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Petroleum and natural gas industries — Field testing of drilling fluids —

Part 1: Water-based fluids

Industries du pétrole et du gaz naturel — Essais in situ des fluides de forage —

Partie 1: Fluides aqueux

Reference number
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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.ch
Web www.iso.ch

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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 3.

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 part of ISO 10414 may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 10414-1 was prepared by Technical Committee ISO/TC 67, *Materials, equipment and offshore structures for petroleum and natural gas industries*, Subcommittee SC 3, *Drilling and completion fluids, and well cements*.

ISO 10414 consists of the following parts, under the general title *Petroleum and natural gas industries — Field testing of drilling fluids*:

— *Part 1: Water-based fluids*

— *Part 2: Oil-based fluids*

Annexes A to H of this part of ISO 10414 are for information only.

Introduction

This part of ISO 10414 is based on API RP 13B-1, second edition, September 1997 [2].

As with any laboratory procedure requiring the use of potentially hazardous chemicals, the user is expected to have proper knowledge and received training in the use and disposal of these chemicals. The user is responsible for compliance with all applicable local, regional and national requirements for worker and local health, safety and environmental liability.

In this part of ISO 10414, where practical, U.S. customary units are included in brackets for information.

Petroleum and natural gas industries — Field testing of drilling fluids —

Part 1: Water-based fluids

1 Scope

This part of ISO 10414 provides standard procedures for the determining following characteristics of water-based drilling fluids:

a) drilling fluid density (mud weight);

b) viscosity and gel strength;

c) filtration;

d) water, oil and solids contents;

e) sand content;

f) methylene blue capacity;

g) pH;

h) alkalinity and lime content;

i) chloride content;

j) total hardness as calcium.

Annexes A, B, C and E provide additional test methods which may be used for

k) chemical analysis for calcium, magnesium, calcium sulfate, sulfide, carbonate, potassium;

l) determination of shear strength;

m) determination of resistivity;

n) drill pipe corrosion monitoring.

Annexes D, F, G and H provide procedures that may be used for

o) removal of air;

p) sampling, inspection and rejection;

q) rig-site sampling;

r) calibration and verification of glassware, thermometers, viscometers, retort kit cup and drilling fluid balances.

2 Term and definition

For the purposes of this part of ISO 10414, the following term and definition applies.

2.1
ACS reagent grade
chemical meeting the purity standards specified by the American Chemical Society (ACS)

3 Abbreviated terms

ACS American Chemical Society

AISI American Iron and Steel Institute

CAS Chemical Abstracts Service

EDTA ethylenediaminetetraacetic acid

HT/HP high temperature, high pressure

meq milliequivalents

OCMA Oilfield Chemical Manufacturer's Association

PTFE polytetrafluoroethylene

QAS quaternary ammonium salt

STPB sodium tetraphenyl borate

TC to contain

TD to deliver

4 Drilling fluid density (mud weight)

4.1 Principle

This test procedure is a method for determining the mass of a given volume of liquid (= density). Drilling fluid density is expressed as grams per cubic centimetre, or kilograms per cubic metre.

4.2 Apparatus

4.2.1 Any **density-measuring instrument** of accuracy to within 0,01 g/cm^3 or 10 kg/m^3.

The mud balance is the instrument generally used for drilling-fluid density determinations. The mud balance is designed such that the drilling-fluid holding cup, at one end of the beam, is balanced by a fixed counterweight at the other end, with a sliding-weight rider free to move along a graduated scale. A level-bubble is mounted on the beam to allow for accurate balancing. Attachments for extending the range of the balance may be used when necessary.

The instrument should be calibrated frequently with fresh water. Fresh water should give a reading of 1,00 g/cm^3 or 1 000 kg/m^3 at 21 °C (70 °F). If it does not, adjust the balancing screw or the amount of lead shot in the well at the end of the graduated arm as required.

4.2.2 **Thermometer**, with a range of 0 °C to 105 °C (32 °F to 220 °F).

4.3 Procedure

4.3.1 The instrument base should be set on a flat, level surface.

4.3.2 Measure the temperature of the drilling fluid and record.

4.3.3 Fill the clean, dry cup with drilling fluid to be tested; put the cap on the filled drilling-fluid holding cup and rotate the cap until it is firmly seated. Ensure that some of the drilling fluid is expelled through the hole in the cap in order to free any trapped air or gas (see annex D for information on air or gas removal).

4.3.4 Holding the cap firmly on the drilling-fluid holding cup (with cap hole covered), wash or wipe the outside of the cup clean and dry.

4.3.5 Place the beam on the base support and balance it by moving the rider along the graduated scale. Balance is achieved when the bubble is under the centreline.

4.3.6 Read the drilling fluid density at the edge of the rider toward the drilling-fluid holding cup. Make appropriate corrections when a range extender is used.

4.4 Calculation

4.4.1 Report the drilling fluid density to the nearest 0,01 g/cm^3 or 10 kg/m^3.

4.4.2 To convert the reading to other units, use the following:

$$\rho = 1\,000 \times \text{g/cm}^3 \quad (1)$$

$$\rho = 16 \times \text{lb/ft}^3 \quad (2)$$

$$\rho = 119{,}8 \times \text{lb/USgal} \quad (3)$$

where ρ is the density, expressed in kilograms per cubic metre.

$$DFG = 9{,}81 \times \text{g/cm}^3 \quad (4)$$

$$DFG = 0{,}022\,6 \times \text{psi/1 000 ft} \quad (5)$$

where DFG is the drilling fluid gradient, expressed in kilopascals per metre.

A list of density conversions is given in Table 1.

Table 1 — Density conversion

Grams per cubic centimetre[a] g/cm^3	Kilograms per cubic metre kg/m^3	Pounds per US gallon (lb/US gal)	Pounds per cubic foot (lb/ft^3)
0,70	700	5,8	43,6
0,80	800	6,7	49,8
0,90	900	7,5	56,1
1,00	1 000	8,345[b]	62,3
1,10	1 100	9,2	68,5
1,20	1 200	10,0	74,8
1,30	1 300	10,9	81,0
1,40	1 400	11,7	87,2
1,50	1 500	12,5	93,5
1,60	1 600	13,4	99,7
1,70	1 700	14,2	105,9
1,80	1 800	15,0	112,1
1,90	1 900	15,9	118,4
2,00	2 000	16,7	124,6
2,10	2 100	17,5	130,8
2,20	2 200	18,4	137,1
2,30	2 300	19,2	143,3
2,40	2 400	20,0	149,5
2,50	2 500	20,9	155,8
2,60	2 600	21,7	162,0
2,70	2 700	22,5	168,2
2,80	2 800	23,4	174,4
2,90	2 900	24,2	180,7

a Same value as relative density.

b Accurate conversion factor.

5 Alternative drilling fluid density method

5.1 Principle

The density of a drilling fluid containing entrained air or gas can be determined more accurately by using the pressurized mud balance. The pressurized mud balance is similar in operation to the conventional mud balance, the difference being that the slurry sample can be placed in a fixed-volume sample cup under pressure.

The purpose of placing the sample under pressure is to minimize the effect of entrained air or gas upon slurry density measurements. By pressurizing the sample cup, any entrained air or gas will be decreased to a negligible volume, thus providing a slurry density measurement more closely in agreement with that which will be realized under downhole conditions.

5.2 Apparatus

5.2.1 Any **density-measuring instrument** of accuracy to within 0,01 g/cm^3 or 10 kg/m^3.

The pressurized mud balance is the instrument generally used for pressurized drilling-fluid density determinations. The pressurized mud balance is designed such that the drilling-fluid holding cup and screw-on lid, at one end of the beam, is balanced by a fixed counterweight at the other end, with a sliding-weight rider free to move along a graduated scale. A level-bubble is mounted on the beam to allow for accurate balancing.

Calibrate the instrument frequently with fresh water. Fresh water should give a reading of 1,00 g/cm^3 or 1 000 kg/m^3 at 21 °C (70 °F). If it does not, adjust the balancing screw or the amount of lead shot in the well at the end of the graduated arm as required.

5.2.2 **Thermometer**, with a range of 0 °C to 105 °C (32 °F to 220 °F).

5.3 Procedure

5.3.1 Measure the temperature of the drilling fluid and record.

5.3.2 Fill the sample cup to a level slightly below the upper edge of the cup (approximately 6 mm).

5.3.3 Place the lid on the cup with the attached check-valve in the down (open) position. Push the lid downward into the mouth of the cup until surface contact is made between the outer skirt of the lid and the upper edge of the cup. Any excess slurry will be expelled through the check-valve. When the lid has been placed on the cup, pull the check-valve up into the closed position, rinse off the cup and threads with water, and screw the threaded cap on the cup.

5.3.4 The pressurizing plunger is similar in operation to a syringe. Fill the plunger by submersing its end in the slurry with the piston rod completely inside. Then draw the piston rod upward, thereby filling the cylinder with slurry. This volume should be expelled with the plunger action and refilled with fresh slurry sample to ensure that this plunger volume is not diluted with liquid remaining from the last clean-up of the plunger mechanism.

5.3.5 Push the nose of the plunger onto the mating O-ring surface of the cap valve. Pressurize the sample cup by maintaining a downward force on the cylinder housing in order to hold the check-valve down (open) and at the same time to force the piston rod inside. A force of approximately 225 N (50 lbf) or greater should be maintained on the piston rod.

5.3.6 The check-valve in the lid is pressure-actuated; when the inside of the cup is pressurized, the check-valve is pushed upward into the closed position. To close the valve, gradually ease up on the cylinder housing while maintaining pressure on the piston rod. When the check-valve closes, release pressure on the piston rod before disconnecting the plunger.

5.3.7 The pressurized slurry sample is now ready for weighing. Rinse the exterior of the cup and wipe dry. Place the instrument on the knife edge. Move the sliding weight to the right or left until the beam is balanced. The beam is balanced when the attached bubble is centred between the two black marks. Read the density from one of the four calibrated scales on the arrow side of the sliding weight. The density can be read directly in units of g/cm^3, lb/gal, and lb/ft^3 or as a drilling fluid gradient in psi/1 000 ft.

5.3.8 To release the pressure inside the cup, reconnect the empty plunger assembly and push downward on the cylinder housing.

5.3.9 Clean the cup and rinse thoroughly with water. For best operation in water-based slurries, the valve should be greased frequently with waterproof grease.

5.4 Calculation

Report the drilling fluid density to the nearest 0,01 g/cm^3 or 10 kg/m^3.

For conversions, use the formula given in 4.5.2.

6 Viscosity and gel strength

6.1 Principle

Viscosity and gel strength are measurements that relate to the flow properties (rheology) of drilling fluids. The following instruments are used to measure viscosity and/or gel strength of drilling fluids:

a) Marsh funnel — a simple device for indicating viscosity on a routine basis;

b) direct-indicating viscometer — a mechanical device for measurement of viscosity at varying shear rates.

NOTE Information on the rheology of drilling fluids may be found in [3].

6.2 Determination of viscosity using the Marsh funnel

6.2.1 Apparatus

6.2.1.1 **Marsh funnel**, calibrated to out-flow 946 ml (1 quart) of fresh water at a temperature of (21 ± 3) °C [(70 ± 5) °F] in (26 ± 0,5) s, with a graduated cup as a receiver.

6.2.1.1.1 **Funnel cone**, of length 305 mm (12,0 in), diameter 152 mm (6,0 in) and a capacity to bottom of screen of 1 500 ml (1,6 quarts).

6.2.1.1.2 **Orifice**, of length 50,8 mm (2,0 in) and inside diameter 4,7 mm (0,185 in).

6.2.1.1.3 **Screen**, with 1,6 mm (0,063 in) openings (12 mesh); fixed at 19,0 mm (0,748 in) below top of funnel.

6.2.1.2 **Graduated cup**, with capacity at least 946 ml (1 quart).

6.2.1.3 **Stopwatch**.

6.2.1.4 **Thermometer**, with a range of 0 °C to 105 °C (32 °F to 220 °F).

6.2.2 Procedure

6.2.2.1 Cover the funnel orifice with a finger and pour freshly sampled drilling fluid through the screen into the clean, upright funnel. Fill until fluid reaches the bottom of the screen.

6.2.2.2 Remove finger and start stopwatch. Measure the time for drilling fluid to fill to 946 ml (1 quart) mark of the cup.

6.2.2.3 Measure temperature of the fluid, in degrees Celsius (degrees Fahrenheit).

6.2.2.4 Report the time (6.2.2.2), to the nearest second, as the Marsh funnel viscosity. Report the temperature (6.2.2.3) of fluid to the nearest degree Celsius (degree Fahrenheit).

6.3 Determination of viscosity and/or gel strength using a direct-indicating viscometer

6.3.1 Apparatus

6.3.1.1 Direct-indicating viscometer

This type of viscometer is a rotational instrument powered by an electric motor or a hand crank. Drilling fluid is contained in the annular space between two concentric cylinders. The outer cylinder or rotor sleeve is driven at a constant rotational velocity. The rotation of the rotor sleeve in the fluid produces a torque on the inner cylinder or bob. A torsion spring restrains the movement of the bob, and a dial attached to the bob indicates displacement of the bob. Instrument constants have been adjusted so that plastic viscosity and yield point are obtained by using readings from rotor sleeve speeds of 300 r/min and 600 r/min.

A direct-indicating viscometer shall meet the following specifications:

a) **Rotor sleeve**

Inside diameter	36,83 mm (1,450 in)
Total length	87,0 mm (3,425 in)
Scribed line	58,4 mm (2,30 in) above the bottom of sleeve, with two rows of 3,18 mm (0,125 in) holes spaced 120° (2,09 radians) apart, around rotor sleeve just below scribed line.

b) **Bob**, closed, with flat base and tapered top

Diameter	34,49 mm (1,358 in)
Cylinder length	38,0 mm (1,496 in)

c) **Torsion spring constant**

386 dyne-cm/degree deflection.

d) **Rotor sleeve speed**

High speed	600 r/min
Low speed	300 r/min

NOTE Other rotor speeds are available in viscometers from various manufacturers.

6.3.1.2 Stopwatch.

6.3.1.3 Suitable container, e.g. the cup provided with the viscometer.

6.3.1.4 Thermometer, with a range of 0 °C to 105 °C (32 °F to 220 °F).

6.3.2 Procedure

6.3.2.1 Place the sample in a container and immerse the rotor sleeve exactly to the scribed line. Measurements in the field should be made with minimum delay (within 5 min, if possible) and at a temperature as near as practical to that of the drilling fluid at the place of sampling, but not differing by more than 6 °C (10 °F). The place of sampling should be stated on the test report.

WARNING — Maximum recommended operating temperature is 90 °C (200 °F). If fluids have to be tested above this temperature, a solid metal bob or a hollow metal bob with a completely dry interior should be used. Liquid trapped inside a hollow bob may vaporize when immersed in high temperature fluid and cause the bob to explode.

6.3.2.2 Record the temperature of the sample.

6.3.2.3 With the sleeve rotating at 600 r/min, wait for viscometer dial reading to reach a steady value (the time required is dependent on the drilling-fluid characteristics). Record the dial reading for 600 r/min.

6.3.2.4 Reduce the rotor speed to 300 r/min and wait for viscometer dial reading to reach a steady value. Record the dial reading for 300 r/min.

6.3.2.5 Stir drilling fluid sample for 10 s at 600 r/min.

6.3.2.6 Allow drilling fluid sample to stand undisturbed for 10 s. Slowly and steadily turn the hand-wheel in the appropriate direction to produce a positive dial reading. The maximum reading is the initial gel strength. For instruments having a speed of 3 r/min, the maximum reading attained after starting rotation at 3 r/min is the initial gel strength. Record the initial gel strength (10-second gel) in pascals (or in pounds per 100 square feet).

6.3.2.7 Restir the drilling fluid sample at 600 r/min for 10 s and then allow the drilling fluid to stand undisturbed for 10 min. Repeat the measurements as in 6.3.2.6 and report the maximum reading as the 10-minute gel in pascals (or in pounds per 100 square feet).

6.3.3 Calculation

$$\eta_P = R_{600} - R_{300} \quad (6)$$

$$YP = 0{,}48 \times (R_{300} - \eta_P) \quad (7)$$

$$\eta_A = R_{600} / 2 \quad (8)$$

where

η_P is the plastic viscosity, in millipascal seconds;

NOTE Plastic viscosity is commonly known in the industry by the abbreviation PV.

YP is the yield point, in pascals;

η_A is the apparent viscosity, in millipascal seconds;

R_{600} is the dial reading at 600 r/min, in pascals (or in lb/100 ft^2);

R_{300} is the dial reading at 300 r/min, in pascals (or in lb/100 ft^2).

NOTE 1 1 cP = 1 mPa·s

NOTE 2 When calculating values in U.S. customary units, the yield point (in lb/100 ft^2) is calculated as follows:

$$YP = R_{300} - \eta_P$$

7 Filtration

7.1 Principle

Measurement of the filtration behaviour and filter cake-building characteristics of a drilling fluid are fundamental to drilling-fluid control and treatment, as are the characteristics of the filtrate such as oil, water or emulsion content. These characteristics are affected by the types and quantities of solids in the fluid and their physical and chemical interactions which, in turn, are affected by temperature and pressure. Therefore, tests are run at both low pressure/low temperature and high pressure/high temperature, and each requires different equipment and techniques.

7.2 Low temperature/low pressure test

7.2.1 Apparatus

7.2.1.1 **Filter press**, consisting mainly of a cylindrical drilling-fluid cell having an inside diameter of 76,2 mm (3 in) and a height of at least 64,0 mm (2,5 in).

This cell is made of materials resistant to strongly alkaline solutions, and is so fitted that a pressure medium can be conveniently admitted into, and bled from the top. It shall also be fitted such that a sheet of 90 mm (3,54 in) diameter filter paper can be placed in the bottom of the cell just above a suitable support. The filtration area is $(45{,}8 \pm 0{,}6)$ cm^2 $[(7{,}1 \pm 0{,}1)$ $in^2]$. Below the support is a drain tube for discharging the filtrate into a graduated cylinder. Sealing is accomplished with gaskets, and the entire assembly supported by a stand. Pressure can be applied with any non-hazardous fluid medium. Presses are equipped with pressure regulators and can be obtained with portable pressure cylinders, midget pressure cartridges or means for utilizing hydraulic pressure. To obtain correlative results, one thickness of the proper 90 mm diameter filter paper (e.g. Whatman No. 50, S&S No. 576[1)] or equivalent) shall be used.

The low temperature/low pressure filter press should have a filter area of 45,2 cm^2 to 46,4 cm^2, which corresponds to a diameter of 75,86 mm to 76,86 mm (2,987 in to 3,026 in). The filter press gasket is the determining factor of the filter area. It is recommended that a filter press gasket used be tested by a conical gauge that has the maximum (76,86 mm) and the minimum (75,86 mm) diameters marked on it. Any filter press gasket found out of these ranges (either larger or smaller than the markings) shall be discarded.

NOTE Results obtained from the use of a filter press with different filter area do not directly correlate with the results obtained when using the standard-sized press.

7.2.1.2 **Timer**, with at least a 30 min interval.

7.2.1.3 **Graduated cylinder** (TC), of volume 10 ml or 25 ml.

7.2.2 Procedure

7.2.2.1 Be sure each part of the cell, particularly the screen, is clean and dry, and that the gaskets are not distorted or worn. Pour the drilling fluid sample into the cell to within 1 cm to 1,5 cm (0, 4 in to 0,6 in) of the top (to minimize CO_2 contamination of filtrate), and complete the assembly with the filter paper in place.

7.2.2.2 Place a dry graduated cylinder under the drain tube to collect the filtrate. Close the relief valve and adjust the regulator so that a pressure of 690 kPa ± 35 kPa (100 psi ± 5 psi) is applied within 30 s or less. The test period begins at the time of pressure application.

7.2.2.3 At the end of 30 min, measure the volume of filtrate collected. Shut off the flow through the pressure regulator and open the relief valve carefully. The time interval, if other than 30 min, shall be reported.

7.2.2.4 Report the volume of filtrate in millilitres (to the nearest 0,1 ml) and the initial drilling fluid temperature in degrees Celsius (degrees Fahrenheit). Save the filtrate for chemical analysis.

7.2.2.5 Remove the cell from the frame, first making certain that all pressure has been relieved. Carefully save the filter paper with a minimum of disturbance to the cake, disassemble the cell and discard the drilling fluid. Wash the filter cake on the paper with a gentle stream of water.

7.2.2.6 Measure and report the thickness of the filter cake, to the nearest millimetre.

7.2.2.7 Although cake descriptions are subjective, such notations as hard, soft, tough, rubbery, firm, etc., may convey important information of cake quality.

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1) Whatman No. 50 and S&S No. 576 are examples of suitable products available commercially. This information is given for the convenience of users of this part of ISO 10414 and does not constitute an endorsement by ISO of these products.

7.3 High temperature/high pressure (HT/HP) test

7.3.1 Apparatus

7.3.1.1 **HT/HP filter press**, consisting of a controlled pressure source (CO_2 or nitrogen), regulators, a drilling-fluid cell able to contain working pressures from 4 000 kPa to 8 900 kPa (600 psi to 1 300 psi), a system for heating the cell, a pressurized collection cell able to maintain proper back-pressure (see Table 2) in order to prevent flashing or evaporation of the filtrate, and a suitable stand. The drilling-fluid cell has a thermometer well, oil-resistant gaskets, a support for the filter medium and a valve on the filtrate delivery tube to control flow from the cell. It may be necessary to replace the gaskets frequently.

WARNING — Rigid adherence to manufacturers' recommendations as to sample volumes, equipment temperatures and pressures is essential. Failure to do so could result in serious injury.

Do not use nitrous oxide cartridges as pressure sources for HT/HP filtration. Under temperature and pressure, nitrous oxide can detonate in the presence of grease, oil or carbonaceous materials. Nitrous oxide cartridges shall be used only for Garrett gas train carbonate analysis.

7.3.1.2 **Filter medium**[2)].

a) Filter paper, Whatman No. 50 or equivalent, for temperatures to 200 °C (400 °F).

b) Porous disc, Dynalloy X-5 or equivalent, for temperatures above 200 °C (400 °F). A new disc is required for each test.

7.3.1.3 **Timer**, with at least a 30 min interval.

7.3.1.4 **Thermometer**, with a range up to 260 °C (500 °F).

7.3.1.5 **Graduated cylinder** (TC), with a volume of 25 ml or 50 ml.

7.3.1.6 **High-speed mixer**.

7.3.2 Procedure for temperatures to 150 °C (300 °F)

7.3.2.1 Place the thermometer in the well in the jacket and preheat to 6 °C (10 °F) above the desired temperature. Adjust the thermostat to maintain the desired temperature.

7.3.2.2 Stir drilling fluid sample for 10 min with a high speed mixer. Close the bottom valve and pour the drilling fluid sample into the drilling fluid cell, being careful not to fill closer than 1,5 cm (0,6 in) from the top to allow for expansion. Install the filter paper.

7.3.2.3 Complete the assembly of the cell and, with both top and bottom valves closed, place it in the heating jacket. Transfer the thermometer to the well in the drilling fluid cell.

7.3.2.4 Connect the high-pressure collection cell to the bottom valve and lock in place.

7.3.2.5 Connect a regulated pressure source to the top valve and collection cell, and lock in place.

7.3.2.6 Keeping the valves closed, adjust top and bottom regulators to 690 kPa (100 psi). Open the top valve, applying 690 kPa (100 psi) to the drilling fluid. Maintain this pressure until the desired temperature is stabilized. The sample in the filter cell should never be heated for a period exceeding a total of 1 h.

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2) Whatman No. 50 and Dynalloy X-5 discs are examples of suitable products available commercially. Dynalloy is a trade name of a product supplied by Memtec America Corporation. This information is given for the convenience of users of this part of ISO 10414 and does not constitute an endorsement by ISO of these products.

7.3.2.7 When the sample reaches the selected test temperature, increase the pressure of the top pressure unit to 4 140 kPa (600 psi) and open the bottom valve to start filtration. Collect the filtrate for 30 min, maintaining the selected temperature within ± 3 °C (± 5 °F). If back-pressure rises above 690 kPa (100 psi) during the test, cautiously reduce the pressure by drawing off a portion of the filtrate. Record the total volume collected, the temperature, pressure and time.

7.3.2.8 Correct the filtrate volume to a filter area of 45,8 cm^2 (7,1 in^2). For example, if the filter area is 22,6 cm^2 (3,5 in^2), double the filtrate volume reported.

7.3.2.9 At the end of test, close top and bottom valves on the drilling fluid cell. Bleed pressure from the regulators.

WARNING — Pressure in the drilling fluid cell will still be approximately 4 140 kPa (600 psi). To avoid possible serious injury, keep cell upright and cool to room temperature, then bleed pressure from cell before disassembling.

7.3.2.10 Remove the cell from the heating jacket, first making certain that the bottom and top valves are tightly shut and all pressure is off regulators. Using extreme care to save the filter paper, place the cell upright, open the valve to bleed pressure from cell contents and open. Discard drilling fluid, and retrieve filter cake. Wash filter cake on the paper with a gentle stream of water.

7.3.2.11 Measure and report the thickness of the filter cake, to the nearest millimetre.

7.3.2.12 Although cake descriptions are subjective, such notations as hard, soft, tough, rubbery, firm, etc., may convey important information of cake quality.

7.3.3 Procedure for temperatures above 150 °C (300 °F)

7.3.3.1 Place the thermometer in the well in the jacket and preheat to 6 °C (10 °F) above the desired temperature. Adjust the thermostat to maintain the correct temperature.

7.3.3.2 Stir drilling fluid sample for 10 min with a high speed mixer. Close the bottom valve and pour the drilling fluid sample into the drilling fluid cell, being careful not to fill the cell closer than 4 cm (1,5 in) from the top to allow for expansion. Install the proper filter medium (see 7.3.1.2).

CAUTION — Not all manufacturers' equipment can be used above 150 °C (300 °F). Failure to know the pressure/temperature rating of equipment in use could result in serious injury. Testing at high temperature and high pressure calls for added safety precautions.

All pressure cells should be equipped with manual relief valves. Heating jackets should be equipped with both an overheat safety fuse and thermostatic cut-off. Vapour pressure of the liquid phase of drilling fluids becomes an increasingly critical design factor as test temperatures are raised. Water vapour pressures at various temperatures are shown in Table 2.

7.3.3.3 Complete the assembly of the cell, and with top and bottom valves closed, place the drilling fluid cell in the heating jacket. Transfer the thermometer to the well in the drilling fluid cell.

7.3.3.4 Connect the high-pressure collection cell to the bottom valve, and lock in place.

7.3.3.5 Connect the regulated pressure source to the top valve and the collection cell, and lock in place.

7.3.3.6 With top and bottom valves closed, apply the recommended back-pressure (see Table 2) for the test temperature to both top and bottom. Open the top valve, applying the same pressure to the drilling fluid while heating. Maintain this pressure until the test temperature is reached and stabilized.

7.3.3.7 When the temperature of the sample reaches the test temperature, increase the pressure on the top by 3 450 kPa (500 psi) over the back-pressure being held, and open the bottom valve to begin filtration. Collect the filtrate for 30 min, holding the test temperature within ± 3 °C (± 5 °F) and maintaining the proper back-pressure. If

the back-pressure should begin to rise, it can be reduced by cautiously drawing off a small portion of the filtrate. The sample in the filter cell should never be heated for a period exceeding a total of 1 h.

7.3.3.8 After the test period, close both top and bottom valves on the pressure cell and bleed pressure from the regulators. Allow a minimum of 5 min for the filtrate to cool to avoid vaporizing, then cautiously drain and record the total volume. Also record the temperature, pressures and time. Be sure to allow sufficient time for all the filtrate to drain from the receiver.

WARNING — Pressure inside the filter cell could be as high as 6 500 kPa (950 psi). To avoid possible serious injury, keep cell upright and cool to room temperature, then bleed pressure from cell before disassembly.

7.3.3.9 Correct the filtrate volume to a filter area of 45,8 cm^2 (7,1 in^2). For example, if the filter area is 22,6 cm^2 (3,5 in^2), double the filtrate volume reported.

7.3.3.10 Remove the cell from the heating jacket, first making certain that the bottom and top valves are tightly shut and all pressure is off regulators. Using extreme care to save the filter paper, place the cell upright, open the valve to bleed pressure from cell contents and open. Discard drilling fluid, and retrieve filter cake. Wash filter cake on the paper with a gentle stream of water.

7.3.3.11 Measure and report the thickness of the filter cake, to the nearest millimetre.

7.3.3.12 Although cake descriptions are subjective, such notations as hard, soft, tough, rubbery, firm, etc., may convey important information of cake quality.

Table 2 — Recommended minimum back-pressure

Test temperature		Vapour pressure		Minimum back pressure	
°C	°F	kPa	psi	kPa	psi
100	212	101	14,7	690	100
120	250	207	30	690	100
150	300	462	67	690	100
Limit of "normal" field testing					
175	350	932	135	1 104	160
200	400	1 704	247	1 898	275
230	450	2 912	422	3 105	450

8 Water, oil and solids contents

8.1 Principle

The retort instrument provides a means for separating and measuring the volumes of water, oil and solids contained in a sample of water-based drilling fluid. In the retort, a known volume of a whole drilling-fluid sample is heated to vaporize the liquid components, which are then condensed and collected in a graduated receiver. Liquid volumes are determined directly from reading the oil and water phases in the receiver. The total volume of solids (suspended and dissolved) is obtained by difference (total sample volume minus liquid volume). Calculations are necessary to determine the volume of suspended solids, since any dissolved solids will be retained in the retort. The relative volumes of low gravity solids and weighting material can also be calculated. Knowledge of the solids concentration and composition is considered basic to viscosity and filtration control in water-based drilling fluids.

8.2 Apparatus

8.2.1 Retort instrument.

Retorts of two sizes (10 ml and 20 ml) are commonly available. Specifications for these retorts are given below.

8.2.1.1 Sample cup.

Standard cup sizes are 10 ml (precision ± 0,05 ml) and 20 ml (precision ± 0,10 ml).

NOTE Other sample cup sizes are available from manufacturers of this equipment.

8.2.1.2 Liquid condenser, of sufficient mass to cool the oil and water vapours below their vaporization temperature prior to leaving the condenser.

8.2.1.3 Heating element, of sufficient wattage to raise the temperature of the sample above the vaporization point of the liquid components within 15 min without causing solids boil-over.

8.2.1.4 Temperature control (optional), capable of limiting the temperature of the retort to 500 °C ± 40 °C (930 °F ± 70 °F).

8.2.2 Liquid receiver (TC), specially designed cylindrical glassware with a rounded bottom to facilitate cleaning and a funnel-shaped top to catch falling drops, meeting the following specifications:

Total volume:	10 ml	20 ml	50 ml
Precision (0 to 100 %):	± 0,05 ml	± 0,05 ml	± 0,05 ml
Frequency of graduation marks (0 to 100 %):	0,10 ml	0,10 ml	0,10 ml

Calibration: To contain “TC” at 20 °C (68 °F)

Scale: ml, cm^3 or volume fraction (as percent)

Material: Transparent, and inert to oil, water and salt solutions at temperatures up to 32 °C (90 °F).

The receiver volume should be verified gravimetrically. The procedure and calculations are provided in annex H.

8.2.3 Fine steel wool, oil-free.

“Liquid steel wool” or similar products should not be used for this application.

8.2.4 High-temperature silicone grease, to be used as a thread seal and a lubricant.

8.2.5 Pipe cleaners.

8.2.6 Putty knife or spatula, with blade shaped to fit the inside dimensions of the sample cup of the retort.

8.2.7 Marsh funnel.

8.2.8 Defoaming agent.

8.2.9 Corkscrew.

8.3 Procedure

8.3.1 Be sure that the retort sample cup, condenser passage and liquid receiver are clean, dry and cooled from previous use. The inside of the sample cup and lid shall be thoroughly cleaned with a putty knife or spatula prior to each test. Periodically, the interior of the sample cup should also be lightly polished with steel wool. The condenser passage should also be cleaned and dried before each test using pipe cleaners. A build-up of material in the condenser can decrease condensation efficiency and cause erroneous liquid readings in a test.

NOTE Procedure will vary slightly depending on type of retort used. See manufacturers' instructions for complete procedure.

8.3.2 Collect a representative sample of water-based drilling fluid and allow it to cool to approximately 26 °C (80 °F). Screen the sample through the 1,68 mm (0,066 in) (12 mesh) screen on the Marsh funnel to remove lost circulation material, large cuttings or debris.

8.3.3 If drilling fluid sample contains gas or air, add two to three drops of defoaming agent to about 300 ml of drilling fluid and stir slowly for 2 min to 3 min to release gases.

8.3.4 Lubricate the threads on the sample cup and condenser tube with a light coating of silicone grease. This prevents vapour loss through the threads and also facilitates disassembly of the equipment and cleaning at the end of the test.

8.3.5 Lightly pack a ring of steel wool into the chamber above the sample cup. Use only enough steel wool to prevent boil-over of solids into the liquid receiver.

NOTE This is determined from experience.

8.3.6 Fill the retort sample cup with degassed water-based drilling fluid, see 8.3.3. See annex D for information on air or gas removal.

8.3.7 Carefully place the lid on the sample cup and allow an overflow of the sample through the hole in the lid to ensure that the correct volume of sample is in the cup.

8.3.8 With the lid held tightly in place, wipe the overflow from the sample cup and lid. Be sure that the sample cup threads are still covered with silicone grease after wiping, and that the hole in the lid is not plugged.

8.3.9 Screw the retort cup onto the retort chamber with its condenser.

8.3.10 Place a clean, dry, liquid receiver under the condenser discharge tube.

8.3.11 Heat the retort and observe the liquid falling from the condenser. Continue heating for 10 min after the last condensate is collected.

8.3.12 Remove the liquid receiver from the retort. Note whether solids are in the liquid which was recovered. If so, the whole drilling fluid has boiled over from the sample cup and the test shall be repeated from 8.3.6.

8.3.13 Read the volumes of water and oil in the liquid receiver after it has cooled to ambient temperature. Record the volumes (or volume percentages) of water and oil collected.

8.3.14 Cool the retort, remove the steel with corkscrew and clean the sample cup with a putty knife or spatula.

8.4 Calculation

8.4.1 Using the measured volumes of oil and water and the volume of the original whole drilling fluid sample (10 ml or 20 ml), calculate as percentages the volume fractions of water, oil and total solids in the drilling fluid.

a) Volume fraction water:

$$V_{\mathrm{w}} = 100 \times \frac{V_{\mathrm{wa}}}{V_{\mathrm{sa}}} \tag{9}$$

where

V_{w} is the volume fraction of water, expressed as a percentage of the total sample volume;

V_{wa} is the volume of water, in millilitres;

V_{sa} is the volume of the drilling fluid sample, in millilitres.

b) Volume fraction oil:

$$V_o = 100 \times \frac{V_{oa}}{V_{sa}} \quad (10)$$

where

V_o is the volume fraction of oil, expressed as a percentage of the total sample volume;

V_{oa} is the volume of oil, in millilitres;

V_{sa} is the volume of the drilling fluid sample, in millilitres.

c) Volume fraction retort solids, V_s:

$$V_s = 100 - (V_w + V_o) \quad (11)$$

where V_s is the volume fraction of retort solids, expressed as a percentage of the total sample volume.

NOTE The percentage (volume fraction) retort solids above is only the difference between water plus oil, and the total sample volume (10 ml or 20 ml). This difference is both suspended solids (weighting material and low-gravity) and dissolved materials (e.g. salt). This percentage (volume fraction) retort solids is the suspended solids only if the drilling fluid is an untreated, fresh-water drilling fluid.

8.4.2 Additional calculations are required to find the percentage (volume fraction) suspended solids and relate them to the relative volumes of low-gravity solids and weighting material. To make these calculations, an accurate drilling fluid mass and chloride concentration are needed.

$$V_{ss} = V_s - V_w\,[(C_s/1\,680\,000) - 1{,}21 \times C_s] \quad (12)$$

where

V_{ss} is the percentage (volume fraction) suspended solids;

C_s is the chloride concentration, in milligrams per litre.

8.4.3 Percentage (volume fraction) low-gravity solids is calculated as:

$$V_{lg} = \frac{1}{(\rho_b - \rho_{lg})}[100\rho_f + (\rho_b - \rho_f)\cdot V_{ss} - 100\rho_m - (\rho_f - \rho_o)\cdot V_o] \quad (13)$$

$$\rho_f = 1 + 0{,}000\,001\,09 \times C_s \quad (14)$$

where

V_{lg} is the percentage (volume fraction) low-gravity solids, in milligrams per litre;

ρ_m is the drilling fluid density, in grams per cubic centimetre;

ρ_f is the density of filtrate, in grams per cubic centimetre;

ρ_b is the density of weighting material, in grams per cubic centimetre;

ρ_{lg} is the density of low-gravity solids, in grams per cubic centimetre (use 2,6 if unknown);

ρ_o is the density of oil, in grams per cubic centimetre (use 0,8 if unknown);

NOTE The ρ_f density calculation [equation (14)] is based on the sodium chloride concentration.

8.4.4 Percentage (volume fraction) weighting material is calculated as:

$$V_b = V_{ss} - V_{lg} \quad (15)$$

where V_b is the percentage (volume fraction) weighting material.

8.4.5 Concentration of low-gravity solids, weighting material and suspended solids can be calculated as:

$$c_{lg} = 10\rho_{lg} \cdot V_{lg} \quad (16)$$

$$c_b = 10\rho_b \cdot V_b \quad (17)$$

$$c_{ss} = c_{lg} + c_b \quad (18)$$

where

c_{lg} is the low-gravity solids concentration, in kilograms per cubic metre;

c_b is the weighting material concentration, in kilograms per cubic metre;

c_{ss} is the suspended solids concentration, in kilograms per cubic metre.

9 Sand content

9.1 Principle

The sand content of drilling fluid is the percentage (volume fraction) of particles of diameter larger than 74 μm. It is measured by a sand-screen set.

9.2 Apparatus

9.2.1 **Sieve**, 75 μm (200 mesh) and 63,5 mm (2,5 in) in diameter.

9.2.2 **Funnel** to fit sieve.

9.2.3 **Glass measuring tube,** marked for the volume of drilling fluid to be added and graduated from 0 % to 20 % in order to read the percentage of sand directly.

9.3 Procedure

9.3.1 Fill the glass measuring tube with drilling fluid to the “drilling fluid” mark. Add water to the next mark. Close the mouth of the tube and shake vigorously.

9.3.2 Pour the mixture onto the clean, wet screen. Discard the liquid passing through the screen. Add more water to the tube, shake, and again pour onto the screen. Repeat until the tube is clean. Wash the sand retained on the screen to free it of any remaining drilling fluid.

9.3.3 Put the funnel upside down over the top of the sieve. Slowly invert the assembly and insert the tip of the funnel into the mouth of the glass tube. Wash the sand into the tube by playing a fine spray of water through the screen. Allow the sand to settle. From the graduations on the tube, read the volume percent of the sand.

9.3.4 Report the sand content of the drilling fluid as a percentage (volume fraction). Report the source of the drilling fluid sample, i.e. above shaker, suction pit, etc. Coarse solids other than sand will be retained on the screen (e.g. lost circulation material) and the presence of such solids should be noted.

10 Methylene blue capacity

10.1 Principle

10.1.1 The methylene blue capacity of drilling fluid is an indication of the amount of reactive clays (bentonite and/or drill solids) present as determined by the methylene blue test. The methylene blue capacity provides an estimate of the total cation exchange capacity of the drilling fluid solids. Methylene blue capacity and cation exchange capacity are not necessarily equivalent, the former normally being somewhat less than the actual cation exchange capacity.

10.1.2 Methylene blue solution is added to a sample of drilling fluid (which has been treated with hydrogen peroxide and acidified) until saturation is noted by formation of a dye “halo” around a drop of solids suspension placed on filter paper. Variations of the procedure used on the drilling fluid can be performed on drill solids and commercial bentonite to allow an estimate of the amount of each type of solid present in the fluid (see API RP 13I [4]).

10.1.3 Drilling fluids frequently contain substances in addition to reactive clays that absorb methylene blue. Pretreatment with hydrogen peroxide (see 10.3.2) is intended to remove the effect of organic materials such as lignosulfonates, lignites, cellulosic polymers, polyacrylates, etc.

10.2 Reagents and apparatus

10.2.1 Methylene blue solution, Reagent grade methylene blue (CAS No. 61-73-4), 3,20 g/l (1 ml = 0,01 milliequivalent).

The moisture content of reagent grade methylene blue shall be determined each time the solution is prepared. Dry a 1 000 g portion of methylene blue to a constant mass at 93 °C ± 3 °C (200 °F ± 5 °F). Make the appropriate correction in the mass of methylene blue to be taken to prepare the solution as follows:

$$m_s = \frac{3,2}{m_{ds}} \tag{19}$$

where

m_s is the mass of sample to be taken, in grams;

m_{ds} is the mass of the dried sample, in grams.

10.2.2 Hydrogen peroxide (CAS No. 7722-88-5): 3 % solution.

10.2.3 Dilute sulfuric acid (CAS No. 7664-93-9): approximately 2,5 mol/l (5 N).

10.2.4 Syringe, (TD) 2,5 ml or 3 ml.

10.2.5 Erlenmeyer flask, of capacity 250 ml.

10.2.6 Burette (TD) 10 ml, **micropipette** 0,5 ml, or graduated **pipette** 1 ml.

10.2.7 Graduated cylinder, (TD) 50 ml.

10.2.8 Stirring rod.

10.2.9 Hot plate.

10.2.10 Filter paper, Whatman No. 1[3] or equivalent.

10.3 Procedure

10.3.1 Add 2,0 ml of drilling fluid (or suitable volume of drilling fluid to require from 2 ml to 10 ml of methylene blue solution) to 10 ml of water in the Erlenmeyer flask. The syringe used should have a capacity of more than 2 ml, generally 2,5 ml or 3 ml. By using a larger syringe, it is not necessary to remove the air trapped in the syringe.To assure that exactly 2,0 ml of drilling fluid is being added, use the following procedure.

a) The air or gas entrained in the drilling fluid shall be removed (see annex D for information on air or gas removal). Stir the drilling fluid to break the gel and quickly draw the drilling fluid into the syringe. Then slowly discharge the syringe back into the drilling fluid, keeping the tip submerged.

b) Again draw the drilling fluid into the syringe until the end of the plunger is at the last graduation on the syringe (e.g. at the 3-ml line on a 3-ml syringe).

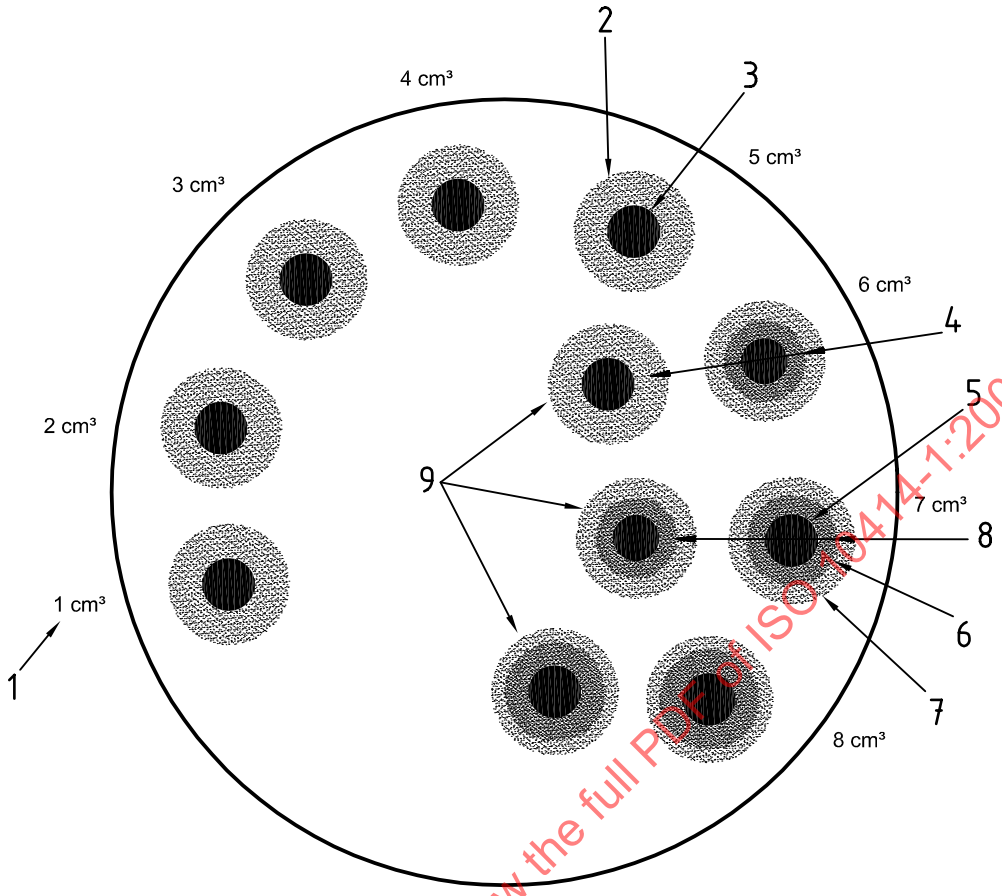
c) Deliver 2,0 ml of drilling fluid by pushing the plunger until the end of the plunger is exactly 2 ml from the last graduation on the syringe. Thus in a 3-ml syringe, it would be at the 1-ml line.

10.3.2 Add 15 ml of 3 % hydrogen peroxide and 0,5 ml of sulfuric acid. Boil gently for 10 min, but do not allow to boil to dryness. Dilute to about 50 ml with water.

10.3.3 Add methylene blue solution to the flask in increments of 0,5 ml. If the approximate amount of methylene blue solution necessary to reach the endpoint is known from previous testing, larger increments (1 ml to 2 ml) can be used at the beginning of the titration. After each addition of methylene blue solution, swirl the contents of the flask for about 30 s. While the solids are still suspended, remove one drop of liquid with the stirring rod and place the drop on the filter paper. The initial endpoint of the titration is reached when dye appears as a blue or turquoise ring surrounding the dyed solids, as shown in Figure 1.

10.3.4 When the blue tint spreading from the spot is detected, shake the flask for an additional 2 min and place another drop on the filter paper. If the blue ring is again evident, the final endpoint has been reached. If the blue ring does not appear, continue as before (see 10.3.3) until a drop taken after 2 min shows the blue tint. Free dye detected immediately after adding 6 ml methylene blue solution is adsorbed after 2 min, and indicates that endpoint has not quite been reached.

3) Whatman No. 1 is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 10414 and does not constitute an endorsement by ISO of these products.



Key

1 Volume of methylene blue solution added
2 Moisture
3 Dyed drilling fluid solids (no free, unadsorbed dye present)
4 Free dye, visible immediately after adding sixth cm^3, is adsorbed after 2 min and indicates that the end point has not quite been reached
5 Dyed drilling fluid solids
6 Free, unadsorbed dye
7 Moisture
8 Endpoint
9 Appearance of spot after 2 min

Figure 1 — Spot tests for endpoint of methylene blue titration

10.4 Calculation

Report the methylene blue capacity of the drilling fluid, calculated as follows:

$$MBT = \frac{V_{mb}}{V_{df}} \tag{20}$$

where

MBT is the methylene blue capacity;

V_{mb} is the volume of methylene blue solution, in millilitres;

V_{df} is the volume of drilling fluid sample, in millilitres.

Alternatively, the methylene blue capacity can be reported as kilograms per cubic metre (or pounds per barrel) bentonite equivalent (*BE*, based on bentonite with a cation exchange capacity of 70 meq/100 g) calculated as follows:

$$BE, \text{ in kilograms per cubic metre} = \frac{14{,}25 \times MBT}{V_{df}} \quad (21)$$

$$BE, \text{ in pounds per barrel} = \frac{5 \times MBT}{V_{df}} \quad (22)$$

NOTE The kilograms per cubic metre (or pounds per barrel) bentonite equivalent from equation (21) or (22) is not equal to the amount of commercial bentonite in the drilling fluid. Reactive clays in the drill solids contribute to this quantity as well as commercial bentonite. See API RP 13I [4] for additional information on estimating the amount of commercial bentonite and drill solids present.

11 pH

11.1 Principle

11.1.1 Field measurement of drilling fluid (or filtrate) pH and adjustments to the pH are fundamental to drilling fluid control. Clay interactions, solubility of various components and contaminants, and effectiveness of additives are all dependent on pH, as is the control of acidic and sulfide corrosion processes.

11.1.2 The term “pH” denotes the negative logarithm of the hydrogen ion, H^+, activity in aqueous solutions (activity and concentration are equal only in dilute solutions): $pH = -\log [H^+]$. For pure water at 24 °C (75 °F) the hydrogen ion activity $[H^+]$ is 10^{-7} mol/litre and pH = 7. This system is termed "neutral" because the hydroxyl ion activity $[OH^-]$ is also 10^{-7} mol/litre. In aqueous systems at 24 °C (75 °F) the ion product, $[H^+] \times [OH^-]$, is 10^{-14} (a constant). Consequently, an increase in H^+ denotes 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”.

11.1.3 The recommended method for measurement of drilling fluid pH is with 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 temperature-compensate the slope and are preferred over the manually adjusted instruments.

Colour-matching pH-paper and sticks are used for field pH measurements, but are not the methods recommended. These methods are reliable only in very simple water-based drilling fluids. Drilling fluid solids, dissolved salts and chemicals, and dark-coloured liquids cause serious errors in pH-paper values. Readability is normally about 0,5 pH unit.

11.2 Reagents and apparatus

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

a) pH = 4,0: potassium hydrogen phthalate at 0,05 mol/l in water. Gives 4,01 pH at 24 °C (75 °F).

b) pH = 7,0: potassium dihydrogen phosphate at 0,020 66 mol/l and disodium hydrogen phosphate at 0,029 34 mol/l in water. Gives 7,00 pH at 24 °C (75 °F).

c) pH = 10,0: sodium carbonate at 0,025 mol/l and sodium bicarbonate at 0,025 mol/l in water. Gives 10,01 pH at 24 °C (75 °F).

Buffers may be obtained from supply houses as pre-made solution, dry-powder packages, or a given formula. Shelf life of all buffers should not exceed six months before disposal. The date of preparation of buffer should be shown on bottles used in the field. Bottles should be kept tightly stoppered.

11.2.2 Distilled or deionized water, in spray bottle.

11.2.3 Mild liquid detergent.

11.2.4 Sodium hydroxide, NaOH (CAS No. 1310-73-2): 0,1 mol/l (approximately); to recondition electrode.

11.2.5 Hydrochloric acid, HCl (CAS No. 7674-01-0): 0,1 mol/l (approximately); to recondition electrode.

11.2.6 Ammonium bifluoride (CAS No. 1341-49-7): 10 % solution (approximately); to recondition electrode.

WARNING — HCl is a strong and toxic acid.

11.2.7 Millivolt-range potentiometer calibrated to show pH units for measuring the potential between a glass-membrane electrode and a standard "reference" electrode.

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

a) pH range: 0 to 14;

b) electronics type: solid state (preferred);

c) power source: batteries (preferred);

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

e) readout: digital (preferred);

f) resolution: 0,1 pH unit;

g) accuracy: ± 0,1 pH unit;

h) repeatability: 0,1 pH unit;

i) adjustments:

   1) "temperature" compensation of electrode system;

   2) "slope" of electrode system (preferred);

   3) "calibration" setting of readout. (Instrument with the above internal temperature compensation is preferred).

11.2.8 Electrode system, a combination of a glass electrode for sensing H^+ ions and a standard voltage reference electrode, preferably constructed as a single electrode.

The body of this probe should be constructed of durable material. A flat-end probe is preferred for better protection and easier cleaning of the electrode. Waterproof connection to the meter is recommended. Specifications are:

a) glass pH electrode response range: 0 to 14 pH units;

b) electrodes: a glass electrode and a silver/silver chloride electrode in combination, having a ceramic or a plastic single or double junction;

   Use double-junction electrode for measuring liquids containing sulfide or bromide ion to avoid damaging (silver) reference electrode system.

c) electrolyte in reference electrode: KCl gel;

d) glass composition: suitable for low sodium ion error;

e) sodium ion error: at pH = 13 or at 0,1 mol Na^+ ion, an error less than 0,1 pH unit.

11.2.9 Soft tissue, to blot electrodes.

11.2.10 Thermometer, glass, 0 °C to 150 °C (32 °F to 300 °F).

11.2.11 Soft-bristle test tube brush, to clean electrode.

11.2.12 Electrode storage vial, to keep electrodes moist.

11.3 Procedure for pH measurement

11.3.1 Obtain a sample of fluid to be tested. Allow it to reach 24 °C ± 3 °C (75 °F ± 5 °F).

11.3.2 Allow buffer solution to reach the same temperature as the fluid to be tested.

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

11.3.3 Clean electrodes by washing with distilled water and blot dry.

11.3.4 Place probe into pH 7,0 buffer.

11.3.5 Turn on meter; wait 60 s for reading to stabilize (see 11.4 if meter reading is not stable).

11.3.6 Measure temperature of pH 7,0 buffer solution.

11.3.7 Set this temperature on “temperature” knob.

11.3.8 Set meter reading to “7,0” using “calibration” knob.

11.3.9 Rinse probe with distilled water and blot dry.

11.3.10 Repeat operations in 11.3.6 through 11.3.9 using either pH 4,0 or pH 10,0 buffer. Use pH 4,0 if “acidic” sample, or pH 10,0 if “alkaline” sample is to be tested. Set meter to number “4,0” or “10,0” respectively, using “slope” adjustment knob. (If no “slope” knob exists, use the “temperature” knob to set “4,0” or “10,0” on meter).

11.3.11 Check the meter again with pH 7,0 buffer. If it has changed, reset to “7,0” with “calibration” knob. Repeat 11.3.6 through 11.3.9. If meter does not calibrate properly, recondition or replace electrodes as given in 11.4.

Discard and do not reuse the sample of buffer solutions used in calibration. Meter should be fully calibrated every day, as per 11.3.2 through 11.3.9, using two buffers. Check with pH 7,0 buffer every 3 h.

11.3.12 If meter calibrates properly, rinse electrode with distilled water and blot dry. Place electrode in sample to be tested and stir gently. Allow 60 s to 90 s for reading to stabilize.

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

11.3.14 Carefully clean the electrode in preparation for next usage. Store in vial of pH 4,0 buffer. Never let the probe tip become dry.

11.3.15 Turn meter off and close cover to protect instrument. Avoid storing instrument at extreme temperatures [below 0 °C (32 °F) or above 50 °C (120 °F)].

11.4 Care of electrode

11.4.1 Cleaning the electrode is necessary periodically, especially if oil or clay particles coat the face of the glass electrode or the porous frit of the reference electrode. Clean electrode with a soft-bristle brush and a mild detergent.

11.4.2 Reconditioning the electrode may be necessary if plugging becomes severe, as indicated by slow response, drifting of readings, or if “slope” and “calibration” cannot be mutually set.

11.4.3 Recondition by soaking electrode for 10 min in 0,1 mol/l HCl, followed by rinsing in water and soaking for 10 min in 0,1 mol/l NaOH and rinsing again.

11.4.4 Check electrode for response by performing calibration in 11.3.1 through 11.3.15.

11.4.5 If electrode continues to perform poorly, soak electrode for 2 min only in 10 % ammonium bifluoride solution. Repeat 11.3.1 through 11.3.15 to check for calibration capability.

11.4.6 Replace electrode system if above steps fail to recondition it.

12 Alkalinity and lime content

12.1 Principle

12.1.1 Alkalinity can be considered as the acid-neutralizing power of a substance. In drilling fluid testing, alkalinity measurements can be made on either the whole drilling fluid (designated with a subscript m) or on the filtrate (designated with a subscript f). The data collected from the alkalinity test can also be used to estimate the concentrations of hydroxyl (OH^-), carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions in the drilling fluid.

12.1.2 Knowledge of the drilling fluid and filtrate alkalinities is important in many drilling operations to ensure proper control of the drilling fluid chemistry. Drilling fluid additives, particularly some deflocculants, require an alkaline environment to function properly. Alkalinity arising from hydroxyl ions is generally accepted as being beneficial, while alkalinities resulting from carbonates and/or bicarbonates may have adverse effects on the drilling fluid performance.

12.1.3 The ions that are primarily responsible for filtrate alkalinities are the hydroxyl (OH^-), carbonate (CO_3^{2-}), and bicarbonate (HCO_3^-) ions. It is important to realize that the carbonate species can change from one form to another form by changing the solution pH. The interpretation of filtrate alkalinities involves calculating differences between the titration values obtained by the following procedures. It is for this reason that special attention to accurate measurement of the various reagents is important in all steps of the procedure. In addition it is important to realize that the following calculations are only estimates of the concentrations of the reported ionic species based on theoretical chemical equilibrium reactions.

12.1.4 The composition of drilling fluid filtrates is often so complex that the interpretation of alkalinities in terms of estimated ionic components may be misleading. Any particular alkalinity value represents all of the ions which will react with the acid in the pH range over which that particular value was tested. Inorganic ions which may contribute to the alkalinity, in addition to the hydroxyl, carbonate and bicarbonate ions, are borates, silicates, sulfides and phosphates. Perhaps more serious in drilling fluids are anionic organic thinners, filtrate reducers, and their degradation products which may contribute to a large portion of the alkalinity value as well as masking the endpoint colour change. These organic materials make a particularly large contribution to the M_f alkalinity and thus render the test highly inaccurate in drilling fluids treated with organic thinners. However, for simple bentonite-base drilling fluid systems containing no organic thinners, the P_f and M_f alkalinities (see 12.3) can be used as guidelines to determine both the presence of carbonate/bicarbonate contamination and the treatment necessary to alleviate the contamination.

12.2 Reagents and apparatus

12.2.1 Sulfuric acid (CAS No. 7664-93-9) solution: standardized 0,02 N (N/50).

12.2.2 Phenolphthalein (CAS No. 518-51-4) indicator solution: 1 g/100 ml in 1:1 alcohol:water solution.

12.2.3 Methyl orange (CAS No. 547-58-0) indicator solution: 0,1 g/100 ml of water.

12.2.4 pH meter (optional).

NOTE pH meter is more accurate than indicator solution.

12.2.5 Titration vessel, 100 ml or 150 ml, preferably white.

12.2.6 Graduated pipettes (TD), 1 ml and 10 ml.

12.2.7 Volumetric pipette (TD), 1 ml.

12.2.8 Syringe (TD), 1 ml.

12.2.9 Stirring rod.

12.3 Procedure — Filtrate alkalinity: P_f, M_f

12.3.1 Measure one or more millilitres of filtrate into the titration vessel. Add two or more drops of the phenolphthalein indicator solution. If the indicator turns pink, add 0,02 N (N/50) sulfuric acid, drop by drop from the graduated pipette, while stirring, until the pink colour just disappears. If the sample is so coloured that the indicator colour change is masked, the endpoint can be taken when the pH drops to 8,3 as measured with a pH meter. (Refer to clause 11 for proper pH measurement).

12.3.2 Report the phenolphthalein alkalinity of the filtrate, P_f, as the number of millilitres of 0,02 N acid required per millilitre of filtrate.

12.3.3 To the sample which has been titrated to the P_f endpoint, add two or three drops of methyl orange indicator solution. Add the standard acid drop by drop from the pipette, while stirring, until the colour of the indicator changes from yellow to pink. The endpoint can also be taken when the pH of the sample drops to 4,3 as measured by a pH meter. (Refer to clause 11 for proper pH measurement.)

12.3.4 Report the methyl orange alkalinity of the filtrate, M_f, as the total millilitres of 0,02 N acid per millilitre of filtrate required to reach the methyl orange endpoint (including that amount required for the P_f endpoint).

12.4 Procedure — Drilling fluid alkalinity: P_m

12.4.1 Measure 1,0 ml of drilling fluid into the titration vessel using a syringe or volumetric pipette. Dilute the drilling fluid sample with 25 ml to 50 ml of distilled water. Add 4 drops to 5 drops of phenolphthalein indicator solution and, while stirring, titrate rapidly with 0,02 N (N/50) standard sulfuric acid solution until the pink colour disappears. If the endpoint colour change cannot be seen, it can be taken when the pH drops to 8,3 measured by a pH meter. (Refer to clause 11 for proper pH measurement.)

If cement contamination is suspected, the titration shall be performed as rapidly as possible and the endpoint reported as the first disappearance of the pink colour.

12.4.2 Report the phenolphthalein alkalinity of the drilling fluid, P_m, as the number of millilitres of 0,02 N (N/50) acid required per millilitre of drilling fluid.

12.5 Calculation of P_f, M_f

The mass concentrations of hydroxyl, carbonate and bicarbonate ions can be estimated as shown in Table 3.

Table 3 — Concentrations of hydroxyl, carbonate and bicarbonate ions, mg/l

	OH^-	CO_3^{-2}	HCO_3^-
$P_f = 0$	0	0	1 220 M_f
$2\,P_f < M_f$	0	1 200P_f	1 220 (M_f –2 P_f)
$2\,P_f = M_f$	0	1 200 P_f	0
$2\,P_f > M_f$	340 (2 P_f – M_f)	1 200 (M_f – P_f)	0
$P_f = M_f$	340 M_f	0	0

12.6 Estimation of lime content

Determine the P_f and P_m of the filtrate and drilling fluid as described in 12.3 and 12.4.

Determine the volume fraction of water in the drilling fluid using the value for volume fraction, expressed as a percentage, of water from the liquid and solids determination (clause 8) in the following equation:

$$F_w = \frac{V_w}{100} \tag{23}$$

where

F_w is the volume fraction of water in the drilling fluid;

V_w is the volume fraction, expressed as a percentage, of water in the drilling fluid (see clause 8).

Report the lime content of the drilling fluid in kilograms per cubic metre (or pounds per barrel) from the following equation:

$$\text{Estimated lime content, kilograms per cubic metre} = 0{,}742 \times (P_m - F_w P_f) \tag{24}$$

$$\text{Estimated lime content, (pounds per barrel)} = 0{,}26 \times (P_m - F_w P_f) \tag{25}$$

where

F_w is the volume fraction of water in the drilling fluid;

P_m is the phenolphthalein alkalinity of the drilling fluid;

P_f is the phenolphthalein alkalinity of the filtrate.

13 Chloride ion content

13.1 Principle

The chloride test measures the chloride ion concentration in drilling fluid filtrate.

13.2 Reagents and apparatus

13.2.1 Silver nitrate (CAS No. 7761-88-8) solution, containing 4,791 g/l (equivalent to 0,001 g chloride ion/ml), stored in an amber or opaque bottle.

13.2.2 Potassium chromate (CAS No. 7789-00-6) indicator solution, 5 g/100 ml of water.

CAUTION — This product is known to be carcinogenic and should be handled with care.

13.2.3 Sulfuric acid (CAS No. 7664-93-9) or nitric acid (CAS No. 7697-37-2) solution, standardized 0,02 N (N/50).

13.2.4 Phenophthalein (CAS No. 518-51-4) indicator solution, 1 g/100 ml of 1:1 alcohol/water solution.

13.2.5 Calcium carbonate (CAS No. 471-34-1), precipitated, chemically pure grade.

13.2.6 Distilled water.

13.2.7 Graduated pipettes (TD), 1 ml and 10 ml.

13.2.8 Titration vessel, 100 ml or 150 ml, preferably white.

13.2.9 Stirring rod.

13.3 Procedure

13.3.1 Measure 1 cm^3 or more of filtrate into the titration vessel. Add 2 drops to 3 drops phenolphthalein solution. If the filtrate turns pink, add acid drop by drop from pipette, while stirring, until the colour has disappeared. If the filtrate was originally deeply coloured, add an additional 2 ml of 0,02 N (N/50) sulfuric acid or nitric acid and stir. Then add 1 g calcium carbonate and stir.

13.3.2 Add 25 ml to 50 ml distilled water and 5 drops to 10 drops potassium chromate solution. Stir continuously, while adding standard silver nitrate solution drop by drop from the pipette, until the colour changes from yellow to orange-red and persists for 30 s. Record the volume of silver nitrate solution required to reach the endpoint. If over 10 ml of silver nitrate solution is used, repeat the test with a smaller sample of filtrate.

NOTE If the chloride ion concentration of the filtrate exceeds 10 000 mg/l, a silver nitrate solution equivalent to 0,01 g chloride ion per millilitre may be used. The factor 1 000 in equation (30) is then changed to 10 000.

13.4 Calculation

Report the chloride ion concentration $c[Cl^-]$ of the filtrate, in milligrams per litre, calculated as follows:

$$c[Cl^-] = 1000 \times \frac{V_{sn}}{V_f} \quad (26)$$

where

V_{sn} is the volume of silver nitrate solution, in millilitres;

V_f is the volume of the filtrate sample, in millilitres.

To convert units:

$$\text{Sodium chloride concentration, } c[NaCl], \text{ in milligrams per litre} = 1{,}65 \times c[Cl^-] \quad (27)$$

Refer to Table 1 for density conversions.

14 Total hardness as calcium

14.1 Principle

The hardness of water or drilling fluid filtrate is due primarily to the presence of calcium and magnesium ions. When EDTA (or its salt) is added to the water or filtrate, it combines with both the calcium and magnesium and the endpoint is determined with a suitable indicator. The total hardness of the water or filtrate is expressed as milligrams calcium per litre. An endpoint obscured by dark components can often be remedied by oxidizing with a reagent such as sodium hypochlorite.

14.2 Reagents and apparatus

14.2.1 EDTA solution (CAS No. 6381-92-6), 0,01 mol/l; standardized disodium ethylenediaminetetraacetate dihydrate (1 ml = 1 000 mg/l $CaCO_3$, 1 ml = 400 mg/l Ca^{2+}).

14.2.2 Buffer solution, 67,5 g ammonium chloride (CAS No. 12125-02-9) and 570 ml ammonium hydroxide (CAS No. 1336-21-6) (15 N) diluted to 1 000 ml with distilled water.

14.2.3 Hardness indicator solution, 1 g/l (Calmagite®[4)] or equivalent); 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid (CAS No. 3147-14-6) in distilled water.

14.2.4 Acetic acid (CAS No. 64-19-7), glacial.

CAUTION — Avoid skin contact.

14.2.5 Masking agent, 1:1:2 volume mixture of triethanolamine (CAS No. 102-71-6):tetraethylenepentamine (CAS No. 112-57-2):water.

14.2.6 Sodium hypochlorite (CAS No. 7681-52-9) solution, 5,25 % mass fraction in deionized water.

Many brands of commercial laundry bleach contain calcium hypochlorite or oxalic acid and should not be used. Ensure the sodium hypochlorite is fresh, as it will deteriorate with time.

14.2.7 Deionized or distilled water.

The deionized water and sodium hypochlorite solution should be tested for hardness by using 50,0 ml of the deionized water and 10 ml of the sodium hypochlorite solution without the test sample, and continuing with 14.3.7 and 14.3.8. If the procedure is then repeated with the test sample utilizing 50 ml deionized water and 10 ml sodium hypochlorite solution in 14.3.2 through 14.3.6, the hardness of the test sample can be determined by subtracting the hardness of the deionized water and hypochlorite.

14.2.8 Titration vessel, 150 ml beaker.

14.2.9 Graduated pipettes (TD), 5 ml and 10 ml.

14.2.10 Volumetric pipettes (TD), 1 ml, 2 ml and 5 ml.

14.2.11 Hot plate (required if filtrate is coloured).

14.2.12 pH paper strip.

4) Calmagite® is an example a suitable product available commercially. This information is given for convenience of users of this part of ISO 10414 and does not constitute an endorsement by ISO of this product.

14.3 Procedure

14.3.1 Measure one or more cubic centimetres of sample into a 150 ml beaker. (If filtrate is clear, or is only lightly coloured, omit steps 14.3.2 through14.3.5.)

14.3.2 Add 10 ml sodium hypochlorite solution and mix.

14.3.3 Add 1 ml glacial acetic acid and mix.

14.3.4 Boil the sample for 5 min. Maintain the sample volume by adding deionized water as required during boiling. Boiling is required to remove excess chlorine. The absence of chlorine can be verified by immersing a strip of pH paper in the sample. If the paper is bleached white, continued boiling is required.

Work in an adequately ventilated area.

14.3.5 Cool the sample.

14.3.6 Rinse the inside of the beaker with deionized water and dilute the sample to 50 ml with deionized water. Add approximately 2 ml buffer solution and swirl to mix.

NOTE The presence of soluble iron may interfere with the endpoint determination. Should this be suspected, a mixture of triethanolamine:tetraethylenepentamine:water (1:1:2 by volume) has proven to be a suitable masking agent. 1 ml of the mixture is used per titration.

14.3.7 Add sufficient hardness indicator (2 drops to 6 drops) and mix. A wine-red colour will develop if calcium and/or magnesium is present.

14.3.8 While stirring, titrate with EDTA solution to the proper endpoint. Calcium indicators will produce a change from red to blue. The endpoint is best described as the point at which additional EDTA produces no further red to blue colour change. The titration volume of EDTA is used in the calculation in 14.4.

14.4 Calculation

$$\text{Total hardness as calcium, in milligrams per litre} = 400 \times \frac{V_{\text{EDTA}}}{V_{\text{S}}} \qquad (28)$$

where

V_{EDTA} is the volume of EDTA solution, in millilitres;

V_{S} is the volume of the sample, in millilitres.

Annex A
(informative)

Chemical analysis of water-based drilling fluids

A.1 Calcium

A.1.1 Principle

When EDTA (or its salt) is added to water or drilling fluid filtrate containing both calcium and magnesium, it combines first with calcium. Calcium can be determined with EDTA when the pH of the sample is sufficiently high, so that magnesium is precipitated as the hydroxide, and an indicator specific for calcium is used. Several indicators will give colour changes when all of the calcium has been complexed by EDTA at a pH of 12 to 13. An endpoint obscured by dark organic components can be remedied by oxidizing with a reagent such as sodium hypochlorite.

A.1.2 Reagents and apparatus

A.1.2.1 **EDTA solution** (CAS No. 6381-92-6), 0,01 mol/l, standardized disodium ethylenediaminetetraacetate dihydrate (1 ml = 1 000 mg/l $CaCO_3$, 1 ml = 400 mg/l Ca^{2+}).

A.1.2.2 **Calcium buffer solution**, 1 mol/l sodium hydroxide (NaOH) (CAS No. 1310-73-2).

A.1.2.3 **Calcium indicator**, Calver® II[5] or hydroxy naphthol blue (CAS No. 63451-35-4).

A.1.2.4 **Acetic acid** (CAS No. 64-19-7), glacial.

CAUTION — Avoid skin contact.

A.1.2.5 **Titration vessel**, 150 ml beaker.

A.1.2.6 **Graduated pipettes** (TD), 1 ml and 10 ml.

A.1.2.7 **Volumetric pipettes** (TD), 1 ml, 2 ml and 5 ml.

A.1.2.8 **Hot plate** (required if filtrate is coloured).

A.1.2.9 **Masking agent,** 1:1:2 volume mixture of triethanolamine (CAS No. 102-71-6):tetraethylenepentamine (CAS No. 112-57-2):water.

A.1.2.10 **pH paper.**

A.1.2.11 **Graduated cylinder** (TC), 50 ml.

A.1.2.12 **Sodium hypochlorite** (CAS No. 7861-52-9) solution, 5,25 % mass fraction in deionized water.

Many brands of commercial laundry bleach contain calcium hypochlorite or oxalic acid and should not be used. Ensure the sodium hypochlorite is fresh, as it will deteriorate with time.

A.1.2.13 **Deionized or distilled water.**

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5) Calver® II is an example a suitable product available commercially. This information is given for convenience of users of this part of ISO 10414 and does not constitute an endorsement by ISO of this product.

The deionized water and sodium hypochlorite solution should be tested for calcium by using 50,0 ml of the deionized water and 10 ml of the sodium hypochlorite solution without the test sample. If the procedure is then repeated with the test sample utilizing 50,0 ml of the deionized water and 10 ml of the sodium hypochlorite solution in A.1.3, the calcium of the test sample can be determined by subtracting the calcium of the deionized water and sodium hypochlorite solution.

A.1.3 Procedure

A.1.3.1 With a volumetric pipette, add 1 ml or more of sample into a 150 ml beaker. This sample volume will be used in the calculation shown in A.1.4. If filtrate is colourless or is only slightly coloured, omit steps A.1.3.2 through A.1.3.5.

A.1.3.2 With graduated pipette, add 10 ml hypochlorite solution and mix.

A.1.3.3 With graduated pipette, add 1 ml glacial acetic acid and mix.

A.1.3.4 Boil the sample for 5 min. Maintain the sample by adding deionized water as required during boiling. Boiling is required to remove excess chlorine. The absence of chlorine can be verified by immersing a strip of pH paper in the sample. If the paper is bleached white, continued boiling is required. A sufficiently boiled sample will show a pH of 5,0.

A.1.3.5 Cool the sample.

A.1.3.6 Rinse the inside of the beaker with deionized water and dilute the sample to approximately 50 ml with deionized water. Add 10 ml to 15 ml of calcium buffer solution, or sufficient sodium hydroxide to produce a pH of 12 to 13.

NOTE The presence of soluble iron may interfere with the endpoint determination. Should this be suspected, a mixture of triethanolamine:tetraethylenepentamine:water (1:1:2 by volume) is a suitable masking agent. Add 1,0 ml of the mixture after A.1.3.6.

A.1.3.7 Add sufficient calcium indicator (0,1 g to 0,2 g) to produce a pink to wine-red colour if calcium is present. Too much indicator will obscure the endpoint.

NOTE The addition of several drops of methyl orange along with the calcium indicator may improve the visibility of the endpoint.

A.1.3.8 While stirring, titrate with standard EDTA to the proper endpoint. Calcium indicators will produce a change from red to blue. The endpoint is best described as that point where additional EDTA produces no further red to blue colour change. The EDTA volume will be used in the calculation in A.1.4.

A.1.4 Calculation

$$\text{Calcium concentration, in milligrams per litre} = 400 \times \frac{V_{\text{EDTA}}}{V_{\text{S}}} \qquad \text{(A.1)}$$

where

V_{EDTA} is the volume of EDTA solution, in millilitres;

V_{S} is the volume of the sample, in millilitres.

A.2 Magnesium

A.2.1 Principle

The magnesium content of the drilling fluid filtrate can be calculated by subtracting the calcium ion content from the total hardness. This gives the magnesium content in terms of calcium which is converted to magnesium by multiplying the value by the ratio of atomic weights (24,3/40 = 0,6).

A.2.2 Procedure

A.2.2.1 Determine the total hardness as calcium (14.3 through 14.4).

A.2.2.2 Determine the calcium content as described in A.1.

A.2.3 Calculation

Magnesium concentration, in milligrams per litre = 0,6 × (Total hardness, mg/l – Calcium content, mg/l) (A.2)

A.3 Calcium sulfate

A.3.1 Principle

The calcium sulfate content of drilling fluid is determined by using the EDTA method as described in A.1 to determine the total calcium in a drilling fluid filtrate and the whole drilling fluid. The total and undissolved calcium sulfate contents of the drilling fluid can then be calculated.

A.3.2 Reagents and apparatus

A.3.2.1 **EDTA solution** (CAS No. 6381-92-6), 0,01 mol/l, standardized disodium ethylenediaminetetraacetate dihydrate (1 ml = 1 000 mg/l $CaCO_3$, 1 ml = 400 mg/l Ca^{2+}).

A.3.2.2 **Buffer solution**, 1 mol/l sodium hydroxide (NaOH) (CAS No. 1310-73-2).

A.3.2.3 **Calcium indicator**, Calver® II[6] or hydroxy naphthol blue (CAS No. 63451-35-4).

A.3.2.4 **Acetic acid** (CAS No. 64-19-7), glacial.

CAUTION — Avoid skin contact.

A.3.2.5 **Masking agent**, 1:1:2 volume mixture of triethanolamine (CAS No. 102-71-6):tetraethylenepentamine (CAS No. 112-57-2):water.

A.3.2.6 **Sodium hypochlorite** (CAS No. 7861-52-9) solution, mass fraction of 5,25 % in deionized water.

Many brands of commercial laundry bleach contain calcium hypochlorite or oxalic acid and should not be used. Ensure the sodium hypochlorite is fresh, as it will deteriorate with time.

6) Calver® II is an example a suitable product available commercially. This information is given for convenience of users of this part of ISO 10414 and does not constitute an endorsement by ISO of this product.

A.3.2.7 Deionized or distilled water.

The deionized water and sodium hypochlorite solution should be tested for calcium by using 10 ml of the deionized water and 10 ml of the sodium hypochlorite solution without the test sample. If the procedure is then repeated with the test sample utilizing 10 ml of the deionized water and 10 ml of the sodium hypochlorite solution in A.3.3, the calcium of the test sample can be determined by subtracting the calcium of the deionized water and sodium hypochlorite solution.

A.3.2.8 Titration vessel, 150 ml beaker.

A.3.2.9 Graduated pipettes (TD), 1 ml and 10 ml.

A.3.2.10 Volumetric pipettes (TD), 1 ml, 2 ml, 5 ml and 10 ml.

A.3.2.11 Hot plate (required, if filtrate is coloured).

A.3.2.12 pH paper.

A.3.2.13 Graduated cylinder (TC), 50 ml.

A.3.2.14 Drilling fluid retort, as described in clause 8.

A.3.3 Procedure

A.3.3.1 Add 5 ml of whole drilling fluid to 245 ml deionized water. Stir the mixture for 15 min and filter through a standard filter press in accordance with 7.2.2. Collect only clear filtrate. Into a 150 ml beaker, add 10 ml of clear filtrate with the 10 ml volumetric pipette and titrate to the EDTA endpoint as described in A.1 and call this volume of EDTA V_t.

A.3.3.2 Titrate 1 ml of the original drilling fluid filtrate (obtained as described in 7.2) to the EDTA endpoint. Call this volume of EDTA V_f.

A.3.3.3 Retort the drilling fluid. Determine the volume fraction of water in the drilling fluid, F_w, by using the value for volume fraction, expressed as a percentage, of water from the liquid and solids determination and the following equation:

$$F_w = \frac{V_w}{100} \qquad \text{(A.3)}$$

where

F_w is the volume fraction of water in the drilling fluid;

V_w is the volume fraction, expressed as a percentage, of water in the drilling fluid (see clause 8).

A.3.4 Calculation

A.3.4.1 The calcium sulfate content of the drilling fluid in kilograms per cubic metre (or pounds per barrel) is calculated by using the following equations:

$$\text{Total calcium sulfate content, in kilograms per cubic metre} = 6{,}79V_t \qquad \text{(A.4)}$$

$$\text{Total calcium sulfate content, in pounds per barrel} = 2{,}38V_t \qquad \text{(A.5)}$$

where V_t is the EDTA titration volume of whole drilling fluid; see A.3.3.1.

A.3.4.2 The (excess) undissolved calcium sulfate content of the drilling fluid in kilograms per cubic metre (or pounds per barrel) may be calculated by using the subsequent equation:

$$\text{Excess calcium sulfate content, kilograms per cubic metre} = 6{,}79\ V_t - 1{,}37\ (V_f \cdot F_w) \quad \text{(A.6)}$$

$$\text{Excess calcium sulfate content, in pounds per barrel} = 2{,}38\ V_t - 0{,}48\ (V_f \cdot F_w) \quad \text{(A.7)}$$

where

F_w is the volume fraction of water in the drilling fluid;

V_t is the EDTA volume of whole drilling fluid, see A.3.3.1;

V_f is the EDTA volume of the drilling fluid filtrate, see A.3.3.2.

A.4 Sulfide

A.4.1 Principle

A.4.1.1 The concentration of soluble sulfides in a drilling fluid can be determined by this method. Soluble sulfides include H_2S and the sulfide (S^{2-}) and bisulfide (HS^-) ions. Drilling fluid filtrate is acidified in a Garrett gas train, converting all sulfides to H_2S which is evolved by bubbling an inert carrier gas through the sample. The gas train separates the gas from the liquid. The gas stream is passed through a Dräger[7)] tube which responds to H_2S by darkening along its length. The darkened length is proportional to the total sulfide in the drilling fluid filtrate. The low-range Dräger tube turns from white to brownish-black and the high-range Dräger tube turns from pale blue to jet-black. No common drilling fluid contaminant will cause these colour changes.

A.4.1.2 Lead-acetate paper disks can be accommodated in the Garrett gas train to determine the presence or absence of sulfide. If the presence of sulfide is indicated by darkening of the lead-acetate paper, a Dräger tube should be used for quantitative analysis.

A.4.2 Reagents and apparatus

A.4.2.1 **Sulfuric acid** (CAS No. 7664-93-9): approximately 2,5 mol/l, ACS reagent grade.

A.4.2.2 **Defoamer** in a dropper bottle.

A.4.2.3 **Carrier gas**, inert to hydrogen sulfide, acid and Dräger tube reagents. Nitrogen is preferred but carbon dioxide is acceptable. (Avoid air or other oxygen-containing gases).

A.4.2.4 **Dräger H_2S analysis tubes:**

a) Low range: marked H_2S 100/a (No. CH-291-01);

b) High range: marked H_2S 0,2 %/A (No. CH-281-01).

7) Dräger tubes are an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 10414 and does not constitute an endorsement of ISO of this product.

A.4.2.5 **Garrett gas train apparatus,** consisting of a transparent plastic gas train, an inert gas supply and pressure regulator, a floating-ball flow meter and a Dräger tube.

Specifications of the Garrett gas train:

a) Body

1) Chamber 1:
   - Depth 90 mm (3,54 in)
   - Diameter 38 mm (1,52 in)

2) Chambers 2 and 3:
   - Depth 90 mm (3,54 in)
   - Diameter 30 mm (1,18 in)

3) Passages between chambers:
   - Diameter 2,0 mm (0,08 in)

4) Material:
   - Transparent material or glass which is inert to acid, sulfides, and hydrogen sulfide gas.

b) Dispersion tube

1) Stem:
   - Diameter 8,0 mm (0,315 in)
   - Length approx. 150 mm (5,9 in)

2) Dispersion frit (bell-shaped, fine):
   - Diameter 30 mm (1,18 in)

3) Material:
   - Low coefficient of expansion, heat-resistant glass.

c) Flow meter, floating ball type preferred, capable of measuring 300 ml/min of CO_2 gas.

d) Flexible tubing, type inert to hydrogen sulfide and carrier gas. Latex rubber or equivalent is preferred.

e) Fittings and rigid tubing, type inert to hydrogen sulfide and acid.

f) Rubber septum.

A.4.2.6 **Lead-acetate paper disk** (see A.4.3.16).

A.4.2.7 **Hypodermic syringes**, 10 ml and 2,5 ml (for acid), and 5 ml and 10 ml (for sample).

A.4.2.8 **Hypodermic needles**, 38 mm (1,5 in) 21-gauge needles.

A.4.3 Procedure

A.4.3.1 Ensure the gas train is clean, dry and on a level surface, with the top removed.

NOTE Moisture in the train can cause the ball in the flow meter to float erratically and may affect the accuracy of the Dräger tube reading.

A.4.3.2 Add 20 ml of deionized water to Chamber 1.

A.4.3.3 Add 5 drops defoamer to Chamber 1.

A.4.3.4 See Table A.1 for sample volume and type of Dräger tube required for the expected sulfide range. Select the proper type Dräger tube. Break the tip from each end of the tube.

A.4.3.5 Install the Dräger tube with the arrow pointing downward into the bored receptacle. Likewise, install the flow meter tube with the word TOP upward. Ensure O-rings seal around the body of each tube.

A.4.3.6 Install the top on the gas train and hand-tighten all screws evenly to seal the O-rings.

Table A.1 — Dräger tube (or equivalent) identification, sample volume, and tube factors to be used for various sulfide ranges

Sulfide range mg/l	Sample volume ml	Dräger tube identification (see tube body)	Tube factor [a] (used in calculation)
1,2 to 24	10,0	H_2S 100/a	0,133
2,4 to 48	5,0	H_2S 100/a	0,133
4,8 to 96	2,5	H_2S 100/a	0,133
30 to 1 050	10,0	H_2S 0,2 %/A	1 330
60 to 2 100	5,0	H_2S 0,2 %/A	1 330
120 to 4 200	2,5	H_2S 0,2 %/A	1 330

[a] If other tubes are used, the tube factors in Table A.1 shall be changed according to manufacturer's specification.

A.4.3.7 With the regulator backed off, connect the carrier gas to the dispersion tube of Chamber 1 using flexible tubing. If a CO_2 cartridge is used, install and puncture cartridge and connect to dispersion tube.

A.4.3.8 Attach the flexible tubing from Chamber 3 outlet to the Dräger tube.

Use only latex rubber or inert plastic tubing. Do not clamp flexible tubing; unclamped tubing provides pressure relief in the event of over-pressurization.

A.4.3.9 Adjust the dispersion tube in Chamber 1 to approximately 5 mm (0,2 in) above the bottom.

A.4.3.10 Gently flow carrier gas for 30 s to purge air from the system. Check for leaks. Shut off the carrier gas.

A.4.3.11 Collect a sufficient volume of solids-free filtrate for analysis. (If a low concentration of soluble sulfides is to be detected, a large volume of filtrate is required. Use Table A.1 as a guide.)

A.4.3.12 Inject a measured volume of the solids-free filtrate sample into Chamber 1 through the rubber septum, using a hypodermic syringe and needle.

A.4.3.13 Slowly inject 10 ml sulfuric acid solution into Chamber 1 through the rubber septum using the hypodermic syringe and needle.

A.4.3.14 Immediately restart the carrier gas flow. The flowrate should be maintained between 200 ml/min to 400 ml/min.

NOTE One CO_2 cartridge should provide about 15 min to 20 min of flow at this rate.

A.4.3.15 Observe changes in appearance of the Dräger tube. Note and record the maximum darkened length (in units marked on the tube) before the front starts to smear. Continue flowing for a total of 15 min although the front may attain a diffuse and feathery colouration. In the high-range tube an orange colour (caused by SO_2) may

appear ahead of the black front if sulfites are present in the sample. The orange SO_2 region should be ignored when recording darkened length.

For best Dräger tube accuracy, the "darkened length" should fill more than half the tube's length, therefore the filtrate "sample volume" shall be carefully selected.

A.4.3.16 A lead acetate paper disk fitted under the O-ring of Chamber 3 can be substituted for the Dräger tube in the gas train. The lead acetate paper will qualitatively indicate the presence or absence of sulfides in the sample. A dark discoloration of the paper is a positive indication of sulfides. After a positive indication, the Dräger tube should be used on a separate sample for quantitative analysis.

A.4.3.17 To clean the gas train, remove the flexible tubing and remove the top. Take Dräger tube and flowmeter out of the receptacles and plug the holes with stoppers to keep them dry. Wash out the chambers with warm water and mild detergent, using a soft brush. Use a pipe cleaner to clean the passages between the chambers. Wash, rinse and blow out the dispersion tube with a dry gas. Rinse the unit with deionized water and allow to drain dry.

A.4.4 Calculation

Using the measured “sample volume” V_s, in millilitres, the Dräger tube's maximum darkened length l and the tube factor f from Table A.1, calculate the sulfide concentration in the sample:

$$\text{Sulfide concentration, in milligrams per litre} = \frac{l \cdot f}{V_s} \qquad \text{(A.8)}$$

NOTE Darkened length in units marked on the tube.

A.5 Carbonate

A.5.1 Principle

The concentration of soluble carbonates in a drilling fluid filtrate can be determined by this method. Total soluble carbonates include CO_2 and the carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions. Drilling fluid filtrate is acidified in a Garrett gas train, converting all carbonates to CO_2, which is then evolved by bubbling an inert carrier gas through the sample. The gas train separates the gas from the liquid. The gas stream is collected in a 1 l gas bag (to allow CO_2 to mix uniformly) and subsequently drawn through a Dräger[8)] tube at a fixed flowrate. The Dräger tube responds to CO_2 by progressively staining purple along its length. A reaction between CO_2 and a hydrazine chemical causes a crystal violet indicator to turn purple. The stain length is proportional to the total carbonate concentration in the filtrate.

A.5.2 Apparatus

A.5.2.1 **Garrett gas train apparatus,** consisting of a transparent plastic gas train, an inert gas supply and pressure regulator, a floating-ball flowmeter and a Dräger tube.

Specifications of the Garrett gas train:

a) Body

1) Chamber 1:
   — Depth 90 mm (3,54 in)

8) Dräger tubes are an example of a suitable product available commercially. This information is given for convenience of users of this part of ISO 10414 and does not constitute an endorsement of ISO of this product.

— Diameter 38 mm (1,52 in)

2) Chambers 2 and 3:
— Depth 90 mm (3,54 in)
— Diameter 30 mm (1,18 in)

3) Passages between chambers:
— Diameter 2,0 mm (0,08 in)

4) Material:
— Transparent material or glass which is inert to acid, sulfides, and hydrogen sulfide gas.

b) Dispersion tube

1) Stem:
— Diameter 8,0 mm (0,315 in)
— Length approx. 150 mm (5,9 in)

2) Dispersion frit (bell-shaped, fine):
— Diameter 30 mm (1,18 in)

3) Material:
— Low coefficient of expansion, heat-resistant glass.

c) Flow meter, floating ball type preferred, capable of measuring 300 ml/min of CO_2 gas.

d) Flexible tubing, inert to hydrogen sulfide and carrier gas. Latex rubber or equivalent is preferred.

e) Fittings and rigid tubing, inert to hydrogen sulfide and acid.

f) Rubber septum.

A.5.2.2 **Carrier gas**, high purity nitrogen (N_2) bottle with low-pressure regulator (preferred), or N_2O gas cartridges

WARNING — Do not use nitrous oxide cartridges as pressure sources for high temperature/high pressure (HTHP) filtration. Under high temperature and pressure, nitrous oxide can detonate in the presence of grease, oil or carbonaceous materials. Use nitrous oxide cartridges only for Garrett gas train carbonate analysis.

A.5.2.3 **Dräger CO_2 analysis tube**, marked CO_2 100/a.

A.5.2.4 **Dräger 1 litre Alcotest gas bag**, No. 7626425, or equivalent.

A.5.2.5 **Dräger Multigas Detector hand-operated vacuum pump**, Model 31, or equivalent.

A.5.2.6 **Stopcock,** 2-way bore, 8 mm (0,315 in) glass with PTFE plug.

A.5.2.7 **Sulfuric acid** (CAS No. 7664-93-9): approximately 2,5 mol/l ACS reagent grade.

A.5.2.8 **Defoamer** in a dropper bottle.

A.5.2.9 **Hypodermic syringes**, 1,0 ml, 5 ml and 10 ml (for acid) and 10 ml (for sample).

A.5.2.10 **Hypodermic needles**, 38 mm (1,5 in) 21-gauge needles.

NOTE Nitrogen is preferred over N_2O as the carrier gas. Because N_2O cools upon expansion and chills the diaphragm in the regulator, prolonged N_2O flow will cause the regulator to perform erratically.

A.5.3 Procedure

A.5.3.1 Ensure that the gas train is clean, dry and on a level surface, with the top removed.

If CO_2 has been used as the carrier gas in the previous test (i.e. sulfide analysis), the regulator, tubing and dispersion tube should be purged with carrier gas at this time.

A.5.3.2 Add 20 ml deionized water to Chamber 1.

A.5.3.3 Add 5 drops of defoamer to Chamber 1.

A.5.3.4 Install the top on the gas train and hand-tighten evenly to seal all O-rings.

A.5.3.5 Adjust the dispersion tube to approximately 5 mm (0,25 in) off bottom.

A.5.3.6 With regulator backed off, connect carrier gas supply to glass dispersion tube of Chamber 1 using flexible tubing.

A.5.3.7 Flow carrier gas through train for 1 min to purge air from the system. Check for leaks in gas train unit.

A.5.3.8 Fully collapse the gas bag and simultaneously check the system for leaks. To do this, connect the gas bag and stopcock to the hand pump. (Use a discarded Dräger tube as connection and start with the bag essentially empty.) Fully depress and release the hand pump. When the bag is completely empty and free of leaks, the pump will remain depressed for several minutes. If leakage is detected, check the pump and all connections. To check the pump alone, insert a sealed Dräger tube into the pump opening and depress bellows. It will remain depressed if pump does not leak.

A.5.3.9 With the bag fully collapsed, install flexible tubing from the stopcock and bag onto the outlet of Chamber 3.

A.5.3.10 Inject a measured volume of solids-free filtrate into Chamber 1 through the septum with a hypodermic syringe and needle. See Table A.2.

A.5.3.11 Slowly inject 10 ml sulfuric acid solution into Chamber 1 through the rubber septum using a clean syringe and needle. Gently shake the gas train to mix acid with sample in Chamber 1.

Table A.2 — Dräger tube, or equivalent, identification, sample volumes and tube factors to be used for various carbonate ranges

Carbonate range mg/l	Sample volume ml	Dräger tube identification (see tube body)	Tube factor [a] f (used in calculation)
25 to 750	10,0	CO_2 100/a	2,5
50 to 1 500	5,0	CO_2 100/a	2,5
100 to 3 000	2,5	CO_2 100/a	2,5
250 to 7 500	10,0	CO_2 100/a	2,5

[a] If other tubes are used, the tube factors in Table A.2 shall be changed according to manufacturer's specification.

A.5.3.12 Open the stopcock on the gas bag. Restart gas flow and allow gas bag to fill steadily during a 10 min interval. When bag is firm to the touch (do not burst it) shut off flow and close the stopcock. Immediately proceed to next step.

A.5.3.13 Break the tip off each end of the Dräger tube.

A.5.3.14 Remove the tubing from Chamber 3 outlet and reinstall it onto the upstream end of the Dräger tube. (Observe that an arrow on the tube indicates gas flow direction.) Attach Dräger hand pump to downstream end of Dräger tube.

A.5.3.15 Open the stopcock on the bag. With steady hand-pressure, fully depress the hand pump. Release pump so that gas flows out of the bag and through the Dräger tube. Operate the pump and count the strokes until the bag is empty. (Ten strokes should empty the bag. More than ten strokes indicates leakage has occurred and test results will not be correct.)

A.5.3.16 Observe a purple stain on the Dräger tube if CO_2 is present in the gas bag, and record the stain length in units marked on the Dräger tube. (Include the faint blue tinge in the purple stain length reading.)

For best Dräger tube accuracy, the "stain length" should fill more than half the tube length, therefore "sample volume" shall be carefully selected.

A.5.3.17 To clean the gas train, remove the flexible tubing and remove the top. Wash out the chambers with warm water and mild detergent, using a brush. Use a pipe cleaner to clean the passages between chambers. Wash, rinse and then blow out the dispersion tube with dry gas. Rinse the unit with deionized water and allow to drain dry. Periodically replace the disposable gas bag to avoid leaks and contamination in the bag. (Bag replacement is suggested after 10 analyses).

A.5.4 Calculation

Using the measured "sample volume," V_s in millimetres, the Dräger tube "stain length" l_{st} and "tube factor" f of 2,5 (see Table A.2) calculate total soluble carbonate (CO_2 + CO_3^{2-} + HCO_3^-) concentration in the filtrate sample using equation (A.9):

$$\text{Carbonate concentration, in milligrams per litre} = \frac{l_{st} \cdot f}{V_s} \qquad \text{(A.9)}$$

A.6 Potassium (concentration above 5 000 mg/l)

A.6.1 Principle

Potassium ion is used in drilling fluids to aid in the stabilization of shales and to control swelling clays. The accurate determination of the potassium ion content is necessary to control the properties of the drilling fluid. This procedure is used to measure the potassium ion content in drilling fluid filtrates at levels above 5 000 mg/l (1,75 lb/bbl). Potassium is precipitated in a centrifuge tube as the perchlorate salt, and the volume of precipitate is measured. The potassium ion content is read from a prepared standard curve.

A.6.2 Reagents and apparatus

A.6.2.1 **Sodium perchlorate** ($NaClO_4$; CAS No. 7601-89-0) solution, 150,0 g/100 ml distilled water.

CAUTION — Sodium and potassium perchlorates are explosive in the dry state if heated or if in contact with organic reducing agents. The perchlorates are not hazardous if kept wet. They will decompose harmlessly in water.

A.6.2.2 **Standard potassium chloride** (CAS No. 7447-40-7) solution, 14,0 g made up to 100 ml with deionized or distilled water.

A.6.2.3 **Centrifuge**, horizontal-swing rotor head (manual or electric) capable of producing approximately 1 800 r/min.

NOTE A fairly constant 1 800 r/min can be obtained with a manual centrifuge as follows. Determine the number of revolutions of the rotor per each turn of the crank; i.e. move the crank very slowly and count the number of revolutions of the rotor head during one turn of the crank. For example, 15 revolutions of the rotor per one turn of the crank. Calculate the number of crank turns required to obtain 1 800 revolutions of the rotor head. In the example, to obtain 1 800 revolutions of the head would require 120 turns of the crank (1 800/15). Thus the crank must be turned 120 times in one minute to obtain the rate of 1 800 r/min. At this rate, in 5 s the handle must be turned 10 times [i.e. (120/60) × (5)]. By counting the crank turns in 5 s and adjusting the rate to obtain the required number of turns, a constant 1 800 r/min should be obtained in 15 s to 20 s. The interval used to adjust to the 1 800 r/min should be included in the centrifuge time of the sample.

A.6.2.4 **Clinical centrifuge tube,** 10 ml Kolmer type.

A.6.2.5 **Graduated volumetric pipettes** (TD), 1 ml, 2 ml and 5 ml.

A.6.2.6 **Hypodermic syringe** or **serological** (graduated) **pipette** (TD), 10 ml.

A.6.2.7 **Distilled or deionized water.**

A.6.3 Preparation of standard calibration curve

A.6.3.1 A standard calibration curve is required for each type of centrifuge. A minimum of three points [10 kg/m^3, 30 kg/m^3 and 50 kg/m^3 (or 3,5 lb/bbl, 10,5 lb/bbl and 17,5 lb/bbl) KCl] is required to obtain an accurate graph.

A.6.3.2 Samples can be prepared by using the standard potassium chloride solution [0,5 ml of standard potassium chloride solution is equivalent to 10 kg/m^3 (3,5 lb/bbl) KCl]. To obtain KCl concentrations of 10 kg/m^3 (3,5 lb/bbl), 30 kg/m^3 (10,5 lb/bbl) and 50 kg/m^3 (17,5 lb/bbl) KCl, use 0,5 ml, 1,5 ml and 2,5 ml of the standard potassium chloride solution, respectively.

A.6.3.3 Dilute each sample to the 7,0 ml mark with distilled water and agitate.

A.6.3.4 Add 3,0 ml of standard sodium perchlorate solution (but do not agitate).

A.6.3.5 Centrifuge at a constant speed (approximately 1 800 r/min) for 1 min and read the precipitate volume immediately.

Counterbalance the centrifuge tube with another tube and liquid of the same mass.

A.6.3.6 Clean the centrifuge tube immediately after use to facilitate ease of cleaning.

A.6.3.7 Plot the volume of precipitate (millilitres) versus potassium chloride content in kilograms per cubic metre (or pounds per barrel) on rectangular graph paper as shown in Figure A.1.

A.6.4 Test procedure

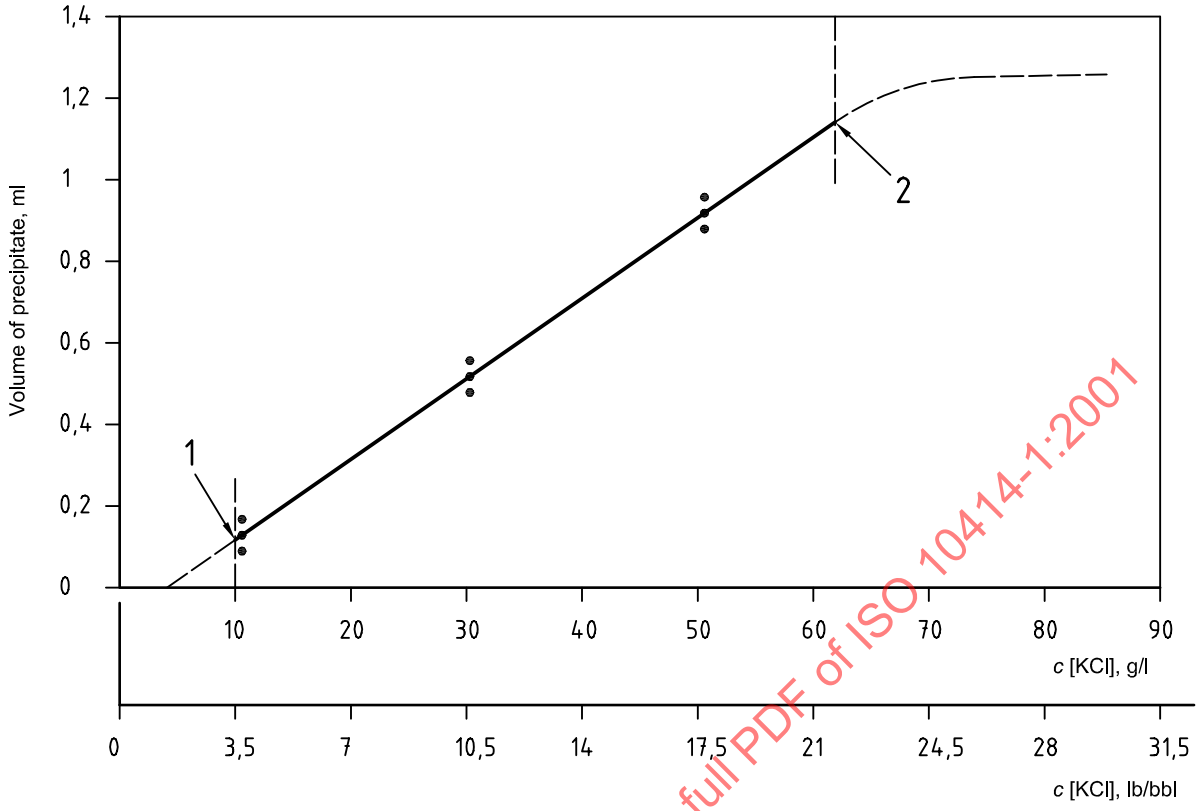
A.6.4.1 Measure the appropriate volume of filtrate into the centrifuge tube (see Table A.3 for range).

A.6.4.2 If less than 7,0 ml filtrate volume is used, dilute to 7,0 ml with distilled water and agitate.

A.6.4.3 Add 3,0 ml of standard sodium perchlorate solution, but do not agitate. If potassium is present, precipitation occurs at once.

A.6.4.4 Centrifuge at constant speed (approximately 1 800 r/min) for 1 min. Read the precipitate volume immediately and record.

Counterbalance the centrifuge tube with another tube and liquid of the same mass.



Key

1 Do not use this procedure for concentrations less than 10 g/l (3,5 lb/bbl).

2 Refer to Table A.3 beyond this point

Figure A.1 — Example of plotted calibration curve for potassium chloride (do not use for calibration)

Table A.3 — Filtrate volumes to be used at various KCl concentrations

KCl concentration range		K^+ in filtrate	Filtrate volume to use
kg/m^3	(lb/bbl)	mg/l	ml
10 to 50	3,5 to 17,5	5 250 to 26 250	7,0
50 to 100	17,5 to 35	26 250 to 52 500	3,5
100 to 200	35 to 70	52 500 to 105 000	2,0
over 200	over 70	over 105 000	1,0

A.6.4.5 Add 2 drops to 3 drops of the sodium perchlorate solution to the tube. If precipitate still forms, the total amount of potassium was not measured. See Table A.3 and use the next smaller filtrate volume. Repeat A.6.4.1 through A.6.4.4.

A.6.4.6 Determine the potassium chloride concentration by comparing the precipitate volume measured with the standard calibration curve as prepared in A.6.3. Report the potassium concentration $c(K^+)$ as kilograms per cubic metre (or pounds per barrel) KCl. The potassium concentration may also be reported as milligrams per litre potassium ion. If the filtrate potassium chloride concentration c(KCl) from the standard calibration curve exceeds a 50 kg/m^3 (or 18 lb/bbl) reading, accuracy of the results is reduced. For more accurate results, use the next smaller filtrate volume as noted in Table A.3, and repeat A.6.4.1 through A.6.4.4.

A.6.5 Calculation

c[KCl], kilograms per cubic metre = (7/V_f) × (x-axis value from standard curve, milligrams per litre) (A.10)

c[KCl], pounds per barrel = (7/V_f) × (x-axis value from standard curve, pounds per barrel) (A.11)

$c[K^+]$ = 525 × (c[KCl], kilograms per cubic metre) (A.12)

$c[K^+]^+$ = 1 500 ×(c[KCl], pounds per barrel) (A.13)

where

c[KCl] is the potassium chloride concentration;

V_f is the volume of filtrate used, in millilitres;

$c[K^+]$ is the potassium ion concentration, in milligrams per litre.

A.7 Potassium (concentration below 5 000 mg/l)

A.7.1 Principle

This procedure is used to measure potassium ion content in drilling fluid filtrates at levels below 5 000 mg/l. Potassium ion is precipitated as the tetraphenylborate salt by adding an excess of standard sodium tetraphenylborate (STPB) solution. The unreacted STPB is then determined by titration with a quaternary ammonium salt (QAS), hexadecyltrimethyl ammonium bromide, using bromophenol blue as an indicator. The endpoint is a colour change from purple-blue to light blue. The potassium ion concentration $c[K^+]$ in the sample is calculated by subtracting the amount of unreacted STPB from the amount of STPB originally added to the sample.

A.7.2 Reagents and apparatus

A.7.2.1 **Standard sodium tetraphenylborate** (STPB) (CAS No. 143-66-8) solution: 8,754 g in 800 ml deionized water. Add 10 g to 12 g aluminum hydroxide, stir 10 min and filter. Add 2 ml 20 % NaOH solution to the filtrate and dilute to 1 l with deionized water.

A.7.2.2 **Quaternary ammonium salt** (QAS) (CAS No. 57-09-0) solution, 1,165 g hexadecyltrimethyl ammonium bromide/500 ml deionized water.

A.7.2.3 **Sodium hydroxide** (CAS No. 1310-73-2) solution, 20 % mass fraction in deionized water.

A.7.2.4 **Bromophenol blue** (CAS No. 115-39-9) **indicator**, 0,04 g tetrabromophenolsulfonphthalein/3 ml 0,1 mol/l NaOH. Dilute to 100 ml with deionized water.

A.7.2.5 **Deionized or distilled water**.

A.7.2.6 **Graduated pipettes** (TD), 2 ml graduated in 0,01 ml subdivisions, 5 ml and 10 ml.

A.7.2.7 **Graduated cylinders**, capacity 25 ml (TD) and 100 ml (TC).

A.7.2.8 **Beakers**, capacity 250 ml.

A.7.2.9 **Funnel**.

A.7.2.10 **Filter paper**.

A.7.3 Procedure

A.7.3.1 Place the proper amount of filtrate into a 100 ml graduated cylinder, using Table A.4 to determine sample size. Be sure to use a pipette to measure the amount of filtrate.

Table A.4 — Filtrate volumes to be used at various KCl concentrations

c[KCl] range		c[K^+] in filtrate	Filtrate volume to use
kg/m^3	(lb/bbl)	mg/l	ml
0,5 to 3,0	0,175 to 1,05	262,5 to 1 575	10,0
3,0 to 6,0	1,05 to 2,1	1 575 to 3 150	5,0
6,0 to 20,0	2,1 to 7,0	3 150 to 10 500	2,0

A.7.3.2 Add 4 ml of NaOH solution (20 % mass fraction; measured with a 5 ml pipette), 25 ml of STPB solution (measured with a 25 ml graduated cylinder), and enough deionized water to bring the level of the solution to 100 ml mark.

A.7.3.3 Mix and allow to stand 10 min.

A.7.3.4 Filter into a 100 ml graduated cylinder. If the filtrate is cloudy, re-filter the solution.

A.7.3.5 Transfer 25 ml of the above filtrate (measured with a 25 ml graduated cylinder) into a 250 ml beaker.

A.7.3.6 Add 10 drops to 15 drops of bromophenol blue indicator.

A.7.3.7 Titrate with QAS solution until colour changes from purple-blue to light blue.

It is important to check the concentration of QAS solution versus the STPB solution at monthly intervals. To determine the equivalent QAS, dilute 2 ml of the STPB solution in a titration vessel with 50 ml deionized water. Add 1 ml of 20 % NaOH solution and 10 drops to 20 drops of the bromophenol blue indicator. Titrate with the QAS solution until colour changes from purple-blue to light blue.

$$\text{Ratio of QAS to STPB} = (V_{QAS})/2 \qquad \text{(A.14)}$$

where V_{QAS} is the QAS volume, in millilitres.

If the ratio is other than 4,0 ± 0,5, calculate a correction factor to be used in the calculation of c[K^+], milligrams per litre.

$$\textit{Correction factor (CF)} = 8/V_{QAS} \qquad \text{(A.15)}$$

A.7.4 Calculation

$$c[K^+] \text{ in filtrate, in milligrams per litre} = \frac{1\,000 \times (25 - V_{QAS})}{\text{mud filtrate, ml}} \quad \text{(A.16)}$$

If correction factor is necessary:

$$c[K^+] \text{ in filtrate, milligrams per litre} = 1\,000\left[\frac{25 - (CF)\,V_{QAS}}{\text{mud filtrate, ml}}\right] \quad \text{(A.17)}$$

$$c[KCl] \text{ in filtrate, in kilograms per cubic metre} = \frac{c[K^+] \text{ in filtrate, mg/l}}{525} \quad \text{(A.18)}$$

$$c[KCl] \text{ in filtrate, in pounds per barrel} = \frac{c[K^+] \text{ in filtrate, mg/l}}{1\,500} \quad \text{(A.19)}$$

Annex B
(informative)

Shear strength measurement using shearometer tube

B.1 Principle

B.1.1 Experience has shown that some drilling fluids tend to develop excessive shear strength under static conditions, especially at elevated temperatures. Excessive shear strength results in high pump pressures to "break circulation," and may therefore result in loss of circulation. High shear strength may also cause difficulties in logging, perforating and other "downhole" operations.

B.1.2 The following technique can be used to determine this tendency and to estimate the extent to which the drilling fluid will develop excessive shear strength. This shear strength measurement is normally made on a static heat-aged drilling fluid sample. Ageing temperatures are therefore selected to be near the estimated bottom hole temperature of the well. Ageing cells or vessels meeting the pressure and temperature requirements for the test are required.

B.2 Apparatus

B.2.1 Stainless steel shearometer tube.

Length	89 mm (3,5 in)
Outside diameter	36 mm (1,4 in)
Wall thickness	0,2 mm (0,008 in)

NOTE A slight outside taper on the bottom of the shear tube has been found to improve reproducibility of the test results.

B.2.2 **Platform** for weights.

B.2.3 **Set of weights,** in gram increments.

B.2.4 **Ruler,** graduated in millimetres (inches).

B.3 Procedure

B.3.1 The shear tube and platform are placed and balanced carefully on the surface of the aged sample cooled to room temperature. It may be necessary to shift the weights on the platform to assure the tube's initial penetration into the drilling fluid is vertical. If a crust develops on the heat-aged sample, this crust should be gently broken before placing the shear tube in place for the test.

B.3.2 Sufficient weights are placed carefully on the platform to start the downward movement of the shear tube. Unless too much mass is added, the tube will stop its downward travel at the point where the shear strength of the aged drilling fluid against the surface of the tube is sufficient to support the applied mass. It is desirable to submerge at least one-half the length of the tube.

B.3.3 Record the total mass in grams which includes the platform and weights. Measure the portion of the tube submerged in the fluid, in centimetres. The length of the tube submerged can be most accurately determined by measuring the length of the non-submerged portion while the tube is at its maximum penetration depth. A small

ruler held at the drilling fluid surface and alongside the tube will facilitate this measurement. The length of the tube minus the exposed length equals the submerged portion.

B.4 Calculation

$$\text{Shear strength } (\gamma), \text{ Pa} = \frac{4{,}40 \times (m_{st} + m_{tot})}{l} - 1{,}02\rho \quad \text{(B.1)}$$

$$\text{Shear strength } (\gamma), \text{ lb/100 ft}^2 = 2{,}083 \times (\gamma, \text{ in Pa}) \quad \text{(B.2)}$$

where

m_{st} is the mass of shear tube, in grams;

m_{tot} is the total shear mass, in grams (sum of platform and weights);

l is the submerged length of shear tube, in centimetres;

ρ is the drilling fluid density, in grams per cubic centimetre.

Annex C
(informative)

Resistivity

C.1 Principle

Control of the resistivity of a drilling fluid and drilling fluid filtrate may be desirable to better evaluate formation characteristics from electric logs.

C.2 Apparatus

C.2.1 **Direct-reading resistivity meter**, or similar resistivity meter.

Follow manufacturer's instructions for current source, calibration, measurement and calculations.

C.2.2 **Calibrated resistivity cell.**

C.2.3 **Thermometer**, reading 0 °C to 105 °C (32 °F to 220 °F).

C.2.4 **Bottle brush**, suitable for size and type of cell.

C.2.5 **Laboratory detergent solution**, appropriate for cleaning metal or plastic surfaces.

C.3 Procedure

C.3.1 Fill the clean, dry resistivity cell with freshly stirred drilling fluid or drilling fluid filtrate. No air or gas should be entrained in the sample.

C.3.2 Connect cell to meter.

C.3.3 Measure the resistivity in ohm metres (direct-reading) or resistance in ohms (not direct-reading). Meter or manufacturer's instructions will indicate type of reading.

C.3.4 Measure the sample temperature to the nearest 0,5 °C (1 °F).

C.3.5 Clean the cell. Scrub with brush and detergent if necessary. Rinse with distilled water and allow to dry.

C.4 Calculation

C.4.1 Report the drilling fluid resistivity (ρ_m) or filtrate resistivity (ρ_{mf}) in ohm metres, to the nearest 0,01 Ω·m.

C.4.2 Report the sample temperature in degrees Celsius (Fahrenheit).

C.4.3 If reading is in ohms, convert to ohm metres by:

$$\rho,\ \Omega\cdot m = (\rho,\ \Omega) \times (\text{cell constant, } m^2/m) \qquad \text{(C.1)}$$

Annex D
(informative)

Removal of air or gas prior to testing

D.1 Principle

The majority of drilling fluids require no special equipment to remove entrained air or gas prior to testing. Usually, gentle agitation together with a few drops of an appropriate defoamer are all that is necessary. Stirring with a spatula or pouring back and forth is sufficient in most cases. When a drilling fluid is encountered that retains air or gas after the preceding steps have been taken, the following procedure can be followed to deaerate the drilling fluid.

NOTE If drilling fluid density is the only property desired, the pressurized fluid density balance described in clause 5 may be used.

D.2 Apparatus

D.2.1 **Device** which can be evacuated.

D.2.2 Commercial liquid drilling fluid **defoamer**.

D.3 Procedure

D.3.1 Fill clean, dry reservoir about one-half full with the air-cut drilling fluid.

D.3.2 Add several drops of defoamer to the drilling fluid surface.

D.3.3 Insert stirrer and cap; cover with gasketed lid.

D.3.4 Affix vacuum line from the pump to the instrument to hold about 83 kPa (620 mmHg) vacuum.

D.3.5 Increase the vacuum to 10 kPa to 16 kPa (75 mmHg to 120 mmHg) and proceed according to the manufacturer's instructions.

D.3.6 When drilling fluid has been deaerated, partially relieve vacuum to about 50 kPa to 65 kPa (375 mmHg to 490 mmHg) vacuum and observe drilling fluid for air bubbles.

D.3.7 If deaeration is not sufficient, repeat D.3.4 to D.3.6 until air is removed.

D.3.8 With cylinder on end, relieve vacuum completely and remove drilling fluid sample for testing.

Annex E
(informative)

Drill pipe corrosion ring coupon

E.1 Principle

E.1.1 The placement of corrosion test rings in the drill string is one of the more common techniques used to evaluate the corrosiveness of drilling fluid environments on the drill string and other steel equipment. Removal and examination of these rings after a period of exposure downhole can be highly informative as to the corrosiveness of the drilling fluid as well as to the type of corrosion encountered. An examination of scales and pits on the exposed rings gives clues as to the cause of the corrosion, thus aiding in choosing proper remedial action.

E.1.2 The ring technique is specifically designed for detection of the type of corrosion characterized by metal loss, whether it be localized pitting or generalized attack. The test ring is not designed to give information relating to hydrogen embrittlement, stress-corrosion cracking or other forms of fracture formation, except in the manner in which pitting may relate to these failures.

E.2 Reagents and apparatus

E.2.1 **Hydrochloric acid**, inhibited (CAS No. 7647-01-0): mass fraction of 15 % in distilled water.

E.2.2 **Acetone**, anhydrous (CAS No. 67-64-1).

E.2.3 **Methanol** (CAS No. 67-56-1).

E.2.4 **Petroleum ether** (CAS No. 8002-05-9).

E.2.5 **Deionized or distilled water**.

E.2.6 **Detergent solution**.

E.2.7 **Ring**.

a) Ring construction:

The ring-type drill string corrosion coupon, or corrosion ring, should be machined to fit in the tool box recess at the end of the pin, and should have a bore the same as that of the tool joint to minimize turbulence.

b) Ring composition:

To avoid galvanic corrosion, the ring should be made from steel identical to that of the tool joint in which it is placed. Such a requirement is impractical and use of a steel that is similar in chemical composition such as AISI 4130 is recommended. The grade of steel used should be identified on the report form. The rings are normally cut from tubes that have not been quenched and tempered. The similarity in composition of the 4130 steel and the tool joint should be adequate to minimize galvanic effects and provide useful data.

c) Ring marking:

The rings should be stencilled with a serial number for permanent identification.

d) Ring preparation:

The rings should be scrubbed with a stiff fibre-bristle brush and detergent solution, rinsed with clean water and with anhydrous acetone or methanol. Allow to dry, weigh to nearest milligram, and record this mass on the report form. Store the ring in a dry container, such as a desiccator, to prevent corrosion. The corrosion rings should be shipped to the field in sealed envelopes or wrappers to minimize atmospheric corrosion.

E.2.8 **Ultrasonic bath** (preferred) or fibre-bristle brush.

E.3 Procedure

E.3.1 Drill pipe corrosion rings should be kept in the drill string for a minimum of 40 h (a normal time for exposure is 100 h). Exposure periods of less than 40 h should not be used because initial corrosion rates may be unusually high and can give misleading data. The ring is usually placed in the tool joint at the top of the first stand above the drill collars and can be left in the drill string for more than one bit run. An additional ring can be placed in the kelly saver sub to monitor corrosion at that point. Care should be taken to ensure that the box recess is clean to prevent interference with proper make-up of the joint and to avoid damage to the ring. In some instances specially manufactured subs have been used for the ring placement in the string. During installation, the ring should be handled with clean, dry gloves.

E.3.2 The drill pipe corrosion coupon form should be filled out completely. Each form should have a space for ring material, drilling fluid properties, type of corrosion, location of ring in the drill string, initial mass, time, depth in, depth out, ring number, colour of scale and any other information of significance in the specific test. The form may be printed on a mailing envelope for the ring or on a separate form to be enclosed with the ring.

E.3.3 The drilling fluid residue should be removed from the coupon by wiping with a cloth when the ring is pulled from the drill string. The ring should be examined for severity of corrosion or mechanical damage. If severe corrosion is evident, the cause of the corrosion should be determined promptly so remedial action can be taken. Following visual observation, place the coupon in the original envelope or wrapper containing vapour-phase corrosion inhibitor for return to the laboratory.

E.3.4 Before proceeding with a quantitative evaluation of corrosion of the ring, the ring should be rinsed with suitable solvent, such as acetone or petroleum ether, to remove the oil applied to the ring on location. Prior to cleaning for weighing, a spot test should be made for corrosion by-products and mineral scale. For example, the surface can be examined qualitatively for sulfides by the inhibited acid test. The rings should be cleaned with a detergent solution and a stiff fibre-bristle brush. It may be necessary to dip the ring for 5 s to 10 s in inhibited 10 % to 15 % hydrochloric acid solution one or more times to remove corrosion products. The ring should be scrubbed with detergent solution after each acid dip. Rinse thoroughly with clean water and then with anhydrous acetone or methanol. Allow to dry prior to weighing. Very abrasive materials or strong, uninhibited acids should not be used. An ultrasonic bath can be useful in cleaning the rings.

NOTE For the inhibited 10 % to 15 % hydrochloric acid, several inhibitive additives may be used to prevent further corrosion of the ring after cleaning with acid. These include chemicals of the classes propargyls, acetylenics, pyridines and amines. Other appropriate chemicals may be suggested by the manufacturer of the corrosion rings.

E.3.5 After the pre-weighed drill pipe corrosion coupon has been properly cleaned and the corrosion film and type of attack noted, the ring should be re-weighed to the nearest milligram and the mass loss determined. If significant loss of metal due to mechanical damage is evident, it should be noted and taken into consideration in evaluation of the ring. The corrosion rate may be reported as kg/m^2·year or mm/year. Formulas for calculating for corrosion rate are given in clause E.5.

E.4 Comments on visual examination

E.4.1 If visual corrosion is evident, it is normally detectable as pitting corrosion. Uniform attack or general corrosion can best be determined by a mass loss measurement. Mechanical damage to the ring is most often evidenced by cuts or dents on the outer surfaces of the ring. In some cases, the ring exhibits a series of dents and worn spots, indicating considerable movement of the ring in the box recess.