviation) of the method was shown to be 10 mg/l. The variance (accuracy) compared to single atomic spectroscopy analyses was -12,7 %.

11.6.3 For high concentrations of iron (range 100 mg/l to 600 mg/l) using standards with incremental iron concentration increases of 100 mg/l, the interlaboratory reproducibility (standard deviation) of the method was shown to be 87 mg/l. The variance (accuracy) compared to single atomic spectroscopy analyses was +3,0 %.

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

12 Daily completion fluid report

12.1 Principle

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

12.1.2 Primary impact areas are:

- a) well control;
- b) formation damage potential;
- c) materials accountability.

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

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

- a) well identification, geometry and zone data;
- b) system properties;
- c) fluids accounting;
- d) cost accounting;
- e) daily commentary,
- f) vendor representative identification.

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

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

12.2 Well identification, geometry and zone data

12.2.1 Well identification — Operator, contractor, rig description, legal description

Well identification includes the following information:

- a) report date;
- b) report number;
- c) operator name;
- d) supervisor name;
- e) contractor;
- f) rig name and number;
- g) well name and number;
- h) geographic location;
- i) country, region/state, county/parish, block.

12.2.2 Geometry

Well geometry includes the following information:

- a) API well number (if applicable);
- b) casing dimensions and lengths;
- c) drill pipe and tubulars dimensions and lengths;
- d) well volume, expressed as capacity, annular, pipe and pipe-in-hole.

12.2.3 Zone data

Well zone data include the following information:

- a) name of current zone or zone of treatment;
- b) bottom-hole temperature of current zone;
- c) bottom-hole pressure of current zone;
- d) true vertical depth of current zone.

12.3 System properties

12.3.1 The system properties to be included in the daily completion fluid report are those tested in accordance with this part of ISO 13503:

- a) actual specific gravity at actual temperature, noting °C (°F);
- b) density, converted to 21 °C (70 °F);
- c) pH at actual temperature, noting °C (°F);
- d) nephelometer turbidity unit (NTU);
- e) percent solids (volume fraction);
- f) iron content, expressed in mg/l.

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

12.4 Fluids accounting

12.4.1 Fluids are identified by fluid type, density, and volume expressed in kg/m³ (bbl).

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

12.4.2 Fluids accounting consists of four (4) 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, volume created from bagged material or water additions.

b) physical inventory;

This represents fluids that have been stated in 12.4.2 a). The fluids are located in the well, on the rig, 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 categorisation of two major areas of fluid use – surface and well. Loss is tallied by day and also cumulatively for categories and sums of categories.

d) fluid volume balance.

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

12.5 Cost accounting

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

The values may be given as:

a) simple total of day and cumulative cost, or;

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

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

12.6 Daily commentary

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

12.7 Vendor representative identification

This portion of the daily completion fluids report includes:

a) representative names;

b) location of plant or stock point;

c) location of office with contact information.

Annex A
(informative)

Completion fluids report form

ANY BRINE COMPANY		DAILY COMPLETION FLUIDS REPORT	
WELL IDENTIFICATION, GEOMETRY AND ZONE DATA			
Report date	Contractor and rig name	Name of current zone	
Report number	Well name and location	BHT of current zone	
Operator name	Country, region/state, county/ parish, block	BHP of current zone	
Supervisor names(s)	Casing and DP/tub dimensions and lengths	TVD of current zone	
	Well volume expressed as capacity, annular, pipe and pipe in hole		
SYSTEM PROPERTIES		FLUIDS ACCOUNTING	
Properties include but are not limited to: Actual specific gravity at actual temperature Density at 21 °C (70 °F) pH at temperature NTU % solids Iron content Additional 3-6 blank lines for optional data		Fluids are identified by fluid type, density and volume in barrels Fluids accounting consists of four (4) main elements: — fluid volume brought to or created on location; — physical inventory; — fluid loss; — fluid volume balance.	
DAILY COMMENTARY		COST ACCOUNTING	
Textual section; summary of daily operations as related to fluids, additives, waste, loss and filter operations Document sample dates/type; orders made and received; certain instructions by operator		Tabulation of all material and service costs for the day and as a cumulative total for the project. The values may be given as a — simple total of day and cumulative cost; or — grouping by primary cost category by day and cumulative; or — detailed account of each product/service that reports quantities used by day and cumulative.	

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 [5], [6], [9] to [11], [13], [18] to [23] and [25]. Consult a brine service company about the potential for hydrate formation for any situation where high pressure and low temperature exist.

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

B.3 Inorganic gases such as hydrogen sulfide and carbon dioxide can also stabilise 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 well bore 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 mud-line temperatures and pressures are conducive to hydrate formation and are the primary focus of hydrate inhibition, cold ambient temperatures at the surface can facilitate hydrate formation in pressurised equipment. Increasing the pressure in all of these situations to “clear the plug” simply makes the situation worse.

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

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

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

B.10 Anti-agglomerates prevent the accumulation of hydrate crystals into masses that can cause plugs. Threshold inhibitors increase the time that hydrates take to form at a given temperature and pressure. Threshold inhibitors produce an effect that is very similar to super-cooling in brine fluids, where the temperature of the fluid can be taken below the crystallization temperature of the brine, but crystallization of the fluid will not occur. As with a brine fluid, super-cooling is not a stable state and catastrophic nucleation can occur at any time.

Annex C (informative)

Buffering capacity of brines

C.1 Principle

C.1.1 Aqueous buffers consist of blends of weak acids and their conjugate bases, or of weak bases and their conjugate acids. Buffering minimises changes to the pH value upon the addition of either acid or base.

C.1.2 An assessment of buffering capacity measures the capacity of the brine to absorb acidic or basic species while maintaining pH control. A common example of a buffer system used in potassium formate brines is the blend of potassium carbonate and potassium bicarbonate.

C.1.3 As a complement to brine pH, buffering capacity is a useful parameter to quantify a brine's resistance to pH change. This is critical for organic brines (e.g. formates and acetates), especially in applications with a potential exposure to acidic gases such as carbon dioxide or hydrogen sulfide.

C.1.4 Important examples are formate brines that should be buffered in a pH range of 9,5 to 11,0. At elevated temperatures, and/or in the presence of catalytic surfaces, some formate/formic acid can react with water to form molecular hydrogen. This reaction occurs at lower temperatures for formic acid than for formate. A buffer pH of 9,5 to 11,0 minimises the concentration of formic acid present.

C.2 Measuring the buffering capacity

C.2.1 Different analytical procedures are employed to assess the buffering capacity of brine, and the choice depends on the chemistry of the buffering system.

C.2.2 In each case, the ratio and the total concentration of buffer components must be determined. For example, the concentration of potassium carbonate and potassium bicarbonate buffer commonly used in potassium formate brines should be quantified.

C.2.3 Specific procedures for determining buffering capacity are under review and will be included in future revisions of this part of ISO 13503.

C.3 Adjusting the buffering capacity

When using brines that require control of pH and buffer capacity, adequate procedures should be employed to assess and adjust the buffer capacity of the brine system.

Annex D (informative)

Pressure crystallization of brines

D.1 Principle

D.1.1 Brine solutions have thermodynamic or true crystallization temperatures (TCT) that have been thoroughly studied and well documented for atmospheric pressures. However, pressure can significantly influence the temperature at which brine crystallises.

D.1.2 The brine fluid can crystallise during high-pressure operations in the field, such as pressure testing of blow-out preventers (BOPs) in deepwater, and subsequently cause extreme difficulties and safety hazards, if the effect of pressure on the brine fluid is not known.

D.1.3 Brines with salt content lower than the eutectic mixture crystallise under pressure at a temperature lower than the TCT, and form ice.

D.1.4 Brines with salt content higher than the eutectic mixture exhibit a solubility of one or more dissolved salts, which can decrease under pressure. For these brines, a threshold pressure exists above which salt crystals will form in the brine fluid at a temperature higher than the TCT. It is under these conditions that operational difficulties and safety hazards can occur.

D.1.5 The resulting TCT at a specified pressure is termed pressure-true crystallization temperature (P-TCT or PCT). PCT is stated as x at y pressure. For example, a PCT of -2 °C at 68 950 kPa (30 °F at 10 000 psi) indicates that the brine fluid will crystallise at 68 950 kPa (10 000 psi) when the fluid temperature is lowered to -2 °C (30 °F).

D.2 Measuring pressure crystallization temperature

D.2.1 Conventional methods for measuring TCT are difficult to apply to PCT if the massive cells required to contain the high pressure make it difficult to agitate the fluid and directly observe the crystallization process.

D.2.2 However, techniques that determine PCT are available, including methods that measure changes in volume, pressure, temperature and optical characteristics, and/or view crystal formation and dissolution. These techniques require the application of safeguards to ensure that artificially low values due to "super-cooling" are avoided.

D.2.3 If a low-temperature high-pressure environment is anticipated, the crystallization temperature of the brine should be less than the most extreme pressure and temperature conditions. If not, the fluid parameters should be altered to compensate and prevent brine crystallization under pressure.

Annex E (informative)

Brine viscosity

E.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 and other fluids (especially at interfaces).

Viscosity measurements can be significant for friction pressure drop, hole-cleaning capability, potentially damaging fluid interfaces, and fluid loss control and formation damage potential. For example, viscosity of a completion brine causes a friction pressure drop in the work string during pumping. If friction pressure drop exceeds power or safety requirement of the tubulars, the completion brine should be reformulated to give lower viscosity.

E.2 Measuring the viscosity

Viscosity is measured using several different instruments and procedures. Depending on the fluid, purposes and limitation of the viscosity measurement, various procedures can provide different results.

A user or manufacturer of brines should be consulted to determine the procedures to use for viscosity measurement and responses for adjusting viscosity.

Annex F (informative)

Principle of corrosion testing

F.1 Corrosion is the destruction of a metal by chemical or electrochemical reaction within its environment. The electrochemical cell is made up of the metallic hardware and the brine that acts as electrolyte. Any metal surface is a composite of electrodes electrically connected through the body of the metal itself.

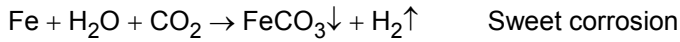
F.2 The area of the metal, which is the source of the ion that goes into the electrolyte, is the anode (oxidation). At the cathode, no metal dissolution occurs; electrons are gained (reduction). In the absence of oxygen and in acidic solutions, hydrogen ions from the water are converted to hydrogen gas. In the presence of oxygen and in alkaline solutions, hydroxyl ions are formed.

F.3 The source of electrical potential or voltage required to induce corrosion to occur is the energy stored in the metal when it was liberated from its ore. Different metals require different amounts of energy for refining, and hence have different corrosion tendencies. For example, zinc and aluminium have greater tendencies to corrode, relative to iron and steel. The relative potential of common alloys to corrode is given in Table F.1.

Table F.1 — Corrosion potential of common materials

Alloy	Corrosion potential V
Graphite	0,50
Platinum	0,44
Ni-Cr-Mo alloy C	0,09 to 0,03
Titanium	0,06 to 0,04
Ni-Fe-Cr alloy 825	0,04 to 0,02
Alloy "20" stainless steels, cast & wrought	0,06 to 0,04
*Stainless steel – types 316, 317 (passive)	–0,1
Ni-Cu alloys 400, K-500	–0,17
*Stainless steel – types 302, 304, 321, 347 (passive)	–0,14
Ni 200	–0,30
*Ni-Cr alloy 600 (passive)	–0,31
Ni-Al bronze	–0,36
Cu-Ni 70-30	–0,17 to –0,24
*Stainless steel – type 430 (passive)	–0,48
80-20 Cu-Ni	–0,48
90-10 Cu-Ni	–0,50
*Stainless steel – types 410, 416 (passive)	–0,58
*Stainless steel – types 316, 317 (active)	–0,79
*Ni-Cr alloy 600 (active)	–0,80
Austenitic Ni cast iron	–0,97
*Stainless steel (type 302, 304, 321, 347 (active)	–1,02
*Stainless steel – types 410, 416 430 (active)	–1,02
Low alloy steel	–1,20
Mild steel, cast iron	–1,32
Al alloys	–1,76
Zn	–2,01
Mg	–3,23
NOTE Alloys are listed in order of the potential exhibited in flowing seawater. The alloys marked (*) can become active and exhibit a potential near –0,5 V in low-velocity or poorly aerated water and at shielded areas. ^[28]	

F.4 Where brines are used, dissolved gases such as oxygen, carbon dioxide and hydrogen sulfide are the primary causes of most corrosion problems. The following electrochemical reactions are of considerable importance and concern.



F.5 The hydrogen ions and gas from either sour or sweet corrosion are known to cause severe problems known as hydrogen embrittlement and hydrogen blistering. Iron sulfide and iron carbonate scale form on metal surfaces and can result in pitting.

F.6 Sweet corrosion is dependent on the concentration of carbon dioxide present, pressure in the system, volume of the brine, composition of the brine, and the temperature. Increased pressure results in increased solubility of carbon dioxide, while increased temperature decreases the solubility of carbon dioxide.

F.7 Oxygen is a severe corrosive agent even at concentrations of less than 1 mg/l. Oxygen corrosion is caused by air entering the fluid at the surface during circulation or by air entering the well annulus at the surface. Dissolved oxygen in brine fluids is limited to 8 mg/l and is rapidly depleted by the corrosion process.

F.8 Aqueous salt solutions provide the medium that completes the galvanic cell and allow corrosion to occur.

F.9 The pH of brine is important. Generally, brine is more corrosive at a lower pH. An example of a low-pH brine is ZnBr_2 above 2,09 specific gravity (17,5 lb/gal).

F.10 Other sources of corrosive species can be contaminants left in the wellbore. Some of these materials can degrade and produce sulfides, nitrates or other corrosive materials.

F.11 When using corrosion-resistant alloys, major concerns include environmentally assisted stress corrosion cracking, sulfide stress cracking, hydrogen embrittlement, and pitting. For low alloy steels, the major concern is general corrosion of the metal, as measured by the amount of steel lost per unit of time.

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