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Petroleum and natural gas industries — Completion fluids and materials —

Part 3:
Testing of heavy brines

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

Partie 3: Essais de saumures denses

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Contents

Page

Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document 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, well cements and treatment fluids,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 12, *Materials, equipment and offshore structures for petroleum, petrochemical and natural gas industries,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO13503-3:2005), which has been technically revised.

This document supplements API RP 13J, 5th edition (2014).

The technical requirements of this document and API RP 13J used to be identical. In the meantime API RP 13J has been technically revised as API RP 13J, 5th edition (2014). The purpose of this edition of ISO 13503 is to bring this document up-to-date, by referencing the current edition of API RP 13J and including supplementary content.

The main changes are as follows:

— the method for measuring crystallization temperature in formate brines is described in this document and differs from the method described in API RP 13J, 5th edition (2014) due to the specific nature of formate brines;

— the method for measuring pH in formate brines is described in this document and differs from the method described in API RP 13J, 5th edition (2014), since the API recommended method is unsuitable for formate brines.

— the method for determining carbonate and bicarbonate concentrations in formate brines is described in this document and differs from the buffer capacity method described in API RP 13J, 5th edition (2014), since the API recommended method is unsuitable for formate brines.

A list of all parts in the ISO 13503 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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Introduction

Crystallization temperature is an important property of well construction and intervention fluids used in cold weather conditions and/or under high pressure. API RP 13J, 5th edition (2014) defines the crystallization temperature of a brine as the temperature at which crystals will appear in a brine solution of a given density as it cools. The definition of the crystallization temperature of a brine provided by API RP 13J, 5th edition (2014) is not suitable for formate brines because of prominent supercooling and metastable phase potassium formate crystals that can form at temperatures much lower than crystallization temperature for stable potassium formate crystals.

Formate brines, especially potassium and cesium formate brines and their blends, behave very differently from most other brines due to strong kinetic effects that complicate crystallization temperature measurements. The following factors complicate crystallization temperature measurements in formate brines:

— crystallization temperatures can be very low and can be lower than the cooling capability of the measuring equipment;

— a significant amount of supercooling;

— existence of metastable potassium formate crystals that form in potassium-rich formate brines.

API RP 13J, 5th edition (2014) recommends measuring pH of a concentrated brine on a neat sample, despite multiple reasons indicating this approach is wrong, including Debye-Hückel and pH buffers (standards) formulas being well outside of its validity range. This causes inconsistent, ambiguous, and meaningless pH results. Diluting a brine sample before a pH measurement eradicates these issues.

API RP 13J, 5th edition (2014) recommends measuring buffer capacity of a concentrated brine by a standard carbonate titration to measure the combined carbonate and hydroxide buffering capacity, followed by titration to a randomly selected target pH of 7,5 (measured in undiluted brine). By selecting such a low target pH (corresponding to a pH of around 6 in diluted brine) the second titration endpoint is at the part of the titration curve masked by the formate/formic acid equilibrium and is unsuitable for determining the bicarbonate concentration, resulting in inconsistent and ambiguous bicarbonate concentration results. These issues can be eradicated by using a method compromising a pH measurement, a possible pH adjustment, and a phenolphthalein titration. Carbonate/bicarbonate concentrations are calculated based on this data.

Petroleum and natural gas industries — Completion fluids and materials —

Part 3:
Testing of heavy brines

1 Scope

This document 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 document supplements API RP 13J, 5th edition (2014), the requirements of which are applicable with the exceptions specified in this document.

This document provides more suitable method descriptions for determining the formate brines pH, carbonate/bicarbonate concentrations and crystallization temperature at ambient pressure compared to the methods provided by API RP 13J, 5th edition (2014).

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

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

API RP 13J, 5th edition (2014), *Testing of heavy brines*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in API RP 13J, 5th edition (2014) and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
crystallization temperature
CT
temperature at which crystals and liquid exists in stable equilibrium

Note 1 to entry: This definition takes precedence over the description of Crystallization Temperature in API RP 13 J, 5th edition (2014), 7.1.3.

4 Supplements to API RP 13J, 5th edition (2014)

4.1 General

The requirements specified in API RP 13J, 5th edition (2014) shall apply, with the exceptions specified in 4.2 to 4.5.

4.2 Method for determining iron content

The requirements specified in API RP 13J, 5th edition (2014), Clause 11 shall apply with the following exception:

The method for determining iron content shall not be used on formate brines.

4.3 Method for determining carbonate and bicarbonate concentrations

4.3.1 General

The requirements specified in API RP 13J, 5th edition (2014), Clause 13 shall apply with the following exception:

— The method for determining buffer capacity shall not be used in formate brines.

— Carbonate and bicarbonate determination method described in 4.3.2 to 4.3.6 shall be applied.

Carbonate and bicarbonate concentrations can be measured in all formate single-salt and blended brines:

— sodium formate brine;

— potassium formate brine;

— cesium formate brine;

— sodium/potassium formate brine blends;

— potassium/cesium formate brine blends.

4.3.2 Determination of carbonate concentration by titration in the titration sample

The following steps shall be executed:

a) If the sample is contaminated with solids, it shall be filtered using an API filter press and nitrogen gas. CO_2 gas shall not be used.

b) The sample shall be diluted with 9 parts of deionized water. Using 5 ml of brine and 45 ml of deionized water is recommended.

c) pH of the diluted brine sample (original sample) shall be measured with a calibrated glass electrode and recorded.

d) If the measured pH is not between 9,5 and 11,0, it shall be adjusted to 10,0 to 10,5 range with a strong acid (HCl, HNO_3 or H_2SO_4) or a strong base (NaOH or KOH). If it is between 9,5 and 11,0, but outside 10,0 to 10,5, it is recommended to adjust it to 10,0 to 10,5 range with a strong acid (HCl, HNO_3 or H_2SO_4) or a strong base (NaOH or KOH).

e) The sample, referred to as the titration sample, shall be titrated down to pH=8,2 using HCl, HNO_3 or H_2SO_4 (0,2 N is the most suitable concentration for formate brines used in the field). It is achieved by dropwise adding an acid solution and recording the volume added and the sample's pH.

f) Once the sample's pH reaches 8,2, the volume acid used shall be recorded (Vacid). The carbonate concentration in the titration sample shall be calculated from Formula (1).

$$[CO_3{}^{2-}]_{titr} = C_{acid} \times V_{acid} / V_{brine} \tag{1}$$

where

$[CO_3{}^{2-}]_{titr}$ is the carbonate concentration, in mol/l, in the titration sample;

C_{acid} is the concentration of HCl, HNO_3 or H_2SO^4, in N used for titration;

V_{acid} is the volume of HCl, HNO_3 or H_2SO^4, in ml, used for titration;

V_{brine} is the volume of brine, in ml, before dilution.

4.3.3 Calculation of carbonate fraction in the titration sample

4.3.3.1 General

Carbonate fraction in the titration sample shall be calculated and the calculation depends on the type of formate brine.

4.3.3.2 Single salt formate brines

Carbonate fraction shall be calculated using Formula (2):

$$f_{carb}(pH) = e^{[a+(b\times\ln(pH)+c)/pH^2]} \tag{2}$$

where $f_{carb}(pH)$ is the molar fraction of buffer that is carbonate as a function of pH.

Table 1 — Formula (2) a, b, and c parameters for sodium, potassium, and cesium formate brines

Brine type	a	b	c	Validity pH-range
sodium formate	-2,36	12,22	-23 029	
potassium formate	-12,29	3 383	-6 638	8,20 to 11,48
cesium formate	-12,55	3 496	-6 881	

4.3.3.3 Na/K formate blend

The following steps shall be followed:

a) Carbonate fraction shall be calculated using Formula (3):

$$f_{carb}(pH) = \varphi_{NaHCOO} \times f_{carb(NaHCOO)}(pH) + \varphi_{KHCOO} \times f_{carb(KHCOO)}(pH) \tag{3}$$

where

$f_{carb(NaHCOO)}(pH)$ is the molar fraction of carbonate in Na formate brine, calculated by Formula (2);

$f_{carb(KHCOO)}(pH)$ is the molar fraction of carbonate in K formate brine, calculated by Formula (2);

φ_{NaHCOO} is the volume-fraction of Na formate brine ($1,30$ g/cm^3 / $10,9$ lb/gal) in the blended brine;

φ_{KHCOO} is the volume-fraction of K formate brine (1,57 g/cm^3 / 13,1 lb/gal) in the blended brine.

b) If the volume fractions of the Na formate and K formate brines are unknown, they shall be estimated based on the density of the blended brine using Formula (4) and Formula (5) [or Formula (6) and Formula (7) if using field units], provided the brine is not heavily diluted with water.

— Metric unit:

$$\varphi_{\text{NaHCOO}} = \frac{1,57-d}{0,27} \tag{4}$$

$$\varphi_{\text{KHCOO}} = \frac{d-1,30}{0,27} \tag{5}$$

where d is the density of the blend, in g/cm^3 or specific gravity.

— Field unit:

$$\varphi_{\text{NaHCOO}} = \frac{13.1-d}{2.2} \tag{6}$$

$$\varphi_{\text{KHCOO}} = \frac{d-10.9}{2.2} \tag{7}$$

where d is the density of the blend, in lb/gal.

4.3.3.4 Cs/K formate blend

The following steps shall be followed:

a) Carbonate fraction shall be calculated using Formula (8):

$$f_{\text{carb}}(\text{pH}) = \varphi_{\text{CsHCOO}} \times f_{\text{carb(CsHCOO)}}(\text{pH}) + \varphi_{\text{KHCOO}} \times f_{\text{carb(KHCOO)}}(\text{pH}) \tag{8}$$

where

$f_{\text{carb(CsHCOO)}}(\text{pH})$ is the molar fraction of carbonate in Cs formate brine, calculated by Formula (2);

$f_{\text{carb(KHCOO)}}(\text{pH})$ is the molar fraction of carbonate in K formate brine, calculated by Formula (2);

φ_{CsHCOO} is the volume-fraction of Cs formate brine (2,20 g/cm^3 18,4 lb/gal) in the blended brine;

φ_{KHCOO} is the volume-fraction of K formate brine (1,57 g/cm^3 / 13,1 lb/gal) in the blended brine.

b) If the volume fractions of Cs formate and K formate brines are unknown, they shall be estimated based on the density of the blended brine using Formula (9) and Formula (10) [or Formula (11) and Formula (12) if using field units], provided the brine is not heavily diluted with water:

— Metric unit:

$$\varphi_{\text{KHCOO}} = \frac{2,20-d}{0,63} \tag{9}$$

$$\varphi_{\text{CsHCOO}} = \frac{d-1{,}57}{0{,}63} \tag{10}$$

where d is the density of the blend, in g/cm^3 or specific gravity.

— Field unit:

$$\varphi_{\text{KHCOO}} = \frac{18.4-d}{5.3} \tag{11}$$

$$\varphi_{\text{CsHCOO}} = \frac{d-13.1}{5.3} \tag{12}$$

where d is the density of the blend, in lb/gal.

4.3.4 Calculation of bicarbonate concentration in the titration sample

Bicarbonate concentration in the titration sample shall be calculated using Formula (13):

$$[\text{HCO}_3^-]_{\text{titr}} = [\text{CO}_3^{2-}]_{\text{titr}}\,\frac{1-f_{\text{carb}}(\text{pH})}{f_{\text{carb}}(\text{pH})} \tag{13}$$

where

$[\text{HCO}_3^-]_{\text{titr}}$ is the bicarbonate concentration, in mol/l, in the titration solution;

$[\text{CO}_3^{2-}]_{\text{titr}}$ is the carbonate concentration, in mol/l, in the titration solution calculated in 4.3.2;

$f_{carb}(\text{pH})$ is the molar fraction of buffer that is carbonate in the titration sample calculated in 4.3.3.

4.3.5 Calculation of total carbonate and bicarbonate concentration

The total carbonate and bicarbonate concentration, which is pH-independent in the relevant pH-range, is the same in the original sample and the titration sample. It shall be calculated using Formula (14):

$$\left[\text{CO}_3^{2-}+\text{HCO}_3^-\right] = [\text{CO}_3^{2-}]_{\text{titr}} + [\text{HCO}_3^-]_{\text{titr}} \tag{14}$$

4.3.6 Calculation of carbonate and bicarbonate concentrations in the original sample (before pH adjustment)

4.3.6.1 General

The method of calculating of carbonate and bicarbonate concentrations ($\left[\text{CO}_3^{2-}\right]$, $\left[\text{HCO}_3^-\right]$) in the original sample depends on the original sample's pH and whether a pH adjustment was performed before the titration.

4.3.6.2 No pH adjustment was performed before the titration

If no pH adjustment was performed [see 4.3.2 d)] before the titration, the original sample is identical to the titration sample and Formulas (15) and (16) apply:

$$\left[\text{CO}_3^{2-}\right] = [\text{CO}_3^{2-}]_{\text{titr}} \tag{15}$$