CHAPTER 3

Testing

Water-Mud Testing 3.3

Water-Mud Testing

The API has recommended standard methods of conducting field and laboratory tests for drilling fluids and detailed procedures may be found in the API publication, "Recommended Practice: Standard Procedure for Field Testing Water-Based (Oil-Based) Drilling Fluids," API RP 13B-1, 13B-2 and supplements (also see 13I for Laboratory Testing Drilling Fluids, 13J for Testing Heavy Brines and supplements).

Section 1. Density of Fluid (Mud Weight)

Instruments

The density (commonly referred to as mud weight) is measured with a mud balance of sufficient accuracy to measure within 0.1 lb/gal (0.5 lb/ft^3 or 5 psi/1,000 ft of depth). For all practical purposes, density means weight per unit volume and is measured by weighing the mud. The weight of mud may be expressed as a hydrostatic pressure gradient in lb/in.^{2} per 1,000 ft of vertical depth (psi/1,000 ft), as a density in lb/gal, lb/ft^3 or Specific Gravity (SG) (see Table 1).

$$SG = \frac{\text{lb/gal}}{8.345} \text{ or } \frac{\text{lb/ft}^3}{62.3} \text{ or } \frac{\text{g}}{\text{cm}^3}$$

Table 1: Conversion table for density units.

MUD BALANCE

Description

The mud balance (see Figure 1) consists principally of a base on which rests a graduated arm with cup, lid, knife edge, level vial, rider and counterweight. The constant volume cup is affixed to one end of the graduated arm, which has a counterweight at the other end. The cup and arm oscillate in a plane perpendicular to the horizontal knife edge, which rests on the support, and are balanced by moving the rider along the arm.

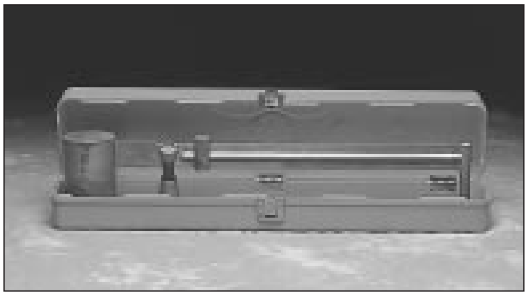


Figure 1: M-I mud balance.

Calibration

1. Remove the lid from the cup and completely fill the cup with pure or distilled water.
2. Replace the lid and wipe dry.
3. Replace the balance arm on the base, with the knife edge resting on the fulcrum.
4. The level-bubble should be centered when the rider is set on 8.33 lb/gal. If not, adjust using the calibration screw in the end of the balance arm. Some balances do not have calibration screws and must have lead shot added or taken out through the calibration cap.

Procedure

1. Remove the lid from the cup, and completely fill the cup with the mud to be tested.
2. Replace the lid and rotate until firmly seated, making sure some mud is expelled through the hole in the lid.
3. Wash the mud from the outside of the cup, and dry it.

4. Place the balance arm on the base, with the knife edge resting on the fulcrum.
5. Move the rider until the graduated arm is level, as indicated by the level vial on the beam.
6. At the edge of the rider closest to the cup, read the density or weight of the mud.
7. Report the result to the nearest scale division, either in lb/gal, lb/ft^3, psi/1,000 ft of depth or Specific Gravity (SG).
8. For balances not showing the desired scale, the equations shown in Table 1 may be used.

Mud gradient:

$$\text{psi/ft} = 0.052 \times \text{lb/gal} = 0.4333 \times \text{SG} = 0.00695 \times \text{lb/ft}^3$$

$$\text{kg/cm}^2\text{/m} = \frac{\text{SG}}{10}$$

$$\text{SG at } 60°\text{F } (15.6°\text{C}) = \frac{141.5}{131.5 + °\text{API}}$$

Where:

°API = American Petroleum Institute gravity

Section 2. Viscosity

Instruments

The Marsh funnel is used for routine field measurement of the viscosity of drilling mud. The Fann V-G meter is used to supplement the information obtained from the Marsh funnel, particularly with respect to the gel characteristics of the mud. The V-G meter is capable of giving the apparent viscosity, plastic viscosity, yield point and gel strengths (initial and timed).

A) MARSH FUNNEL

Description

The Marsh funnel (see Figure 2) is 6 in. in diameter at the top and 12 in. long. At the bottom, a smooth-bore tube 2 in. long having an inside diameter of 3⁄16 in. is attached in such a way that there is no constriction at the joint. A wire screen having 1⁄16-in. openings, covering one-half of the funnel, is fixed at a level of ¾ in. below the top of the funnel.

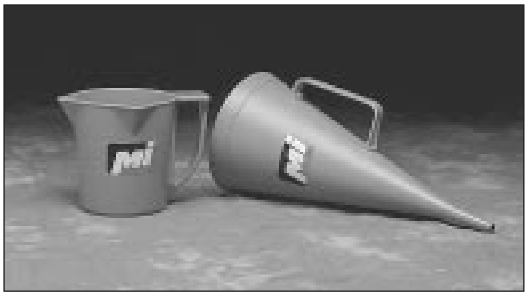


Figure 2: Marsh funnel.

Calibration

Fill the funnel to the bottom of the screen (1,500 ml) with freshwater at 70±5°F. Time of outflow of 1 qt (946 ml) should be 26 sec ±0.5 sec.

Procedure

1. With the funnel in an upright position, cover the orifice with a finger and pour the freshly collected mud sample through the screen into a clean funnel until the fluid level reaches the bottom of the screen (1,500 ml).

2. Immediately remove the finger from the outlet and measure the time required for the mud to fill the receiving cup to the 1-qt mark on the cup.
3. Report the result to the nearest second as Marsh funnel viscosity. Report fluid temperature in degrees Fahrenheit or Centigrade.

B) ROTATIONAL VISCOMETER

Description

Direct-indicating viscometers are rotational types of instruments 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 RPM (rotational velocity). The rotation of the rotor sleeve in the fluid produces a torque on the bob or inner cylinder. 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 600 and 300 RPM.

Specifications: Direct-indicating viscometer

Rotor sleeve

Inside diameter	1.450 in. (36.83 mm)
Total length	3.425 in. (87.00 mm)
Scribed line	2.30 in. (58.4 mm) above the bottom of sleeve.

Two rows of ⅛-in. (3.18-mm) holes spaced 120 degrees (2.09 radians) apart, around rotor sleeve just below scribed line.

Bob

Diameter	1.358 in. (34.49 mm)
Cylinder length	1.496 in. (38.00 mm)

Bob is closed with a flat base and a tapered top.

Torsion spring constant

386 dyne-cm/degree deflection

Rotor speeds:	High speed:	600 RPM
	Low speed:	300 RPM

The following are types of viscometers used to test drilling fluids:

1. Hand-cranked instrument has speeds of 600 and 300 RPM. A knob on the hub of the speed-change lever is used to determine gel strength.
2. The 12-volt, motor driven instrument also has speeds of 600 and 300 RPM. A governor-release switch permits high shearing before measurement, and a knurled hand-wheel is used to determine gel strength.
3. The 115-volt instrument (see Figure 3) is powered by a two-speed synchronous motor to obtain speeds of 600, 300, 200, 100, 6 and 3 RPM. The 3-RPM speed is used to determine gel strength.

Figure 3: V-G meter laboratory model.

4. The variable speed 115- or 240-volt instrument is powered to obtain all speeds between 625 and 1 RPM. The 3-RPM speed is used to determine gel strength.

1) PROCEDURE FOR APPARENT VISCOSITY, PLASTIC VISCOSITY AND YIELD POINT DETERMINATION

1. Place recently agitated sample in a thermocup and adjust surface of mud to scribed line on the rotor sleeve.
2. Heat or cool the sample to 120°F (49°C). Stir slowly while adjusting the temperature.
3. Start the motor by placing the switch in the high-speed position with the gear shift all the way down. Wait for a steady indicator dial value, and record the 600 RPM reading. Change gears only when motor is running.
4. Change switch to the 300-RPM speed. Wait for a steady value and record 300-RPM reading.
5. Plastic viscosity in centipoise = 600 reading minus 300 reading (see Figure 4).
6. Yield Point in lb/100 ft^2 = 300 reading minus plastic viscosity in centipoise.
7. Apparent viscosity in centipoise = 600 reading divided by 2.

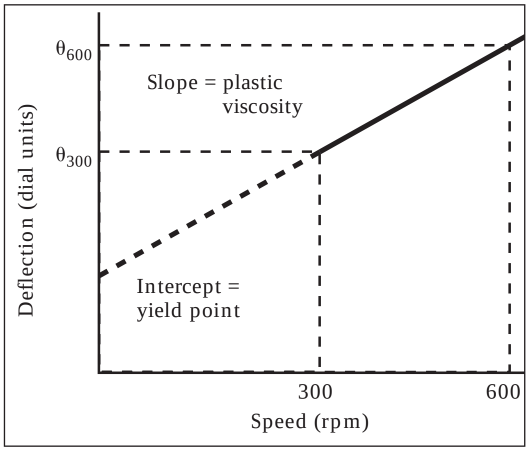


Figure 4: Typical flow curve for a drilling mud.

2) PROCEDURE FOR GEL STRENGTH DETERMINATION

1. Stir sample at 600 RPM for approximately 15 sec and slowly lift the gear assembly to the neutral position.
2. Shut motor off and wait 10 sec.
3. Flip switch to the low-speed position and record maximum deflection units in lb/100 ft^2 as initial gel. If the dial indicator does not return to zero with motor off, do not reposition.
4. Repeat 1 and 2, but allow 10 min, then place switch in the low-speed position and read maximum deflection units as the 10-min gel. Report measured temperature.

Care of Instrument

Clean instrument by running at high speed with rotor sleeve immersed in water or other solvent. Remove rotor sleeve by twisting slightly to release lock pin. Wipe bob and other parts thoroughly with clean, dry cloth or paper towel.

CAUTION: The bob is hollow and can be removed for cleaning. Moisture will occasionally collect within the bob and should be dried out with a pipe cleaner. Immersion of the hollow bob in extremely hot mud (>200°F) could result in a very dangerous explosion.

NOTE: Never immerse meter in water.

Section 3. Filtration

Description

The filtration or wall-building property of a mud is determined by means of a filter press. The test consists of determining the rate at which fluid is forced through the filter paper. The test is run under specified conditions of time, temperature and pressure. The thickness of the solid filter cake deposited is measured after the test.

The filter press being used should meet specifications as designated in the API Recommended Practice and conducted in the manner suggested. The API fluid loss is conducted at surface temperature at 100 psi pressure, and is recorded as the number of milliliters lost in 30 min.

Instruments

This instrument (see Figure 5) consists of a mud cell assembly, pressure regulator and gauge mounted on the top of the carrying case or the top part of the car laboratory unit. The cell is attached to the regulator by means of a coupling adapter by simply inserting the male cell coupling into the female filter press coupling and turning clockwise ¼ turn. Some cells do not have this locking device, and are just inserted into the proper coupling. The cell is closed at the bottom with a lid fitted with a screen (or grid), by placing the lid firmly against the filter paper and turning to the right until hand tight. This forces the sheet of filter paper against the O-ring previously fitted in the base of the cell. Pressure is supplied by a small cartridge of carbon dioxide gas. A bleed-off valve is provided to release the pressure prior to uncoupling the cell. Do not use N_2O, nitrous oxide (Whippets).

Figure 5: An example of an API filter press.

A) API FLUID LOSS

Procedure

1. Have air or gas pressure of 100 psi available.
2. Remove the lid from the bottom of the clean and dry cell. Place the O-ring in an undamaged groove, then invert to fill. Any mechanical damage could prevent it from sealing. Seal the inlet with a finger.
3. Fill the cell with mud to within ¼ inch of O-ring groove. Place filter paper (Whatman No. 50 or equivalent) on top of O-ring. Place the lid on the filter paper with the flanges of the lid between the flanges of the cell, and turn clockwise until hand tight. Turn the cell over and insert the male cell coupling into the female filter press coupling and turn either direction to engage.
4. Place a suitable graduated cylinder under the filtrate opening to receive the filtrate.

5. Open the inlet valve applying pressure to the cell. (A rapid fluctuation downward of the needle can be seen as pressure fills the cell.)
6. The normal API test period is 30 min. At the end of the test, close the valve. Pressure will be shut off at the source, and the pressure will bleed off automatically. Remove the cell.
7. Report the fluid loss in milliliters unless otherwise specified.
8. Disassemble the cell, discard the mud and use extreme care to save filter paper with a minimum of disturbance of the cake. Wash the cake gently to remove excess mud. Measure the thickness of the filter cake and report in 32nds of an inch.

B) HIGH-TEMPERATURE, HIGH-PRESSURE (HTHP) FILTRATION

MB style (API #II) HTHP filter press

Description

The instrument (see Figures 6 and 7) consists of a heating jacket with thermostat, cell plate assembly, primary pressure assembly and back-pressure receiver. The capacity of the mud cell is 160 ml with a filter area of 3.5 in.^{2}. Filtrate receiver holds 15 ml, and up to 100 psi backpressure can use a glass tube. If a higher back pressure is to be used, a stainless-steel tube should replace the glass.

A routine test can be conducted at 300°F and 500 psi differential pressure. High-temperature fluid loss is recorded as double the number of milliliters lost in 30 min.

Procedure

1. Plug heating jacket cord into proper power source and allow instrument to preheat. Place thermometer in well in heating jacket and adjust thermostat to obtain 10°F above desired test temperature.
2. Close the inlet valve on the cell and invert the cell.

Figure 6: HTHP filter press (disassembled).

3. Take the mud from the flow line and fill to within ½ in. of the O-ring groove to allow for expansion.
4. Place one circle of filter paper in groove and place the O-ring on top of paper. Use Whatman No. 50 paper or equivalent.
5. Place the cell plate assembly over the filter paper and align the safety locking lugs.
6. Evenly tighten cap screws finger tight and close the discharge valve.
7. With cell plate assembly down, place cell in heating jacket with all valves closed. Transfer the thermometer to the cell's thermometer well.
8. Place CO_2 cartridge in primary pressure assembly and tighten cartridge holder until cartridge is punctured. The regulator and bleed-off valve should be closed.
9. While lock ring is lifted, slide primary pressure assembly onto the top "slide coupling" and release the lock ring.
10. Place 100 psi pressure on top valve, then open it to pressurize unit. This pressure will minimize boiling while sample is heating.
11. Always use the back-pressure receiver to prevent vaporization of the filtrate at test temperatures near boiling or higher. Place and activate a CO_2 cartridge into the back-pressure receiver assembly.

12. Slide back-pressure assembly into place with slotted lock ring.
13. Apply 100 psi pressure to the bottom pressure unit with this valve still closed.
14. After the temperature has reached the desired range (300°F), as noted by the cell thermometer, increase pressure on top cell regulator from 100 to 600 psi while maintaining 100 psi on the bottom regulator. Open bottom cell valve one turn, and start timing test.
15. Maintain 100 psi on the receiver during the test. If it rises, drain a little filtrate to maintain the 500 psi differential. Maintain temperature ±5°F.
16. After 30 min filtration, close bottom cell valve and then close top cell valve.
17. Back off both regulator T-screws and bleed pressure from both regulators.
18. Drain filtrate into graduated cylinder and read volume. Double the reading to report. Remove receiver.
19. Disconnect primary pressure assembly by lifting lock ring and slip assembly off.
    CAUTION: Cell still contains pressure.
20. Maintain cell in upright position and cool to room temperature, then bleed off cell pressure; do not blow mud through valve.

Figure 7: HTHP filter press (MB style - API #II).

21. Invert cell, loosen cap screws (use Allen-head wrench if necessary) and disassemble. Thoroughly clean and dry all parts.

API #I STYLE HTHP FILTER PRESS (HOLLOW TAPERED-TIP STEM)

The standard HTHP fluid loss test is run at a temperature of 300°F (148°C) and a differential pressure of 500 psi.

Description

1. Heating jacket mounted on a stand.
2. A sample cell rated to a working pressure of 1,000 psi (filter area of 3.5 in.^{2}).
3. Thermometer or electronic thermocouple (readings to 500°F [260°C]).
4. Top assembly regulator with the ability to regulate 1,000 psi from any pressure source used.
5. Filtrate receiver (100 ml recommended) designed to withstand a working back pressure of at least 500 psi.
6. Graduated cylinder for filtrate collection.

NOTE: Extreme caution should be used in running an HTHP test. Maintain all equipment in a safe working condition.

Testing at temperatures of 300°F (149°C) or less

1. Plug heating jacket into correct voltage for the unit. Place thermometer in the thermometer well on the outside of jacket.
2. Preheat jacket to 10°F above the test temperature and maintain if needed, by adjusting the thermostat. Check all O-rings and replace as needed.
3. Agitate the mud sample for 10 min and pour into the cell making sure the valve stem on the cell body is closed. The cell should not be filled closer than ½ in. from the top of the lip.
4. Place a piece of filter paper (Whatman No. 50 or equivalent) on top of the lip.

5. Seat lid properly, align and tighten Allen screws. Make sure that both valve stems are closed and then place the cell into the heating jacket. With a twisting motion lock the cell in the jacket. *NOTE: The cell body fits in the jacket with the end containing the filter paper on the bottom.*
6. Transfer the thermometer to the cell body thermometer well.
7. Place the pressure unit on the top valve and lock into place with a locking pin.
8. Place the bottom low-pressure receiver to the bottom valve and lock into place (see Figure 8).
9. Apply 100 psi to both pressure units and open top valve stem ¼ turn counterclockwise.
10. When the test temperature is reached, increase the pressure of the top pressure unit to 600 psi and open the bottom valve stem ¼ turn clockwise to begin filtration. The filtrate is to be collected in a graduated cylinder for a period of 30 min.
11. While testing, the test temperature should be maintained within ±5°F. Drain some filtrate when the back pressure exceeds 100 psi.
12. After 30 min close both valves and back the regulator T-screws off. Bleed the filtrate and pressure from the bottom receiver and then bleed the pressure from the top regulator. Remove top regulator and receiver. Remove the cell from the heating jacket and cool to room temperature in an upright position. *CAUTION: Cell still contains pressure.*
13. While allowing the cell to cool, measure the amount of collected filtrate and double the results. Record as milliliters of filtrate along with the test temperature.
14. After the cell has cooled, bleed the pressure carefully from the top stem opposite the filter paper. Close the valve and then open the other end carefully to bleed off any pressure.

Figure 8: HTHP filter press (API #I style) (disassembled).

Aging Temperature		**Water Vapor Pressure**		**Coefficient of Volume Expansion for Water at Saturation Pressure**	**Suggested Applied Back Pressure**	
°F	°C	kPa	psi		kPa	psi
212	100	101	14.7	1.04	689	100
250	121	207	30	1.06	689	100
300	149	462	67	1.09	689	100
350	177	931	135	1.12	1,104	160
400	205	1,703	247	1.16	1,898	275
450	232	2,917	422	1.21	3,105	450

Note: Do not exceed equipment manufacturer's recommendations for maximum temperatures, pressures and volumes.

Table 2: Vapor pressure and volume expansion of water between 212 and 450°F with suggested back pressure.

Disassemble after there is no remaining pressure, and discard mud sample. Visually observe and note the condition of the filter cake. It can be measured in 1⁄32 of an inch.

Testing at temperatures between 300 to 400°F (149 to 233°C)

The same basic procedure is used except the 500-ml cell and nitrogen pressure manifold is suggested:

1. When heating the sample, 450 psi can be placed on both pressure units. When the test begins, the top pressure is raised to 950 psi and the bottom pressure is maintained at 450 psi.
2. Temperatures over 350 to 400°F require the use of porous stainless-steel disc (Dynalloy X5 or equivalent) in place of filter paper (see API RP 13B-1 and 13B-2).
3. Time for heating sample should not exceed 1 hour.

C) FILTER-CAKE COMPRESSIBILITY

The test is run using the same procedure at 300°F (149°C), but 200 psi is applied to the cell body and 100 psi is applied to the bottom receiver. The 100 and 500 psi differential values are compared.

Section 4. Sand Content

Instruments

The sand content of mud is estimated by the use of a sand-screen set. The screen test, because of its simplicity of operation, is widely used in the field.

Figure 9: Sand content set.

SAND CONTENT SET

Description

The sand content set (see Figure 9) consists of a 2½-in. diameter sieve, 200 mesh (74 micron), a funnel to fit the sieve and a glass measuring tube marked for the volume of mud to be added in order to read the percentage of sand directly in the bottom of the tube, which is graduated from 0 to 20%.

Procedure

1. Fill the glass measuring tube to the indicated mark with mud. Add water to the next mark. Cover the mouth of the tube with the thumb and shake vigorously.
2. Pour the mixture onto the screen, add more water to the tube, shake and again pour onto the screen. Repeat until the wash water is clear. Wash the sand clean that is retained on the screen.
3. Fit the funnel down over the top of the sieve. Insert the tip of the funnel into the mouth of the glass tube. Wash the sand from the screen into the tube by means of a fine spray of water. Allow the sand to settle. From the graduations on the tube, read the percent by volume of sand.

Section 5. Liquid and Solid Content

Instruments

A mud retort with "oven" heating capability is used to determine the quantity of liquids and solids in a drilling fluid. Internal-probe heater retorts are not recommended. A sample of mud (either 10-, 20- or 50-ml retorts are available) is placed in the cup and the lid added to expel some fluid. This ensures a correct volume. It is heated until the liquid components have been vaporized. The vapors are passed through a condenser and collected in a graduated cylinder that usually is graduated in percent. The volume of liquid, oil and water, is measured directly in percent. The solids, both suspended and dissolved, are determined by subtracting from 100% or by reading the void space at the top.

Description

A) PROCEDURE: RETORT

1. Allow the mud sample to cool to room temperature.
2. Disassemble retort assembly and lubricate sample cup threads with high-temperature grease (Never-Seez®). Fill sample cup almost level full of the fluid to be tested. Put sample cup cover in place by rotating firmly, squeezing out excess fluid to obtain the exact volume — 10, 20 or 50 ml required. Clean spills from cover and threads.
3. Pack fine steel wool into the upper expansion chamber, then screw sample cup into expansion chamber. The steel wool should trap the solids boiled out. Keep assembly upright so that mud does not flow into the drain tube.
4. Insert or screw the drain tube into hole at end of condenser, seating firmly. The graduated cylinder which is calibrated to read in percent should be clipped in place on the condenser.

Figure 10: Retort.

5. Plug power cord into the correct voltage and keep power on until distillation stops, which may require 25 min depending on the characteristics of oil, water and solids content.
6. Allow the distillate to cool to room temperature.
7. Read the percentage of water, oil and solids directly from the graduate. A drop or two of aerosol solution will help define the oil-water interface, after reading the percent solids.
8. At end of the test, cool completely, then clean and dry retort assembly.
9. Run a pipe cleaner through condenser hole and retort drain tube to clean and maintain full openings. *NOTE: Do not allow drain tube to become restricted.*

Percent by volume solids analysis, weight method (calculation by weight difference using conventional retort)

1. Equipment needed:
   Mud balance.
   Conventional 20 cm^3
   (oven-type) retort.
   Analytical balance accurate
   to 0.01 g.

2. Four measurements are taken:
   - A. Mud weight.
   - B. Weight of retort (including steel wool and cup).
   - C. Weight of retort with whole mud.
   - D. Weight of retort with mud solids.

Procedure

1. Ready the retort with steel wool and sample cup. Determine the weight in grams. This is value B.
2. Disassemble retort and add mud to fill sample cup. Measurement of volume or use of lid is unnecessary as volumes are calculated in this weigh-in/out procedure. Weigh the reassembled retort. This is value C.
3. Run retort as usual collecting distillate (water and any oil).
4. Allow the retort to cool and reweigh the assembly. This is value D.

Calculation

Calculate:

1. Mud density (g/cm^3); SG_{MUD} = mud wt (lb/gal) x 0.11994.
2. Grams of mud in retort: g of mud = Value C – Value B.
3. Grams or cm^3 water distilled: Value C – Value D.

Compute volume % solids:

$$\text{Fraction of solids} = \frac{(C - B) - SG_{MUD} \times (C - D)}{C - B}$$

% solids = 100 x volume fraction solids

Example:
Four measurements from a field mud:
A) 12.70 lb/gal
B) 317.45 g
C) 348.31 g
D) 332.69 g

Thus:

$$\#1 = 12.70 \text{ lb/gal} \left[0.1194 \ \frac{\text{g/cm}^3}{\text{lb/gal}}\right] = 1.523 \text{ g/cm}^3$$

#2 = 348.31 – 317.45 = 30.86 g of mud

#3 = 348.31 – 332.69 = 15.62 g of water

$$\text{Volume fraction solids} = \frac{30.86 - 1.52 \times 15.62}{30.86} = \frac{7.12}{30.86} = 0.2307$$

% solids = 100 x 0.2307 = 23.07%

B) METHYLENE BLUE CAPACITY

Field procedure for determining cation exchange capacity

Equipment

1. Syringe, 3 ml, burette 10 ml.
2. Micropipette, 0.5-ml.
3. Erlenmeyer flask, 250-ml with rubber stopper.
4. Burette or pipette, 10-ml.
5. Graduated cylinder, 50-ml.
6. Stirring rod.
7. Hot plate.
8. Filter paper: 11 cm diameter, Whatman No. 1 or equivalent.

Reagents

1. Methylene blue solution:
   1 ml = 0.01 milliequivalents
   3.74 g USP-grade methylene blue ($C_{16}H_{18}N_3SCl \cdot 3H_2O$) per liter.
2. Hydrogen peroxide, 3% solution.
3. 5 N sulfuric acid solution.

Procedure

1. Add 2 ml of mud (or suitable volume of mud to require 2 to 10 ml of reagent) to 10 ml of water in the Erlenmeyer flask. Add 15 ml of 3% hydrogen peroxide and 0.5 ml of 5 N sulfuric acid solution and mix by swirling before heating. Boil gently for 10 min. Dilute to about 50 ml with water. *NOTE: Drilling muds frequently contain substances in addition to bentonite that absorb methylene blue. Treatment with hydrogen peroxide is intended to remove the effect of organic materials such as CMC, polyacrylates, lignosulfonates and lignites.*
2. Add methylene blue solution, 0.5 ml at a time, from the burette or pipette to the flask. After each addition, insert rubber stopper and shake contents of the flask for about 30 sec. While the solids are still suspended, remove a drop from the flask with a glass rod and place on filter paper. The endpoint of the titration is reached when the dye appears as a greenish-blue ring surrounding the dyed solids.
3. When the greenish-blue tint spreading from the spot is detected, shake the flask an additional 2 min and place another drop on the filter paper. If the greenish-blue ring is again evident, the endpoint has been reached. If the ring does not appear, continue as before until a drop taken after shaking 2 min shows the greenish-blue tint.
4. Record the ml of methylene blue solution used.
5. Methylene blue capacity of mud
   English system MBC (lb/bbl) =
   (cm^3 of methylene blue/cm^3 of mud) x 5
   Metric system MBC (kg/m^3) =
   (cm^3 of methylene blue/cm^3 of mud) x 14

C) METHYLENE BLUE CAPACITY OF SHALE

Methylene blue capacity (bentonite equiv.)

English system MBC (lb/bbl) = CEC x 5

Metric system MBC (kg/m^3) = CEC x 14

Cation exchange capacity for shales

Approximately 1 g of dried ground shale is accurately weighed and placed in a 150-ml Erlenmeyer flask and 50 ml of deionized water is added. The shale slurry is gently boiled with 0.5 ml 5 N sulfuric acid for 10 min. The slurry is allowed to cool and is titrated in 0.5 ml increments with 0.01 N methylene blue solution.

$$\text{CEC in milliequivalents/100 g shale} = \frac{\text{ml of methylene blue}}{\text{g of shale titrated}}$$

D) Flocculent efficiency test

Procedure

1. Measure 100 ml of drill water directly from rig flow line into a graduated cylinder.
2. Add 1 ml of 1%* flocculent solution to the graduated cylinder.
3. Invert the graduated cylinder slowly 3 to 4 times and set it on a flat surface.
4. Record the time (in sec) required to form the flocs and settle to the 40 cm^3 line on the graduated cylinder.
5. Repeat the procedure with each flocculent. If no flocs form, then a flocculent would not be required at that time. Repeat this test daily or every other day.
6. The flocculent with the fastest time is the correct one to use.

NOTE: To determine if flocculent is needed in clear water drilling, collect a sample of water where it returns to the suction pit and run a floc test.

**1% flocculent solutions are made by adding 1 g of the correct flocculent to 100 ml of distilled water and stirring until dissolved.*

Section 6. Hydrogen Ion Concentration (pH)

Purpose

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 effectiveness of additives are all dependent on pH, as in control of acidic and sulfide corrosion processes.

Two methods are used for measuring the pH of freshwater drilling mud: a modified colorimetric method, using plastic backed test strips (sticks); and the potentiometric method, employing the glass-electrode electronic pH meter. The plastic strip method is frequently used for field pH measurements, but is not the preferred method. It is reliable only in very simple water muds. Mud solids, dissolved salts and chemicals, and dark-colored fluids cause errors in pH plastic strip values.

A) Indicator sticks

Description

The "colorpHast pH indicator" sticks (see Figure 11) are coated with indicators of such nature that the color is dependent on the pH of the fluid in which the stick is placed. Standard color charts are supplied for comparison with the test stick, allowing estimation of pH to 0.5 pH units over the entire pH range.

Procedure

1. Place an indicator stick in the mud and allow it to remain until the color has stabilized, usually less than a minute. Rinse the stick off with deionized water but do not wipe.
2. Compare the colors of the stick with the color standard provided and estimate the pH of the mud.
3. Report the pH of the mud to the nearest 0.5 pH units.

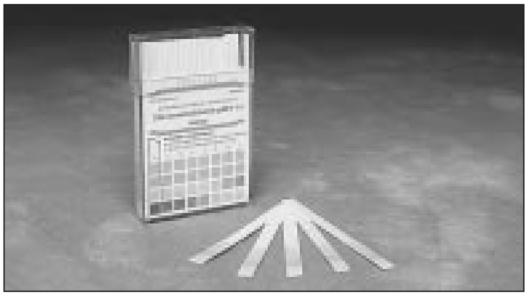


Figure 11: pH indicator sticks.

B) pH METER

Description

The recommended method for pH measurement of drilling fluid is with the glass-electrode electronic pH meter similar to the Orion model No. 201. This meter is accurate and gives reliable pH values, being essentially free of interferences. Measurements can be made quickly and easily, automatically adjusting slope and temperature compensation.

Equipment

1. pH meter (e.g. Orion 201).
2. Glass pH electrode.
3. Buffer solutions (4, 7 and 10 pH).
4. Accessory equipment:
   a. Soft-bristle brush.
   b. Mild liquid detergent.
   c. NaOH, 0.1 M, to recondition electrode.
   d. HCl, 0.1 M, to recondition electrode.
   e. Distilled or deionized water.
   f. Soft tissues to blot electrodes.
   g. Glass thermometer, 32 to 212°F.

Procedure

1. Obtain sample of fluid to be tested and allow it to reach 75±5°F (24±3°C).
2. Allow buffer solutions to also reach the same temperature as the fluid to be tested. For accurate pH measurement of the test fluid, buffer solution and reference electrode must all be at the same temperature. The pH of the buffer solution indicated on the container label is only at 75°F (24°C). If attempting to calibrate at another temperature, the actual pH of the buffer at this temperature must be used. Tables of the buffer pH values at various temperatures are available from the supplier and should be used in the calibration procedure.
3. Clean electrodes-wash with distilled water and blot dry.
4. Place probe into pH 7.0 buffer solution.
5. Turn on meter, wait 60 sec for reading to stabilize. If meter reading does not stabilize, see cleaning procedures.
6. Measure temperature of pH 7.0 buffer solution.
7. Set this temperature on “temperature” knob.
8. Set meter reading to “7.0” using “calibration” knob.
9. Rinse and blot probe dry.
10. Repeat operations in Steps 6 through 9 using pH 4.0 or 10.0 buffer. Use pH 4.0 for low pH sample or pH 10.0 for alkaline sample. Set meter to “4.0” or “10.0” respectively, using the “temperature” knob.
11. Check the meter with pH 7.0 buffer again. If it has changed, reset to “7.0” with “calibration” knob. Repeat Steps 6 through 11. If meter does not calibrate properly, recondition or replace electrodes as given in cleaning procedures.
12. If meter calibrates properly, rinse and blot dry the electrodes. Place in sample to be tested. Allow about 60 sec for reading to stabilize.
13. Record measured pH along with the temperature of sample tested. Indicate whether mud or filtrate was tested.
14. Carefully clean the electrodes in preparation for next usage. Place in storage bottle with electrode through the cap. Use pH buffer 7.0 to store the electrode. Deionized water is usually not desired to store the electrode. If it is not used for a prolonged time remove any batteries.
15. Turn meter off and close cover to protect instrument.

Figure 12: Orion or suitable pH meter.

Cleaning procedures

1. Cleaning the electrodes will be necessary periodically, especially if oil or clay particles coat the face of the glass electrode or the porous face of the reference electrode. Clean the electrodes with the soft-bristle brush and mild detergent.
2. Reconditioning electrodes may be necessary if plugging becomes severe, as indicated by slow response, drifting of readings, or if "slope" and "calibration" cannot be mutually set.
3. Recondition by soaking electrodes for 10 min in 0.1 molar HCl followed by rinsing in water and soaking for 10 min in 0.1 molar NaOH and rinsing again.
4. Check electrodes for response by performing calibration steps.
5. Only qualified individuals should attempt this next step. If no response, soak electrode for a maximum of 2 min in 10% $NH_4F \bullet HF$ solution *(CAUTION: This is a strong and toxic acid)*. Repeat calibration steps.
6. Replace electrode system if above steps fail to recondition it.

Section 7. Chemical Analysis of Water-Base Drilling Fluids

A) ALKALINITY (P_f, M_f, P_m AND LIME CONTENT)

Equipment

The following materials are required to determine the alkalinity and lime content of drilling fluids:

1. Standardized acid solution, 0.02 N (N/50); sulfuric or nitric acid *(NOTE: Standardized 0.1N (N/10) acid solution may also be used, but it is converted to the equivalent ml 0.02 N by multiplying by 5).*
2. Phenolphthalein indicator solution.
3. Methyl orange/brom cresol green indicator solution. API recommends methyl orange (yellow to pink).
4. Titration vessel, 100 to 150 ml, preferably white.
5. Graduated pipettes: one 1-ml and one 10-ml.
6. Stirring rod.
7. One 1-ml syringe.
8. Glass-electrode pH meter (suggested).

1) PROCEDURE FOR FILTRATE ALKALINITY (P_f AND M_f)

1. Measure 1-ml filtrate into the titration vessel, and add 5 ml deionized water.
2. Add 2 or more drops of phenolphthalein indicator. If the solution turns pink.
3. Add 0.02 N acid drop by drop from the pipette with stirring, until the pink color just disappears. If the sample is so colored that the color change of the indicator is masked, the endpoint is taken when the pH drops to 8.3, as measured with the glass electrode pH meter. (The sample can be diluted with distilled water.)
4. Report the phenolphthalein alkalinity of the filtrate, P_f, as the number of ml of 0.02 N acid required per ml of filtrate to reach the end point.

5. To the same sample used for measuring P_f, add 3 to 4 drops of methyl orange/brom cresol green indicator; a green color will develop.
6. Titrate with 0.02 N acid until the color changes to yellow. This will occur at pH of 4.3.
7. The M_f is reported as the total ml of acid used for P_f plus this last titration.

Example:

If 0.5 ml acid was used to titrate the phenolphthalein endpoint, the P_f is 0.5.

If an additional 0.3 ml acid was used to titrate to the methyl orange endpoint, the M_f is 0.8.

$BaCl_2$ procedure:

1. Measure 1 ml of filtrate into a titration vessel.
2. Add 2 drops of 10% barium chloride solution *(NOTE: $BaCl_2$ is poisonous; do not pipette with mouth).*
3. Repeat Steps 2 through 4 for the P_f titration.
4. As a rule of thumb, if the $BaCl_2$ $P_{Alkalinity}$ is one-half or less than the previous P_f titration, carbonate contamination exists.

Example:

If 1 ml acid was used to titrate to the endpoint for P_f, the P_f is 1.0.

If 0.4 ml acid was used to titrate to the $P_{Alkalinity}$ endpoint with $BaCl_2$, the $BaCl_2$ value is 0.5. Thus, carbonate contamination exists because the $BaCl_2$ is less than one-half the P_f.

2) PROCEDURE FOR MUD ALKALINITY (P_m)

Measure 1 ml of mud into the titration vessel using the syringe. Dilute the mud sample with 25 ml of distilled water. Add 5 drops of phenolphthalein indicator and, while stirring, titrate quickly with 0.02 N acid or 0.1 N acid until the pink color disappears. If the sample is so colored that the color change of the indicator is masked, the end point is taken when the pH drops to 8.3 as measured with the glass electrode.

Report the phenolphthalein alkalinity of the mud, P_m, as the number of ml of 0.02 N (N/50) acid required per ml of mud. If 0.1 N acid is used, $P_m = 5 \times$ ml of 0.1 N acid per ml mud.

3) PROCEDURE FOR LIME CONTENT

Determine the P_f and P_m, as described in the preceding paragraphs.

Determine the volume fraction of water in the mud, F_w (decimal fraction of water), using the value from the retort test.

Report the lime content of the mud in lb/bbl calculated from the following equation:

Lime (lb/bbl) = $0.26 \times (P_m - F_w P_f)$.

4) FILTRATE ALKALINITY: P_1 AND P_2

Equipment

1. Standard sulfuric acid solution, 0.02 N (N/50).
2. Sodium hydroxide solution, 0.1 N (N/10).
3. Barium chloride solution, 10%.
4. Phenolphthalein Indicator.
5. Deionized water.
6. pH strips or glass electrode pH meter.
7. Titration vessel, 100 to 150 ml, preferably white.
8. Pipette: one 1-ml, one 2-ml and one 10-ml.
9. Graduated cylinders: one 25-ml and one 5- or 10-ml.
10. Stirring rod.

Procedure: P_1 - P_2

1. Measure 1 ml of filtrate into the titration vessel and add 24 ml of deionized water.
2. Add 2 ml of 0.1 N sodium hydroxide and stir well. Measure the pH with the pH strip or pH meter. If the pH is 11.4 or greater, proceed to the next step. If the pH is less than 11.4, add another 2 ml of 0.1 N sodium hydroxide.

3. Using the graduated cylinder, measure 2 ml of barium chloride and add to the titration vessel. Add 2 to 4 drops of phenolphthalein with stirring.
   NOTE: Do not use your mouth to pipette; the barium chloride solution is poisonous.
4. Immediately titrate the mixture with standard sulfuric acid to the first disappearance of the pink color (or to pH 8.3 with the pH meter). The color may reappear after a short time; do not continue the titration.
5. Report the alkalinity, P_1, as the ml of 0.02 N sulfuric acid required to titrate to the phenolphthalein endpoint.

Procedure: P_2 (blank)

1. Omit the filtrate, but otherwise repeat the procedure for P_1, using exactly the same quantities of water and reagents. Titrate using the same procedures as for P_1.
2. Report the alkalinity, P_2, as the ml of 0.02 N sulfuric acid required to titrate to the phenolphthalein end point.

Calculations

Within limitations, the various ionic alkalinities can be calculated as follows:

When $P_1 > P_2$

OH^- (mg/l) = $340 \times (P_1 - P_2)$
CO_3^{2-} (mg/l) = $1,200 \times [P_f - (P_1 - P_2)]$

When $P_1 < P_2$

HCO_3^- (mg/l) = $1,220 \times (P_2 - P_1)$
CO_3^{2-} (mg/l) = $1,200 \times P_f$

B) GARRETT GAS TRAIN (GGT) TEST FOR CARBONATES

Purpose

This procedure uses the Garrett Gas Train, analyzing the soluble carbonates on a filtrate sample of water-base drilling fluid. The CO_2 Dräger tube responds to the CO_2 gas passing through it by turning purple. The stain length is primarily sensitive to the amount of CO_2 present, but it is also sensitive to the flow rate and the total gas volume passed through the tube. Therefore, for more accurate results, the gas exiting the gas train must first be captured in a 1-l bag to allow the CO_2 to mix uniformly with the carrier gas. The CO_2 Dräger tubes are very sensitive to incorrect use. The filtrate must be free of solids. Therefore, the first spurt of the filtrate should be discarded, because it may contain $CaCO_3$ particles that can cause errors on the high side. The contents of the bag are passed from the bag through the Dräger tube using 10 strokes of the Dräger hand pump. This technique will draw exactly 1 l of gas through the tube.

Equipment

1. Deionized water.
2. Octyl alcohol defoamer.
3. Sulfuric acid, approximately 5 N, reagent grade.
4. Garrett Gas Train apparatus.
5. Dräger CO_2 analysis tube, “CO_2 100/a” labeled 100 to 3,000 ppm. Factor = 2.5 (be sure to check to see if the factor has changed).
6. Dräger 1-l bag, #762425.
7. Dräger “Multigas Detector” hand vacuum pump.
8. Glass stopcock, 8 mm, 2-way bore.
9. Hypodermic syringes: one 10-ml with 21 gauge needle (for acid), one 10-ml, one 5-ml and one 2.5-ml.
10. N_2O gas cartridges (e.g. Whippets). Bottled nitrogen or helium gas can also be used. Do not use Whippets in any other test.

Procedure

1. Be sure the gas train is clean, dry and on a level surface.
2. With the regulator backed off, install and puncture a N_2O cartridge. Do not use compressed air or a CO_2 cartridge.
3. Add 20 ml deionized water to Chamber 1.

Figure 13: Garrett Gas Train.

4. Add 5 drops of defoamer to Chamber 1.
5. Install the top on the gas train and hand-tighten evenly to seal all O-rings.
6. Attach the flexible tubing from the regulator onto the dispersion tube of Chamber 1.
7. Inject with syringe an accurately measured sample of filtrate into Chamber 1, (see Figure 13). Flow carrier gas through train for 1 min to purge air from system. Stop gas flow.
8. Install one end of a piece of flexible tubing into the stopcock which is fitted directly into the gas bag. Have the gas bag fully collapsed. Fit the other end of the tubing onto the outlet tube of Chamber 3.
9. Slowly inject 10 ml sulfuric acid into Chamber 1 through the rubber septum using the hypodermic syringe and needle. Gently shake the gas train to mix acid with sample in Chamber 1.
10. Open the stopcock on the gas bag. Restart N_2O flow gently and allow gas bag to fill. When bag is full do not burst it, shut off N_2O flow and close the stopcock. Immediately proceed to Step 11.
11. Remove the tubing from Chamber 3 outlet and re-install it onto the upstream end of the CO_2 Dräger tube after breaking off the ends of the Dräger tube (observe that the arrow indicates gas flow direction). Attach Dräger hand pump to other end of Dräger tube.
12. Open stopcock on bag. With hand pressure, fully depress the hand pump, then release so that gas flows out of the bag and through the Dräger tube. Operate the hand pump 10 strokes, which should essentially empty the gas bag.
13. Observing a purple stain on the Dräger tube means CO_2 was present in the gas bag. Record the stain length in units marked on the Dräger tube.

1) DRÄGER TUBE IDENTIFICATION

1 Carbonate Range (mg/l)	2 Sample Volume (ml)	3 Dräger Tube Identification	4 Tube Factor
25 - 750	10	CO_2 100/a	2.5*
50 - 1,500	5	CO_2 100/a	2.5*
100 - 3,000	2.5	CO_2 100/a	2.5*
250 - 7,500	1	CO_2 100/a	2.5*

*NOTE: Tube factor “2.5” applies to new tubes, CO_2 100/a (cat. no. 8101811) with scale 100 to 3,000. Old tubes use tube factor 25,000 with scale 0.01 to 0.3%.

Table 3: Sample volumes and tube factor to be used for various carbonate ranges.

Calculations

Using the measured sample volume, the Dräger tube’s purple stain length and tube factor or 2.5 (see Table 3), calculate the soluble carbonates in the filtrate sample using the following equation:

$$CO^{2-}\ (\text{mg/l}) = \frac{\text{tube stain length x 2.5}}{\text{ml of sample filtrate}}$$

NOTE: The gas train apparatus MUST be cleaned after each use or the acid used will cause severe damage to the equipment. 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 tubes with air or N_2O gas. Rinse the unit with deionized water and allow to drain dry. Do not use the Nitrous oxide for any other test, or as a gas source.

It can cause an explosion if misused in other applications. (NEVER use them as a gas source for High-Temperature, High-Pressure (HTHP) cell or filtration — only GGT for carbonates.)

C) CHLORIDE (Cl^-)

Purpose

The salt, or chloride, test is very significant in areas where salt can contaminate the drilling fluid. This would include the majority of the world's oilfields. The salt may come from makeup water, sacks, stringers, beds or saltwater flows.

Equipment

The following materials are required to determine the chloride ion concentration in the mud filtrate.

1. Silver nitrate solution, 0.0282N or 0.282N (strong) $AgNO_3$, stored in an amber or opaque bottle.
2. Potassium chromate indicator solution.
3. Acid solution 0.02 N sulfuric or nitric acid.
4. Distilled water.
5. Two graduated pipettes: one 1-ml and one 10-ml.
6. Titration vessel, 100 to150 ml, preferably white.
7. Stirring rod.

Procedure

1. Measure 1 or 2 ml of filtrate into a titration vessel.
2. Add the amount of acid required in the P_f titration.
3. Add 25 ml of distilled water and 10 drops of potassium chromate solution. Stir continuously and titrate with standard silver nitrate solution drop by drop from the pipette, until the color changes from yellow to orange-red and persists for 30 sec.
4. Record the number of ml of silver nitrate required to reach the endpoint. (If over 10 ml of 0.282N silver nitrate solution are used, consider repeating the test with a smaller, accurately measured sample of filtrate or use a dilution with factor.)

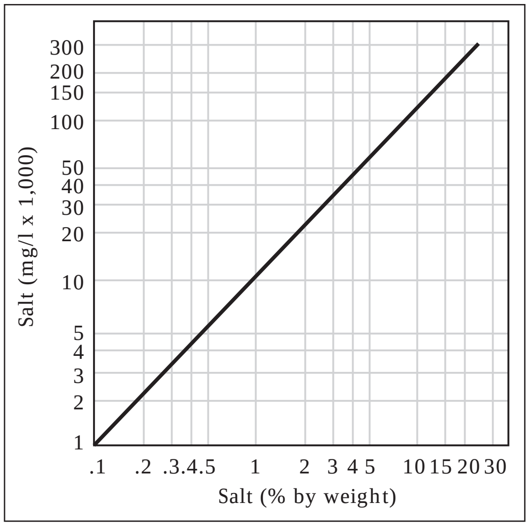


Figure 14: Salt milligrams per liter vs. salt percent by weight.

Calculations

If the chloride ion concentration of the filtrate is less than 10,000 mg/l, use the 0.0282 N silver nitrate solution equivalent to 0.001 g Cl^- ion per ml.

Report the chloride ion concentration of the filtrate in milligrams per liter, calculated as follows:

$$Cl^- \text{ (mg/l)} = \frac{\text{ml of 0.0282 N silver nitrate x 1,000}}{\text{ml of filtrate}}$$

If the chloride ion concentration of the filtrate is greater than 10,000 mg/l, use the 0.282 N silver nitrate (equivalent to 0.01 g Cl^- ion per ml). Report the chloride concentration of the filtrate in mg/l, calculated as follows:

$$Cl^- \text{ (mg/l)} = \frac{\text{ml of 0.282 N silver nitrate x 10,000}}{\text{ml of filtrate}}$$

For any normality silver nitrate:

$$Cl^- \text{ (mg/l)} = \frac{\text{N x 35,000 x ml used}}{\text{ml of filtrate sample}}$$

D) CALCIUM - QUALITATIVE

Purpose

Water containing a large amount of dissolved calcium and magnesium salts is referred to as "hard water." The common evidence of hardness in water at home is the difficulty of producing a lather with soap. In many oil fields, the water available for use is quite hard. Drilling clays have low yields when mixed in hard water. The harder the water, the more bentonite it takes to make a satisfactory gel mud. In extreme cases it has been found economical to treat the water chemically before using it for mixing mud, but it is not generally economical to do this. Frequently, however, where there is a choice of two or more sources of water for the rig, it may be desirable to make a simple test to select the softer of the two.

Field engineers are familiar with the effects on the mud when anhydrite (calcium sulfate) or gyp formations are drilled. Calcium may be picked up in drilling cement plugs and sometimes in penetrating sections of limey shale. Any extensive calcium contamination can result in high water loss and high gels. The detrimental effect of cement on increased P_m is due to the high alkalinity (lime) content.

Equipment

The following materials are required to qualitatively determine the presence of calcium and/or magnesium.

1. Test tube.
2. Dropper bottle of saturated solution of ammonium oxalate.

Procedure

Place 1 to 3 ml of filtrate in test tube. Add a few drops of saturated ammonium oxalate. The formation of a white precipitate indicates the presence of calcium. Record as light, medium or heavy.

E) TOTAL HARDNESS

1) CALCIUM AND MAGNESIUM TOGETHER

QUANTITATIVE

Equipment

1. EDTA (Standard Versenate) solution 0.01 M (1 ml = 400 mg Ca^{2+} or 1,000 mg $CaCO_3$).
2. Strong buffer solution (ammonium hydroxide/ammonium chloride).
3. Calmagite Indicator solution.
4. Titration dish, 100 to 150 ml, preferably white.
5. Three graduated pipettes: one 1-ml, one 5-ml and one 10-ml.
6. Graduated cylinder, 50 ml.
7. Distilled water.
8. Stirring rod.
9. 8N NaOH or KOH solution.
10. Calcon Indicator or Calver II.
11. Porcelain spoon/spatula.
12. Masking Agent: 1:1:2 mixture volume triethanolamine: tetraethylenepentamine: water (API).

Determining the total hardness of water or mud filtrate can be done by performing Part A as shown. This test is performed to obtain the ppm total hardness reported as calcium for the mud report form.

It may be required to determine the concentration of magnesium as well as calcium. In this case, use the procedure described in 2) CALCIUM AND MAGNESIUM SEPARATELY. This measures calcium specifically, rather than reporting the Mg^{2+} as Ca^{2+}. After the calcium is known, the magnesium concentration is calculated from the difference in the two titrations. Caustic soda (called "calcium buffer solution" here) precipitates the magnesium as the hydroxide, and the calcium is titrated with an indicator that is specific for calcium.

Procedure (total hardness as Ca^{2+})

1. Add approximately 20 ml of distilled water to titration vessel.
2. Add 1 ml of the water or filtrate to be tested.

3. Add 1 ml of strong buffer solution (NH_4OH base).
4. Add about 6 drops of Calmagite and mix with a stirring rod. A wine red color will develop if calcium and/or magnesium is present.
5. Using a pipette, titrate with Standard Versenate Solution, stirring continuously, until the sample first turns to blue with no undertint of red remaining. Record the number of ml of Standard Versenate solution used. (If magnesium is to be measured as in Procedure 2, record this value as "A" ml.)

Calculations

Total hardness as Ca^{2+} (mg/l) =

$$\frac{\text{ml of Standard Versenate x 400}}{\text{ml of sample}}$$

$CaCO_3$ (mg/l) =

$$\frac{\text{ml of Standard Versenate x 1,000}}{\text{ml of sample}}$$

Occasionally in dark-colored filtrate, it is difficult to see the endpoint to determine total hardness. The following method can be used to better observe the endpoint. Calculations remain the same.

1. Add approximately 20 ml of distilled water to titration vessel.
2. Add 1 ml filtrate to titration dish (0.5 ml accurately measured can be used if the endpoint cannot be seen with a 1 ml sample).
3. Add 1 ml Masking Agent.
4. Add 1 ml of strong buffer solution.
5. Add 6 drops Calmagite Indicator and stir.
6. Using a pipette, titrate with Standard Versenate solution until the color changes to blue/green. Record the number of ml used and calculate the same as before.

Calculations

Total hardness as $CaCO_3$ (mg/l) =

$$\frac{\text{ml of Standard Versenate x 1,000}}{\text{ml of sample}}$$

2) CALCIUM AND MAGNESIUM SEPARATELY

1. Add approximately 20 ml of distilled water to the titration vessel.
2. Add the same amount of water or filtrate to be tested as performed in the previous hardness test.
3. Add 1 ml Masking Agent.
4. Add 1 ml of 8N NaOH or KOH and ¼ porcelain spoonful (0.2 g) of Calcon Indicator and mix with a stirring rod.
5. Titrate with Standard Versenate solution until the indicator turns from wine red to blue with no undertint of red remaining. Record the number of ml of Standard Versenate required (record this value as "B" ml).

Calculations

$$\text{Calcium (mg/l)} = \frac{\text{B x 400}}{\text{ml of sample}}$$

$$\text{Magnesium (mg/l)} = \frac{\text{(A – B) x 243}}{\text{ml of sample}}$$

F) HARDNESS IN DARK FILTRATES

1) TOTAL HARDNESS IN DARK FILTRATES

QUANTITATIVE

Purpose

Occasionally there is difficulty in accurately titrating for hardness concentration in dark-colored filtrates due to the subtle change in color of the filtrate when the endpoint is reached. Thus, the following method has been developed and is recommended only when the previous hardness test procedure becomes difficult or impossible.

Equipment

1. Acetic acid: glacial (caution).
2. Calcon or Calver II Indicator (specific for Ca^{2+}).
3. Sodium hypochlorite 5.25% (Clorox®).
4. Calmagite Indicator.
5. Sodium hydroxide; 8N NaOH.
6. Masking Agent.
7. Standard Versenate solution 0.01 Molar.
8. Strong buffer solution.

9. Beaker, 100-ml.
10. Graduated cylinders, two 10-ml.
12. Graduated pipette, 10-ml.
13. Hot plate.
14. Volumetric pipette, 1-ml.
15. Porcelain spoon/spatula for solid indicator addition.

Method I (includes all metals which are titrated by Versenate solution)

CAUTION: Work in well-ventilated area. Do not breathe fumes.

1. Using a 1-ml volumetric pipette, transfer 1 ml of filtrate to a 100-ml beaker.
2. Add 10 ml Clorox (be sure it is fresh as it will deteriorate with time). Swirl to mix.
3. Add 1 ml of acetic acid and swirl to mix.
4. Heat to boiling on high heat and boil for 5 min. Maintain volume by adding deionized water.
5. Remove the beaker from the hot plate and let it cool to room temperature. Wash down sides of the beaker with deionized water.
6. Add 1 ml strong buffer solution and swirl to mix.
7. Add 6 drops of Calmagite and mix. A wine red color will develop if hardness is present.
8. Using a pipette, titrate with Standard Versenate solution, stirring continuously, until the sample turns to blue with no undertint of red remaining. The color change will be purple to slate gray with dark filtrates. Record the number of ml Standard Versenate solution used.

Calculations

Total hardness as Ca^{2+} (mg/l) =
ml Standard Versenate x 400

Method II (includes calcium and magnesium reported as Ca^{2+})

1. Using a 1-ml volumetric pipette, transfer 1 ml of filtrate to a 100-ml Pyrex® beaker.
2. Add 10 ml Clorox (be sure Clorox is fresh). Swirl to mix.
3. Add 1 ml of acetic acid and mix.
4. Heat to boiling and boil for 5 min. Maintain volume by adding deionized water.
5. Remove the beaker from the hot plate and let it cool to room temperature. Wash down the sides of the beaker with deionized water.
6. Add 1 ml of strong buffer solution and swirl to mix.
7. Add 1 ml of Masking Agent and mix.
8. Add 6 drops of Calmagite and mix. A wine red color will develop if calcium and/or magnesium is present.
9. Using a pipette, titrate with Standard Versenate, stirring continuously, until the sample turns blue with no undertint of red remaining. Record the number of ml of Standard Versenate used. This is Value A.

Calculations

Total hardness as Ca^{2+} (mg/l) = A x 400

2) CALCIUM AND MAGNESIUM SEPARATELY

1. Using a 1-ml volumetric pipette, transfer 1 ml of filtrate to a 100-ml Pyrex beaker.
2. Add 10 ml Clorox and swirl to mix.
3. Add 1 ml acetic acid and mix.
4. Heat to boiling and boil for 5 min. Maintain volume by adding deionized water.
5. Remove the beaker from the hot plate and let it cool to room temperature. Wash down the side of the beaker with deionized water.
6. Add 1 ml calcium buffer (sodium hydroxide) and mix (precipitates Mg^{2+}).
7. Add 1 ml Masking Agent and mix.
8. Add ¼ spoonful (0.2 g) of Calcon Indicator and mix. A wine red color will develop if calcium is present.
9. Titrate with Standard Versenate until the indicator turns from wine red to blue with no under tint of red remaining. Record the number of ml Standard Versenate required. This is Value B.

Calculations

Calcium (mg/l) = B x 400

Magnesium (mg/l) = (A - B) x 243

G) SULFATE

1) QUALITATIVE

Purpose

The sulfate ion is present in many natural waters due to the solvent action of water on the minerals in the earth. Anhydrite (calcium sulfate) is a slightly soluble contaminant encountered in drilling in certain areas. Frequently it is desirable to know the sulfate ion content in the filtrate. Sulfate ion concentrations around 2,000 mg/l could contribute to high viscosity and fluid-loss control problems.

Equipment

The following materials are required to qualitatively determine the presence of sulfate:

1. Test tube.
2. Dropper bottle of 10% barium chloride solution. *(POISON. Do not pipette by mouth.)*
3. Dropper bottle of strong nitric acid.

Procedure

Place about 3 ml of filtrate in a test tube. Add a few drops of barium chloride solution. The formation of a white precipitate indicates the presence of sulfates and/or carbonates. Add a few drops of concentrated nitric acid. If the precipitate dissolves, it is carbonate; if not, it is sulfate. Record the amount of precipitate remaining after the acid treatment as light, medium or heavy.

2) AVAILABLE (UNREACTED) CALCIUM SULFATE

Purpose

When running gyp muds it is necessary to know how much available gyp (calcium sulfate) is available in the system.

Equipment

1. Masking Agent: 1:1:2 mixture by volume of triethanolamine: tetraethylenepentamine: water.
2. Deionized water.
3. Calmagite Indicator.
4. Standard Versenate solution 0.01 Molar.
5. Strong buffer solution.
6. Beaker, 400-ml.
7. Calibrated beaker at 250 ml volume mark.
8. Hot plate.
9. Pipettes: 1-ml, 2-ml and 10-ml. 5-ml syringe.
10. Titration vessel, 100- to 150-ml, preferably white.
11. Mud still (retort).

Procedure

1. Add 5 ml of mud to calibrated beaker, then add 245 ml water to make final volume at 250-ml calibration mark.
2. Heat to 160°F and stir for about 15 to 20 min. Stir while heating if possible. (If there are no heating facilities available, stir for 30 min.)
3. Cool with stirring and make up the volume to exactly 250 ml with water using the calibrated container.
4. Filter with the filter press, discarding first cloudy portion of filtrate, and retain only clear filtrate.
5. To 10 ml of filtrate add 1 ml of Strong Buffer and 6 drops of Calmagite Indicator.
6. Titrate with Standard Versenate solution, stirring continuously until sample turns blue (or green for dark-colored filtrate) with no undertint of red remaining. Record the number of ml Standard Versenate solution used (Vt).
7. Clean the titration vessel and add approximately 20 ml water.
8. Add 1 ml of filtrate from the mud.
9. Add 1 ml of Strong Buffer solution.
10. Add 1 ml of Masking Agent.
11. Add 6 drops of Calmagite and mix with a stirring rod.
12. Titrate with Standard Versenate solution, stirring continuously until sample turns to blue (or green for dark-colored filtrate) with no undertint of red remaining.

13. Record the number of ml of Standard Versenate solution used (Vf).

Calculations

Available $CaSO_4$ (lb/bbl) =

$$2.38 \text{ x } V_t - [0.2 \text{ x } (F_w \text{ x } V_f)]$$

Where:

V_t = Number of ml Standard Versenate solution used to titrate 10 ml of clear filtrate in Step 6.

V_f = Number of ml Standard Versenate solution used to titrate 1 ml of mud filtrate in Step 13.

F_w = Freshwater fraction of mud obtained with mud still. Water %/100 = Fw.

H) POTASSIUM (K^+)

When it is necessary to determine the potassium ion concentration, either of the following procedures can be used effectively. Procedure I may be accurately used for any concentration of potassium ion. Procedure II is a quick method, used for high concentrations of potassium.

1) PROCEDURE I — POTASSIUM BELOW 5,000 mg/l (STPB METHOD)

Equipment

1. Standard Sodium Tetraphenyl Borate (STPB) solution.
2. Quaternary Ammonium Salt (QAS) solution, hexadecyltrimethyl ammonium bromide.
3. Sodium hydroxide (NaOH) solution (20%); 20 g/80 ml deionized water.
4. Bromophenol blue indicator.
5. Serological (graduated) pipettes: one 2-ml in 0.1-ml subdivisions, two 5-ml and two 10-ml.
6. Graduated cylinders: two 25-ml and two 100-ml.
7. Funnel: 100-ml.
8. Filter paper.
9. Beakers: two 250-ml and deionized water.

Procedure

1. Place the proper amount of filtrate into a 100-ml graduate, using Table 4 to determine sample size. Be sure to use a pipette to measure the amount of filtrate and/or diluted sample.
2. Add 4 ml of NaOH with a 5-ml pipette, 25 ml of STPB solution measured with a 25-ml graduate and enough deionized water to bring the level of the solution up to the 100-ml mark.
3. Mix and allow to stand 10 min.
4. Filter into a clean 100-ml graduated cylinder. If the filtrate is cloudy, the solution must be refiltered.
5. Transfer 25 ml of clear filtrate (measured with a 25-ml cylinder) into a 250-ml beaker.
6. Add 15 drops of bromophenol blue indicator.
7. Titrate with QAS solution until color changes from purple-blue to light-blue. Record ml of QAS solution used. Continue titration to 25 ml to ensure end point has been reached and no purple-blue color remains. If possible, use magnetic stirrer with light. Do not use a titration dish.

Ratio of QAS to STPB = ml QAS ÷ 2

If ratio is other than 4.0±0.05, it must be used as a correction factor in the calculation of mg/l K^+.

Calculations

$$K^+ \text{ (mg/l)} = \frac{(25 - \text{ml of QAS}) \text{ x } 1{,}000}{\text{ml of filtrate}}$$

If correction factor is necessary:

$$K^+ \text{ (mg/l)} = \frac{\left[25 - \left(\frac{\text{ml of QAS x 4}}{\text{ratio of QAS to STPB}}\right)\right] \text{ x } 1{,}000}{\text{ml of filtrate*}}$$

* For calculation, use ml filtrate from Procedure No. 1, labeled ml filtrate * (calculations). This procedure is called a back titration. Step 2 precipitates the potassium from solution. The potassium ion is filtered out in Step 4. Titration with the QAS solution determines the amount of unreacted STPB solution.

2) PROCEDURE II — POTASSIUM ION (SODIUM PERCHLORATE METHOD)

Equipment

1. Standard sodium perchlorate solution: 150.0 g $NaClO_4$ per 100 ml distilled water.

   NOTE: Sodium perchlorate is explosive in the dry state, if heated to a high temperature or allowed to contact organic reducing agents. The perchlorate is not hazardous if kept water wet. They will decompose harmlessly if dispersed in a bucket of water and then disposed of properly.
2. Standard potassium chloride solution, 14.0 g KCl made up to 100 ml with distilled water.
3. 10 ml clinical centrifuge tubes, Kolmer-type only; Corning 8360.
4. Centrifuge, horizontal-swing rotor head (manual or electrical) capable of producing approximately 1,800 RPM.
5. Standard calibration curve for potassium chloride.

Preparation

1. Calibrate the centrifuge.
   a. If electrical centrifuge is used, calibrate to 1,800 RPM using rheostat.
   b. If manual centrifuge is used, fairly constant 1,800 RPM can be obtained as follows:
      1. Determine the number of revolutions of the rotor per each turn of the crank; i.e., very slowly turn the crank and count the number of revolutions of the rotor head during one turn of the crank.
      2. Determine the number of crank turns it takes to get 1,800 revolutions of the rotor head.
      3. To maintain a constant speed for 1 min, take the required number of crank turns and divide by 12. This will give the number of crank turns needed per 5 sec.
      4. Now, look at the second hand of your watch. Start cranking rapidly and count the number of crank turns in 5 sec. If the number is greater than 10, slow down a little and count turns for another 5 sec. Continue adjusting your speed until the required number of turns is achieved and becomes natural.
2. Preparation of standard calibration curve for potassium chloride (see Figure 15 or use the following to prepare curve).
   a. Prepare standards over the range of 1 to 8% KCl by adding appropriate ml of standard potassium chloride solution (0.5 ml for each 3.5 lb/bbl) to centrifuge tube and dilute to 7 ml with distilled water.
   b. Add 3 ml of sodium perchlorate solution to each tube.

Estimated ppm K^+	Sample Preparation	Filtrate (ml)
Over 100,000	Take 1 ml filtrate, add 9 ml distilled water. Mix and use 1 ml solution for sample.	0.10
50,000 - 100,000	Take 1 ml filtrate, add 9 ml distilled water. Mix and use 2 ml solution for sample.	0.20
20,000 - 50,000	Take 1 ml filtrate, add 9 ml distilled water. Mix and use 5 ml solution for sample.	0.50
10,000 - 20,000	Take 1 ml undiluted filtrate.	1.00
4,000 - 10,000	Take 2 ml undiluted filtrate.	2.00
2,000 - 4,000	Take 5 ml undiluted filtrate.	5.00
250 - 2,000	Take 10 ml undiluted filtrate.	10.00

NOTE: It is important to check the concentration of QAS solution vs. the STPB solution at monthly intervals. To determine the equivalent QAS, dilute 2 ml of the STPB solution in titration vessel with 50 ml distilled water. Add 1 ml sodium hydroxide solution and 10 to 20 drops of the bromophenol blue indicator. Titrate with the QAS solution until the color changes from purple-blue to light-blue.

Table 4: Potassium sample sizes.

c. Centrifuge for 1 min at 1,800 RPM and read the precipitate volume immediately.
d. Rinse tubes and dispose of the liquid properly.
e. Plot ml of precipitate vs. potassium chloride content (lb/bbl) on rectangular graph.

Procedure

1. Measure 7 ml of filtrate into centrifuge tube. Add 3 ml of the sodium perchlorate solution to the tube (if potassium is present, precipitation occurs at once). *DO NOT AGITATE!* Centrifuge at constant speed, approximately 1,800 RPM for 1 min and read the precipitate volume immediately. Rinse the precipitate from the tube into a bucket of water.

   NOTE: To ensure all potassium has been removed, add 2 to 3 drops of the sodium perchlorate to the centrifuge tube after centrifuging. If a precipitate is formed, the total amount of potassium ion was not measured; sample must be diluted as in Note 2.
2. Determine the potassium chloride concentration by comparing the precipitate volume measured with the standard curve (see Figure 15).
3. Report the potassium concentration as lb/bbl KCl or kg/m^3.

Calculations

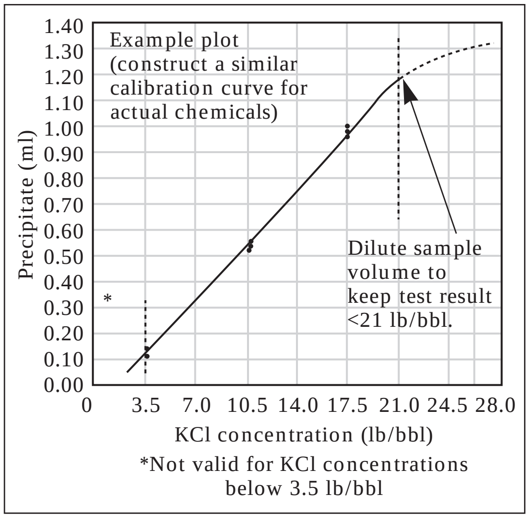
The potassium concentration may also be reported as a weight % of KCl.

$$\text{KCl (wt \%)} = \frac{\text{lb/bbl}}{3.5}$$

$$\text{K}^+ \text{ (mg/l)} = 1{,}500 \times \text{KCl (lb/bbl)}$$

NOTE 2: These two calculations assume a filtrate specific gravity of 1.00.

If the concentration of KCl exceeds 21 lb/bbl, the accuracy can be improved by performing an appropriate dilution to keep the test result in the 3.5 to 21 lb/bbl range. The volume in the tube should be made up to 7 ml with distilled water and agitated before adding the sodium perchlorate solution. If filtrate volumes other than 7 ml are used, the KCl concentration should be calculated as follows:



*Not valid for KCl concentrations below 3.5 lb/bbl

Figure 15: KCl concentration calibration curve.

$$\text{KCl (lb/bbl)} = \frac{7}{\text{ml of filtrate}} \text{ (value from standard curve)}$$

This method was developed as a field procedure and should be used in that respect. It is to aid in maintaining the potassium ion in the mud filtrate at or above a certain level. It can best be used when potassium ion concentration is above 5,000.

I) NITRATE ION CONCENTRATION

Purpose

Fluids recovered from DST/formation tests are often difficult to identify as being either filtrate or connate water. The use of the nitrate ion in the mud filtrate as a tracer permits a better evaluation to be made.

Equipment

Nitrate Test Kit (A.J. Chemical) plus tablespoon for measuring lime.

Procedure

1. Measure a 5-ml sample of near colorless filtrate into a test tube. If the filtrate is dark, the color must

be removed by either dilution or lime treatment (see Note 1 and Table 3).

2. Add contents of a NO_3-11 ampoule and shake for 3 min.
3. Let settle and decant liquid into a second test tube.
4. Add contents of a NO_3-12 ampoule to the decanted liquid in the second test tube.
5. Shake and let stand in rack for 10 min for full color development.
6. After full color development, pour sample into a 10-ml graduate and add deionized water to make the volume up to 10 ml. Mix thoroughly.
7. Transfer sample back to the second test tube.
8. Prepare a blank by taking a 5-ml sample which is treated identically to the sample in Step 1 with respect to dilution and lime treatment, and add 5 ml of deionized water to give the same dilution as indicated in Step 6.
9. Place the colored unknown in the right hole of the comparator box.
10. Place the blank in the left hole of the comparator box.
11. While looking through the holes, rotate the wheel slowly until color intensities match. If sample color is darker than wheel color at 80 (see Note 2), estimate the dilution needed (see Table 5) to reduce nitrate ion concentration to within color wheel range and repeat test.
12. Record the dial reading.

Calculations

Clear filtrates:

$$\text{mg/l } NO_3^- = \frac{\text{dial reading x dilution factor}}{10}$$

Colored filtrate requiring one lime treatment:

$$\text{mg/l } NO_3^- = \frac{\text{dial reading x dilution factor}}{10} - (6 \text{ x mg/1 } NO_3^- \text{ in lime*})$$

Colored filtrate requiring two lime treatments:

$$\text{mg/l } NO_3^- = \frac{\text{dial reading x dilution factor}}{10} - 1 - (42 \text{ x mg/l } NO_3^- \text{ in lime*})$$

*This value is marked on the lime container.

NOTE 1: The 5-ml sample taken at Step 1 does not have to be absolutely colorless. A slight color can be tolerated if the proper blank is used as specified in Step 8. Quite often the color is reduced to a satisfactory level by the dilution that may be required to lower the NO_3^- concentration so it will fall within the range of the color wheel at Step 11. An extremely dark filtrate, however, will have to be decolorized. This is accomplished by diluting 5 ml of filtrate with deionized water, adding 1 tablespoon of calcium hydroxide, shaking well and then filtering with funnel. This gives an initial dilution factor of 6. If the filtrate is too dark, take 1 ml and dilute to 5 ml with deionized water to see if this would be a satisfactory sample to use as Step 1. If not take 5 ml and repeat the above dilution and treatment, and then filter again. This will give a dilution factor of 36. No further decolorization should be necessary; however, further dilution with deionized water may be necessary (see Table 5). But this may not be known until completion of Step 11.

NOTE 2: The readings above 80 on the color wheel give erroneous results. Therefore, samples having readings above 80 should be diluted and rerun.

Dilution tables

This table is to aid in selecting the proper dilution of the original filtrate (no lime treatment) or the additional dilution after lime treatment, if the approximate NO_3^- concentration of original mud filtrates is known. Dilution Factors (DF) for use in calculations are also shown.

No lime treatment.

NO_3^- (mg/l)	Dilution (ml)	Dilution Factor
0 - 8	None	1
8 - 20	2 - 5	2.5
20 - 40	1 - 5	5
40 - 80	1 - 10	10
80 - 200	1 - 25	25
200 - 500	1 - 50	50

One lime treatment.

mg/l	Dilution (ml)	Dilution Factor
0 - 20	None	6
20 - 100	2 - 5	15
100 - 200	1 - 5	30
200 - 450	1 - 10	60

Two lime treatments.

mg/l	Dilution (ml)	Dilution Factor
0 - 120	None	36
120 - 550	2 - 5	90

Table 5.

The dilution factor column indicates the amount of filtrate used and the final volume to which it is diluted with deionized water.

J) PHPA POLYMER CONCENTRATION

Purpose

PHPA polymers are mud additives which help stabilize shales in a wellbore. The following analysis will determine the free polymer available to adsorb on the wall of the hole.

Equipment

1. Hot plate/magnetic stirrer with magnetic stir bars.
2. Two, 125-ml Erlenmeyer flasks.
3. Distilled water.
4. Boric acid solution, 2% by weight.
5. Methyl Red Indicator.
6. 6 N sodium hydroxide solution.
7. 2 to 3 ft of 0.25-in. ID Tygon tubing.
8. No. 6 rubber stopper with a 0.25-in. hole.
9. 0.02 N sulfuric acid solution.
10. Silicone defoamer (i.e. Dow-Corning 84 AFC-78).
11. 0.25-in. OD glass tubing — fire polished (2 pieces about 3 to 4 in. long).

Procedure

1. Attach the two pieces of glass tubing to each end of the Tygon tubing. Insert one end into the rubber stopper so the end of the tube is exactly flush with the bottom of the stopper.
2. To one Erlenmeyer flask, add 25 ml of the boric acid solution, and 6 drops of Methyl Red Indicator. This is the collection flask. Note the original color which should be pink/red, but not yellow.
3. To the other Erlenmeyer flask (this is the reaction flask) add 50 ml distilled water, 2 ml of silicone defoamer and 10 ml whole mud. If the active POLY-PLUS® concentration is more than 1.5 lb/bbl, or if the liquid POLY-PLUS is more than 4.5 lb/bbl, use 5 ml whole mud, then double the result.
4. Place the reaction flask containing the mud on the hot plate and begin stirring. Add 3 ml of the 6 N sodium hydroxide solution and immediately fit the flask with the rubber stopper.
5. Submerge the other end of the tubing (Pasteur pipette, if used) into the 2% boric acid/methyl red solution.
6. Heat for 45 to 60 min, allowing a gentle boiling. Approximately 25 ml should condense in the collection flask during this time, with a color change from pink to yellow.

7. Adjust heat for neither too hot, nor cool enough to allow fluid to be pulled back. If the heat from the hot plate cycles from on to off, the cooling will allow the boric acid solution to be sucked from the flask. After the 25 ml is collected, remove stopper, and drain any liquid into the collection flask. Titrate the collection flask contents back to the original red/pink color with the 0.02 N H_2SO_4 solution and record the amount of acid used.
8. The concentration of POLY-PLUS can be determined from the correct graph. Remember to double the result if a 5-ml sample is used.

Additional guidelines and trouble-shooting

1. It is important that the glass tubing be flush with the bottom of the rubber stopper. If the glass tube protrudes below the stopper, the caustic solution being distilled will collect around the exposed tube and be sucked up and over to the boric acid solution. This will give high erroneous values in the determination.
2. Be sure the indicator used is methyl red. This indicator will change from a pale amber yellow to a pink or pinkish-red when going from high pH to low pH. Also, the boric acid solution should turn the indicator pink, not yellow. If it doesn't turn pink, obtain a fresh sample of boric acid. If this is not possible, use 0.02 N sulfuric acid and add dropwise until the solution just turns pink. Use this solution to collect the distillate. This step will ensure that in the final titration, only the acid required to titrate the ammonia will be measured. Any addition of acid to correct the boric acid is ignored.
3. If the mud foams or boils over, use more defoamer. Try to estimate the range of the active polymer so the proper amount of whole mud can be used.
4. The temperature setting for distilling the solution should be adjusted so it does not cause boil-over (which invalidates the test). It should boil the solution gently causing water (or distillate) to condense at the top of the glass tubing. That way, the mud is not boiled over into the receiving flask but distillate merely collects in the tubing and runs down to the boric acid solution. Again, the temperature setting should be high enough so a steady boil is maintained, preventing the mud flask from cooling and sucking boric acid into this flask.

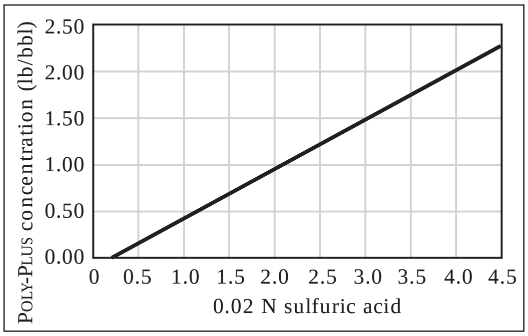


Figure 16: POLY-PLUS (liquid) concentration test.

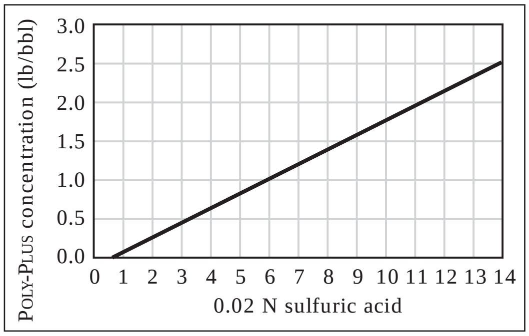


Figure 17: POLY-PLUS (dry) concentration test.

5. Be sure that the end of the glass tubing is below the surface of the boric acid solution. It is even better if a Pasteur pipette is used at this end instead of a glass tube. The opening is smaller therefore the chance of allowing ammonia to escape is reduced.
6. When the final titration is performed, be sure to titrate back to the original color of the boric acid solution. If a light pink was noted, do not continue to titrate to a darker pink or reddish color.

Section 8. Chemical Analysis Relating to Corrosion

A) SULF-X (ZnO) AND BASIC ZINC CARBONATE ($ZnCO_3 \cdot Zn(OH)_2$)

Purpose

Zinc oxide and zinc carbonate may be used to scavenge hydrogen sulfide in drilling fluids. In order to determine the available ZnO or $ZnCO_3$ in the mud, the following may be used:

Equipment

1. Acetic acid, glacial.
2. Ammonium fluoride, 10%.
3. Ammonium hydroxide, concentrated.
4. Masking Agent.
6. Deionized water.
7. Formaldehyde solution (4%).
8. Calmagite Indicator solution.
9. Standard Versenate solution.
10. Beaker, 150-ml.
11. Graduated cylinders: one 10-ml, one 25-ml and one 100-ml.
12. Field mixer with powerstat or magnetic stirrer with stirring bar.
13. Syringes: one 10-ml and one 20-ml.
14. Plastic funnel, 4 in.
15. Fluted filter paper (S & S No. 588 size 18.5 cm).
16. pH strips.
17. Volumetric pipettes: one 10-ml and one 20-ml.

Procedure

1. Stir the mud sample, then measure 10 ml using syringe.
2. Place in 150-ml beaker.
3. Dilute to 40 ml with deionized water.
4. Add 10 ml glacial acetic acid *(CAREFUL: Use a vent hood, if available).*
5. Stir 10 min with mixer or stirrer. If neither is available, hand mix with stirring rod. Thorough mixing is essential as the reaction is slow to take place.
6. Add 15 ml ammonium hydroxide *(CAREFUL).*
7. Check pH. If pH is above 9, proceed to next step. If pH is below 9, add additional ammonium hydroxide in 5-ml increments until pH is above 9, then proceed.
8. Add 3 ml of Masking Agent.
9. Add 10 ml of ammonium fluoride solution.

   NOTE: Ammonium fluoride is poisonous; do not pipette with your mouth. Never mix ammonium fluoride with an acidic solution.
10. Transfer the solution to the 100-ml graduated cylinder and dilute to the 100-ml mark with deionized water.
11. Mix well and filter into a dry, clean beaker.
12. Take 20 ml of filtrate and place in a clean beaker.
13. Dilute with deionized water to about 40 ml.
14. Add 6 drops of Calmagite Indicator. If solution is blue, proceed directly to Step 15. If solution is red, titrate slowly with Standard Versenate to the regular

blue endpoint. The amount of Versenate indicator does not need to be recorded.

15. Add 5 ml ammonium hydroxide.
16. Check the pH. It should be between 10 and 11. If pH is below 10, add additional ammonium hydroxide in 5-ml increments until pH of 10 is reached.
17. Add 5 ml formaldehyde solution.
18. Let stand at least 2 min. Solution will turn from blue to wine-red if zinc is present.
19. Titrate with Versenate indicator until wine-red changes to blue.

Calculations

$$\text{ZnO (lb/bbl)} = \frac{28.5 \text{ x ml of Standard Versenate}}{\text{ml of sample x ml of filtrate}}$$

$$\text{ZnCO}_3 \text{ (lb/bbl)} = \frac{44 \text{ x ml of Standard Versenate}}{\text{ml of sample x ml of filtrate}}$$

B) IRON SULFIDE SCALE (QUALITATIVE)

Purpose

To test for iron sulfide on steel equipment, a special reagent solution is used. While the presence of iron sulfide frequently indicates the presence of H_2S downhole, it by no means proves the existence of H_2S gas.

Equipment

Iron sulfide test solution, containing 15% HCl, 1% sodium arsenite and 0.05% detergent used as a wetting agent.

Procedure

A few drops of the acid solution is placed on the equipment or scale being formed. If a bright yellow precipitate of arsenic sulfide is formed, the sample contains iron sulfide. The precipitate looks like miniature “scrambled eggs.”

Since some iron will be dissolved by the acid, a yellow-orange solution may result. This should not be mistaken for the yellow precipitate formed by the sulfide. If bubbles are released, then the scale may have been carbonate from carbon dioxide, possibly.

CAUTION: This test should be used only on steel equipment; do not use on aluminum or metal plating because poisonous fumes may be formed.

NOTE: Information taken from “Corrosion of Oil and Gas Well Equipment,” Sponsored by National Association of Corrosion Engineers International and American Petroleum Institute, 300 Corrigan Tower Building, Dallas, TX, 1958, page 85.

C) HYDROGEN SULFIDE (H_2S)

Purpose

It is possible for the poison gas, H_2S to enter the drilling fluid causing corrosion. The gas is deadly poison to living beings. Two different methods are presented for determination of H_2S in parts per million. The first method is rapid, and requires a minimum of equipment. The results are less accurate, and should be used to indicate H_2S as present or not. Use the second method (GGT) to determine ppm of H_2S in the drilling fluid by the use of the filtrate analysis.

1) PROCEDURE I: HACH TEST

Equipment

1. A special calibrated test bottle with cap containing hole to release gas.
2. Hydrogen sulfide test paper to fit in cap.
3. Hypodermic syringe, one 10-ml.
4. Deionized water.
5. Alka-Seltzer® tablets (fresh).
6. Color comparison chart for ppm H_2S.
7. Octanol defoamer.
8. Hydrochloric acid, approximately 6 N.

Procedure

1. With a syringe transfer 8.3 ml mud to test bottle. Add 16.7 ml deionized water and swirl until mixed. Volume is 25 ml now. To reduce foaming, a drop of defoamer should be added at this point. Do not let the fluid touch and stain the paper.
2. Place a circle of H_2S test paper inside the test bottle cap (that has

a hole in it for gas to escape through the paper).

3. Add an Alka-Seltzer tablet to the sample and immediately screw the cap containing the test paper on the bottle. Gently swirl to stir.
4. After 15 min, remove the test paper and compare to the color chart. The ppm H_2S obtained from chart is multiplied by three to obtain the ppm H_2S in the mud.

This test will detect as little as 0.3 ppm H_2S. The test is only good for dissolved sulfide in mud. To determine an insoluble sulfide, such as iron sulfide, it must be put into solution with acid. Five drops of hydrochloric acid at Step 3 will enable any iron sulfides to be determined.

NOTE: If the H_2S of mud is greater than 15 ppm, more dilution will be necessary. For concentrations between 15 and 125 ppm, use 1 ml mud and 24 ml deionized water and multiply ppm H_2S obtained from chart by 25.

For concentrations between 125 and 1,250 ppm, mix 1 ml mud in 9 ml deionized water in a small beaker, and take 1 ml of mix and add 24 ml deionized water for the test; multiply ppm H_2S obtained from chart by 250. Since filtrate is used in GGT, these results will not compare.

2) PROCEDURE II: GARRETT GAS TRAIN

Purpose

The Garrett Gas Train purges the H_2S from the filtrate prior to capturing the gas in a Dräger tube.

Equipment

Section 1. Garrett Gas Train and accessories.

Section 2. Dräger H_2S analysis tubes:
- A) Low range-H_2S 100/a (100 to 2,000 labeled) Factor = 0.12.
- B) High range H_2S 0.2%/A (labeled 0.2 to 7%) Factor = 1,500.

Section 3. CO_2 cartridges (or other gas which is inert to H_2S and does not contain air or oxygen, nitrogen is permitted).

Section 4. Lead acetate paper disks (optional).

Section 5. Sulfuric acid, approximately 5 N, reagent grade.

Section 6. Octanol defoamer.

Section 7. Hypodermic syringes: one 10-ml with 21-gauge needle for acid, one 40-ml and one 5-ml.

Procedure

1. The gas train must be clean, dry and on a level surface, since the passages must be clear and moisture may cause the flow meter ball to float erratically.
2. Install a new CO_2 cartridge.
3. Add 20 ml deionized water to Chamber 1.
4. Add 5 drops of defoamer to Chamber 1.
5. Select the correct sample volume and Dräger tube for the expected sulfide range from the following table. Break the tip from each end of the tube.
6. Install the tube with the arrow pointed downward in the receptacle bored in the corner of the train. Also, install the clean, dry flow meter tube with the word “TOP” upward, and the ball in the bored receptacle in the side of the train. Be sure that the O-rings seal around both tubes after they have been inserted.
7. Measure out the filtrate sample into Chamber 1. Chambers 2 and 3 remain empty and serve as foam traps.
8. Place O-rings on the chamber grooves and install the top of the gas train. Hand tighten all screws evenly to seal the train.
9. Attach the flexible tubing to the dispersion tube and the Dräger tube. The tubing does not need to be clamped to the tubes and will provide pressure relief in the event of over-pressurization.

Sample Volumes and Tube Factor to be Used for Various Sulfide Ranges			
Sulfide Range (mg/l)	**Sample Volume (cm^3)**	**Dräger Tube Identification (see tube body)**	**Tube Factor**
1.2 - 24	10.0	H_2S 100/a (100 - 2,000 range)	0.12*
2.4 - 48	5.0	H_2S 100/a (100 - 2,000 range)	0.12*
4.8 - 96	2.5	H_2S 100/a (100 - 2,000 range)	0.12*
30 - 1,050	10.0	H_2S 0.2%/A	1,500**
60 - 2,100	5.0	H_2S 0.2%/A	1,500**
120 - 4,200	2.5	H_2S 0.2%/A	1,500**

*Tube factor 0.12 applies to new tubes, H_2S 100/a (Cat. No. CH-291-01), with scale 100 to 2,000. Old tubes use tube factor 12.0 with scale 1 or 2 to 20.

**Tube factor 1,500 applies to new tubes, H_2S 0.2%/A (Cat. No. CH-281-01), with scale 0.2 to 7.0%. Old tubes with 1 to 17 cm scale use tube factor 600 times ratio: “batch factor”/0.40.

Table 6: Dräger tube identification and selected ranges.

10. Adjust the dispersion tube to approximately 0.5 cm above the bottom.
11. Gently flow CO_2 for 15 sec to purge air from the system, then stop flow. Be sure to start the gas flow slowly so as not to blow the ball out of the flow meter tube. You may also want to lightly cover the tube with a finger to make sure the ball is not lost.
12. Slowly inject 10 ml of sulfuric acid into Chamber 1 through the rubber septum using the hypodermic syringe and needle.
13. Immediately restart CO_2 flow. Adjust the rate so the ball in the flow meter tube is between the red lines (200 to 400 cm^3/min). One CO_2 cartridge should provide 15 to 20 min of flow at this rate.
14. Continue flowing for a total of 15 min. Record the maximum darkened length before any preceding “front” starts to smear. Using high-range tubes, and sulfites in the filtrate, an orange color may be seen. The orange region should be ignored when recording the darkened length.
15. The gas train MUST be cleaned to avoid permanent damage caused by the acid used. To clean, remove the flexible tubing and the top of the train. Take out the flow meter and Dräger tube and plug the holes with stoppers to keep dry. Wash out the chambers with mild detergent and a soft brush. Use a pipe cleaner to clean out the passages between chambers. Rinse the unit with deionized water and allow to drain dry.

Calculations

Using the sample volume, the Dräger tube’s maximum darkened length and the factors, calculate the sulfides in the sample:

$$\text{Sulfides (mg/l)} = \frac{\text{darkened length x tube factor}}{\text{ml of sample volume}}$$

D) PHOSPHATE

Purpose

The active ingredient in the inhibitors CONQOR® 404 and SI-1000™ is an organic phosphate. However, inorganic phosphates may also be present in the drilling fluid, thus the test must differentiate between organic and inorganic phosphates.

The following two procedures are basically the same, but using different HACH kits.

NOTE: Starch in the fluid may prevent the detection of either organic or inorganic phosphates.

1) Procedure I: Using HACH Direct Reading colorimeter

Equipment

1. Deionized water.
2. Phenolphthalein indicator.
3. PhosVer III pillows.
4. Potassium persulfate pillows.
5. Sodium hydroxide, 8 N NaOH.
6. Sulfuric acid, 5 N H_2SO_4.
7. Erlenmeyer flask, 50-ml.
8. Graduated cylinder, 25-ml.
9. HACH Direct Reading colorimeter.
10. Hot plate.
11. Pipettes: one 1-ml, one 5-ml and one 10-ml.

a) Inorganic phosphate

1. Pipette 5 to 10 ml filtrate into the 50-ml flask. Add deionized water to the 20-ml mark.
2. Add 1 ml sulfuric acid.
3. Boil for 15 min maintaining the volume at about 20 ml.
4. Cool.
5. Add one drop phenolphthalein indicator.
6. Add sodium hydroxide dropwise until sample almost changes to pink. If too much is added and the pink persists, add sulfuric acid dropwise until the pink color just disappears.
7. Pour sample into a 25-ml graduated cylinder and add deionized water to the 25-ml mark.
8. Pour into square mixing bottle.
9. Add the contents of one PhosVer III pillow. Swirl and let stand for 1 to 2 min (not over 2 min).
10. Insert phosphate meter scale or transmittance scale into the HACH Direct Reading colorimeter and use the 2408 color filter.
11. Fill another square colorimeter bottle with the untreated filtrate for the blank. Make certain it is the same concentration as the sample. If 5 ml is used for the sample, use 5 ml of the filtrate diluted to 25 ml for the blank.
12. Insert the blank in the colorimeter. Adjust the light control for a meter reading of 0 mg/l or 100% transmittance depending on which scale is being used.
13. Place the prepared sample in the colorimeter and read mg/l PO_4^{3-} or transmittance. If the mg/l PO_4^{3-} reading is greater than 2.0 or if the transmittance reading is less than 10%, repeat the procedure using less filtrate in Step 1.
14. Record mg/l PO_4^{3-} reading for use in calculations. If the transmittance scale is used, refer to the graph of transmittance vs. mg/l PO_4^{3-}.

b) Total phosphate (inorganic plus organic)

1. Pipette 5 to 10 ml filtrate into the 50-ml flask. Add deionized water to the 20-ml mark.
2. Add 1 ml sulfuric acid.
3. Add the contents of one potassium persulfate pillow.
4. Boil for 30 min.
5. Boil down to not less than 10 ml volume. Add deionized water, if necessary.
6. Proceed as in Steps 4 through 11 above.

   NOTE: If the filtrate color disappears due to the potassium persulfate oxidation, do not use the colored filtrate for the blank in Step 11. In this case, use deionized water.
7. Insert the blank in the colorimeter. Adjust the light control for a meter reading of 0 mg/l or 100% transmittance depending on which scale is being used.
8. Place the prepared sample in the colorimeter and read mg/l PO_4^{3-} or % transmittance. If the mg/l PO_4^{3-} reading is greater than 2.0 or if the transmittance reading is less than 10%, repeat the procedure using less filtrate in Step 15.
9. Record mg/l PO_4^{3-} reading for use in calculations. If the transmittance scale is used, refer to the graph of transmittance vs. mg/l PO_4^{3-}.

Calculations

Inorganic phosphate (mg/l) =

$$\frac{\text{mg/l of } PO_4^{3-} \text{ from chart x 25}}{\text{ml of filtrate}}$$

Total phosphate (mg/l) =

$$\frac{\text{mg/l of } PO_4^{3-} \text{ from chart x 25}}{\text{ml of filtrate}}$$

Organic phosphate =
total phosphate – inorganic phosphate

2) PROCEDURE II: HACH PHOSPHATE KIT (PO-24)

Equipment

1. Deionized water.
2. Phenolphthalein indicator.
3. PhosVer III pillows.
4. Potassium persulfate pillows.
5. Sodium hydroxide, 8 N NaOH.
6. Sulfuric acid, 5 N H_2SO_4.
7. Erlenmeyer flask, 50-ml.
8. Graduated cylinder, 25-ml.
9. HACH phosphate kit PO-24.
10. Hot plate.
11. Pipettes: one 1-ml, one 5-ml and one 10-ml.

a) Inorganic phosphate

1. Pipette 5 to 10 ml filtrate into the 50-ml flask. Add deionized water to the 20-ml mark.
2. Add 1 ml sulfuric acid.
3. Boil for 15 min maintaining the volume at about 20 ml.
4. Cool.
5. Add one drop of phenolphthalein indicator. Add sodium hydroxide dropwise until sample almost turns pink. If too much sodium hydroxide is added and the pink persists, add sulfuric acid dropwise until pink color just disappears.
6. Pour sample into square mixing bottle and add water up to the 20-ml mark.
7. Add a PhosVer III pillow to the sample. Swirl and let stand for 1 to 2 min.
8. Pour sample into the color viewing tube.
9. Insert this tube into the color comparator in the opening nearest the middle.
10. Put a blank in the other tube. Make sure it is the same concentration as the sample. If 5 ml is used for the sample, use 5 ml of the filtrate diluted to 20 ml for the blank.
11. Hold the comparator up to a light and view through the two openings in the front. Rotate the color disc until a match is obtained. If the color is too dark, repeat the procedure using less filtrate in Step 1.
12. Record reading for use in calculations.

b) Total phosphate (inorganic plus organic)

13. Pipette 5 to 10 ml filtrate into flask and add deionized water to the 20-ml mark.
14. Add 1 ml sulfuric acid.
15. Add contents of one potassium persulfate pillow.
16. Boil for 30 min.
17. Boil down to not less than 10 ml volume. Add deionized water if necessary.
18. Proceed as in Steps 4 through 10 above.

    NOTE: If the filtrate color disappears due to the potassium persulfate oxidation, do not use the colored filtrate for the blank in Step 10. In this case, use deionized water.
19. Hold the comparator up to a light and view through the two openings in the front. Repeat the procedure using less filtrate in Step 13.
20. Record reading for use in calculations.

Calculations

Inorganic phosphate (mg/l) =

$$\frac{\text{reading Step 12 x 2}}{\text{ml of filtrate Step 1}}$$

Total phosphate (mg/l) =

$$\frac{\text{reading Step 20 x 2}}{\text{ml of filtrate Step 13}}$$

Organic phosphate =
total phosphate – inorganic phosphate

E) OXYGEN SCAVENGER: SO_3^{2-} CONTENT

Purpose

Oxygen scavengers that contain ammonium bisulfite or sodium sulfite are added to some drilling fluids to reduce dissolved oxygen to a minimum. To assure the complete removal of dissolved oxygen, an excess of the sulfite (SO_3^{2-}) ion should be maintained in the mud.

Two procedures are listed below: one used for normal filtrates and the other used for dark filtrates. Use Procedure I first as it is more accurate. However, if the color change cannot be seen use Procedure II. Do not dilute filtrate with deionized water as this may add dissolved oxygen.

Procedure: Light filtrates

Equipment

1. Deionized water.
2. Hydrochloric acid, 6 N HCl.
3. Standard "iodine" solution 0.008 N ($KI\text{-}KIO_3$).
4. Standard sodium thiosulfate solution, 0.008 N.
5. Starch indicator solution.
6. Test tube.
7. Flasks, two 125-ml.
8. Pipettes: one 1-ml and one 2-ml.

NOTE: If any sulfide is present, it will also be titrated in this test. Determine hydrogen sulfide by some other method and subtract mg/l H_2S x 2.4 from the mg/l SO_3^{2-} obtained. If the SO_3^{2-} content of the mud is apparently increasing when no sulfite is being added, H_2S should be suspected. (With sulfide present, the Cl^- ion test may show an increase as it will react with the ion also.)

Standardization of sodium thiosulfate solution.

Sodium thiosulfate does not have a long shelf life. Every two weeks it should be checked against the $KI\text{-}KIO_3$ solution as follows. This is important as a weaker sodium thiosulfate solution will give you lower sulfite content and a deterioration factor must be used.

1. Pipette 2 ml of the "iodine" solution into a 125-ml beaker.
2. Add 2 drops of hydrochloric acid.
3. Dilute with 10 ml deionized water.
4. Titrate with the sodium thiosulfate until most of the yellow color disappears.
5. Add 5 drops of starch indicator.
6. Continue titrating until the blue color just disappears.
7. Record total ml of thiosulfate solution required to calculate deterioration factor.
8. Use this factor in the equation for determining mg/l SO_3^{2-} on dark colored filtrates:

$$\text{Factor} = \frac{\text{ml of } KI\text{-}KIO_3 \text{ solution}}{\text{ml of sodium thisulfate}}$$

1) PROCEDURE I: LIGHT FILTRATES

The mud sample for this test should be collected above the shaker. Because of the instability of sulfite, the filtrate should be collected and the test performed immediately.

1. Pipette 5 ml of filtrate into test tube. (If amount of filtrate is limited, a 1-ml sample may be used.)
   CAUTION: Do not dilute sample for this test.
2. Add 5 drops of starch indicator and 2 drops of hydrochloric acid.
3. Titrate with "iodine" solution until a permanent blue color develops.

Calculations

$$SO_3^{2-}\ (\text{mg/l}) = \frac{\text{ml of iodine solution x 320}}{\text{ml of filtrate}}$$

2) PROCEDURE II: DARK FILTRATES

Use procedure for light filtrates if possible, as it is simpler and more accurate. However, if the color change cannot be seen, do not dilute the sample; proceed with the dark filtrate procedure. If the filtrate is not too dark, a sample larger than 1 ml may be used.

1. Pipette 2 ml of "iodine" solution into each of two 125-ml flasks.
2. Add 20 ml deionized water to each flask.
3. Pipette 1 ml or more of the filtrate to both flasks. Flask No. 1 will be the blank. Use white sheet of paper for background to better see color change.
4. To Flask No. 2, only add 4 drops of hydrochloric acid and 5 drops of starch indicator solution. The solution will turn to a dark blue-black color.
5. Titrate with sodium thiosulfate dropwise until the blue-black color disappears and the color matches the blank solution in Flask No. 1.

Calculations

$$SO_3^{2-}\ (\text{mg/l}) = \frac{(\text{ml of iodine solution} - (\text{factor x ml of sodium thiosulfate})) \text{ x } 320.2}{\text{ml of filtrate}}$$

Section 9. Resistivity

Resistivity of the mud, filtrate and filter cake is sometimes needed in order to help evaluate the electric logs.

Equipment

1. Mud, filtrate and filter cake.
2. Direct reading resistivity meter for drilling fluids.
3. Calibrated resistivity cell.
4. Thermometer, 32 to 220°F

Procedure

1. Fill the clean, dry resistivity cell with freshly stirred mud or filtrate. Try to ensure no air bubbles are entrained. Fill the cell to the correct volume according to the manufacturer's procedure.
2. Connect the cell to the meter.
3. Measure the resistance in ohm-meters if using the direct reading meter. The value should be set to ohms if a "not direct meter" is being used.
4. Note the temperature of the measurement.
5. Clean the cell, rinse with deionized water and dry.

Calculations

1. Report the mud resistivity Rm or filtrate resistivity Rmf in ohm-meters to nearest 0.01 units.
2. Report the sample temperature in °F.
3. If the reading is in ohms, convert to ohm-meters by:

   Resistance (ohm-meter) =
   R (ohms) x K (cell constant, m^2/m)

Section 10. Glycol Testing Procedure (Field procedure to determine the glycol content of a drilling fluid)

A) REFRACTOMETER

Equipment

1. Refractometer for determining the glycol volume percent range used in the mud system. Several types of refractometers can be used. A commonly used type is the Atago N10E. The instrument measures glycol contents in the 0 to10% range. If for some reason a range outside of this is desired, check with the manufactures specifications for a different range.
2. 10-, 20- or 50-ml retort, oil-free steel wool, complete with glassware.

Reagents

Glycol used in the drilling fluid.
Distilled or deionized water.
Graduated cylinders, storage bottles.

Procedure I

1. Prepare a glycol in water calibration curve. This curve is made by adding various volumes percent of glycol in deionized water (typically 1 to 6% by volume is used). Run each mixture through the retort and plot on a linear graph paper the corresponding BRIX reading vs. the original volume percent of glycol added. BRIX is the name of the unit of refractometer measurement for determination of the glycol.
2. Run a retort on the drilling fluid.
3. Record the volume percent liquid.
4. Shake up the liquid collected in the graduated cylinder from the retort.
5. Place 2 to 4 drops of the liquid from the retort on the clean refractometer prism surface. Make sure the entire prism is covered with the liquid and close the cap. Look into the refractometer window with the prism pointed toward a bright light source (see Figure 18).

Figure 18: Refractometer.

6. Record the BRIX reading and using the glycol calibration curve, convert the reading to glycol volume percent in the mud.
7. Glycol percent whole mud = glycol percent from calibration curve x liquid fraction of the mud. Liquid fraction of the mud is F_w.

B) DUAL-TEMPERATURE RETORT ANALYSIS FOR GLYCOL SYSTEMS

Glycol as the primary inhibitor in the GLYDRIL™ 2000 system will deplete from the system as it is adsorbed onto shales. It is therefore important to measure and control the level of the glycol in the drilling mud. This test procedure can be used to measure the concentration of all types of glycols. This is not an API defined test, but uses the API retort procedure.

Equipment

API standard retort test kit, a 50-ml is preferable for accuracy. It must be fitted with a temperature control, which will permit heating at 302°F (150°C) and 950°F (510°C).

Procedure II

1. Place a known volume of mud into the lower cup of the retort cell. It is important that this sample contain as little entrained air as possible. Insert fine, oil-free steel wool as required into the upper part of the cell.

Assemble the cell and seal the threads with high-temperature grease (Never-Seez) or equivalent to reduce leakage through the threads.

2. Set temperature controller to 302°F (150°C). Heat the retort until all the water has been collected (approximately 90 min). Note this volume as V1.
3. Re-adjust the temperature controller to 950°F (510°C), and continue to distill over the remainder of the liquid phase. Note the final volume as V2.

Volume % of glycol =

$$\frac{(V2 - V1) \times 100}{\text{Sample volume of mud}}$$

NOTE: the presence of other liquids with high boiling points, such as lubricants or oil will interfere with the results of this test.

C) CHEMICAL DETERMINATION OF GLYCOL USING CENTRIFUGE

Procedure

1. Collect 8 ml of filtrate and transfer this to a graduated centrifuge tube.
2. Add 3 g of NaCl salt to the tube and shake it well until most of the salt is dissolved.
3. Centrifuge the tube for 3 min.
4. The glycol will have separated out of the saturated NaCl solution and will have formed a layer on the top. The volume of this layer can be found from the graduations on the tube. Note this volume (V).

Volume % glycol in filtrate =

$$\frac{V \times 100}{\text{volume filtrate (ml)}}$$

Volume percent glycol in whole mud = volume % glycol in filtrate x liquid fraction of mud (F_w). Where liquid fraction (F_w) equals %/100 from mud, and is obtained from the retort.

Section 11. KLA-GARD® Concentration

QUANTITATIVE DETERMINATION

A procedure has been developed for approximating the concentration of excess KLA-GARD. The test procedure is based on the strong reaction of KLA-GARD and the chemical Reinecke salt with the formation of a white precipitate. Detailed procedures and the materials needed for conducting the test are described below.

Equipment and materials needed

1. Reinecke salt.
2. Containers with caps.
2. Sample of KLA-GARD.
3. Syringe (optional).
4. Micro-filters (optional).
5. Distilled water.

Procedure

Section 1. KLA-GARD standard solutions: Prepare standard KLA-GARD solutions for comparison testing. To prepare a 1 lb/bbl (3 kg/m^3) KLA-GARD solution add 1 gram KLA-GARD to 350 ml of tap water. Known concentrations, from 1 lb/bbl (3 kg/m^3) to the highest level used, should be prepared. For example, 1, 3, 5, 7 and 9 lb/bbl (3, 9, 14, 20 and 26 kg/m^3) standard solutions should be prepared for most applications. These standard solutions should be labeled with the date they were prepared; they will only last approximately one month unless a bactericide is used.

Section 2. Reinecke salt indicator: To prepare the indicator solution, dissolve approximately 3% by weight of the Reinecke salt into distilled water (tap water can be utilized if distilled is not available). Only small amounts of the indicator solution should be prepared because the shelf life is only 7 to 10 days at temperatures below 65°F (18°C). At temperatures above that, the shelf life of the indicator solution decreases rapidly. For this reason, we recommend the indicator solution be stored in a refrigerator and that new solutions be prepared often. To prepare a small quantity of the indicator solution, dissolve 0.75 g of the Reinecke salt into 24.25 g of distilled water. Allow to dissolve for at least 4 hr before use, then thoroughly shake the solution before using it. It is normal for some insoluble material to remain on the bottom of the container after standing. This can be filtered out as explained below.

Section 3. When testing for the KLA-GARD concentration, a sample of drilling fluid filtrate and a clear sample of the Reinecke salt solution are required.

Section 4. Prepare a clarified quantity of the Reinecke salt solution by drawing about 5 ml into a syringe, then forcing the solution through a micro-filter securely attached to the syringe. Collect the clear fluid in a small vial. If the above equipment is not available, the Reinecke salt solution can still be used without filtering.

Section 5. Having prepared the indicator solution, conduct the KLA-GARD test as follows:

A) In small vials (one for each of the prepared KLA-GARD standard solutions), place 40 drops of distilled water and 8 drops of salt indicator solution and shake well. To these vials, add 8 drops of the KLA-GARD standard solutions (a different standard to each vial) and shake for 5 sec. Seal and label the vials with the known KLA-GARD concentrations.

B) In a small vial, place 40 drops of distilled water and 8 drops of Reinecke salt indicator solution and shake well. To this vial, add 8 drops of the mud system filtrate and shake for 5 sec. Seal and label the vial.

Section 6. Allow the precipitates to settle for about 30 min. Compare the height of the precipitate for the filtrate (unknown) to the standards. Re-check results after 1 hr.

Section 7. By matching the height of the precipitate in the system filtrate to the height of the precipitate in one of the standards, the concentration of KLA-GARD can be estimated.

Section 8. If viscosity or other factors in the filtrate interfere with the test, use 80 drops of water instead of 40 drops for both the filtrate and the standards and repeat the test.

Section 12. Permeability Plugging Test Procedure

Equipment

1. Cylindrical cell, one fitted to accept ¼-inch thick porous disc.
2. Heating jacket.
3. Spacer ring.
4. Two end caps (one with screen for hydraulic end).
5. Two stems: one with quick connect for hydraulic hose, the other with valve for top of cell.
6. Hydraulic pump with quick connect hose and coupling.
7. Hydraulic fluid.
8. Piston with O-rings to separate hydraulic fluid from mud.
9. T-bar wrench for piston positioning.
10. Reservoir receiver cell with bleed-off valve.
11. Back pressure regulator attachment.
12. Two thermometers.
13. Two safety locking pins.

Procedure

1. Preheat the heating jacket to the desired temperature. Open the cell and check all O-rings and replace any damaged O-rings. Apply a thin coating of silicone grease on the two O-rings on the floating piston. Screw the floating piston onto the T-bar wrench and install the piston into the bottom of the cell, working it up and down to ensure that the piston moves freely in the cell.

   NOTE: the bottom of the cell is the end with the shorter recess. Position the piston so that it is near the bottom edge of the cell and unscrew it from the wrench. This will be the inlet end or may also be called the hydraulic end.
2. Before unscrewing the T-bar wrench, position the piston flush with the edge of the recess. Place an O-ring in the recess of the inlet end of the cell. Install the hydraulic cell end cap (bottom cap) into the inlet end of the cell. Use a silicone grease to lightly cover the O-ring on the end cap to allow for easier installation. Install the set screws, check for alignment marks, align properly and tighten snugly into the recesses of the cell cap. Use the hardened steel set screws and coat them with Never-Seez to facilitate their tightening and removal. Use the T-wrench from the other end to push the floating cap down against the end cell cap to remove any trapped air.
3. Install and tighten the inlet valve stem with the nipple of the quick-connect on it. The valve stem can be filled by attaching it to the hydraulic pump and slowly operate the pump with the release valve closed. When the stem is full, open the pump pressure relief valve and use the T-wrench from the other end to push the floating cap down against the end cell cap to remove any trapped air.
4. Turn the cell upright and fill cell with 300 ml of drilling mud. This will be the outlet end. Place an O-ring into the recess in the top end of the cell. Install the hydraulic hose and with the hand pump, pump the mud to just within the edge of the recess and then place a disk on top of the O-ring then disconnect hose. *NOTE: The disks must be soaked for at least 5 to 10 min in freshwater prior to use when testing a water-base mud. If an oil or synthetic mud is being tested, then the disks must be soaked 5 to 10 min in the representative base oil prior to use. Disks must never be re-used.*
5. Install the end cap on the outlet end. Use a silicone grease to lightly cover the O-ring on the end cap to allow for easier installation. Be sure that the set screw recesses are aligned with the set screws and

then tighten the set screws snugly against the cap. Next, install the outlet valve stem with a safety valve into the end of the cell cap and close the valve. Then holding the valve assembly, place the cell into the heating jacket until it bottoms out. Rotate the cell clockwise until the cell locks in place over the alignment pin that is in the bottom of the heating jacket.

6. Install a metal thermometer in the thermometer well in the top of the cell. Place the filtrate reservoir onto the top of the valve stem assembly ensuring that the small valve O-ring is in good condition and lock the reservoir in place by installing the safety retaining pin. Next install the back pressure receiver device onto the top of the valve stem and lock into place with the safety retaining pin. Connect the quick connect from the hydraulic pump to the valve stem on the inlet end of the cell before applying pressure. Apply 200 psi on the cell and leave the valve on the pump closed. As the cell is heating up, there will be an increase in pressure in the cell due to the heating up of the hydraulic oil in the cell. Maintain the 200 psi pressure by releasing the built-up pressure by opening the valve on the hydraulic pump.
7. Heat the cell to the desired temperature. The test temperature for this series of tests will be 150°F. Record the time it takes to heat up to the desired temperature. Close the pressure release valve on the pump and apply the desired pressure to the cell with the hydraulic pump. Apply 1,500 psi working hydraulic pressure to the cell with the hydraulic pump.

   NOTE: When working with the heated, pressurized cell, ensure that all are wearing safety glasses. The mud and/or filtrate will be near the temperature at which the test is run and slowly opening the reservoir drain valve will minimize any splattering of the fluid and potential contact with eyes, fingers and hands.
8. Once the desired hydraulic pressure is applied, apply some pressure to the back pressure receiver not to exceed 50 psi and slowly open the safety valve. After 30 sec, slowly open the drain valve on the reservoir and collect the mud and/or filtrate that comes out into a small glass beaker and continue to collect the fluid until the reservoir just blows dry. This should be recorded as the spurt loss.
9. Close the drain valve on the receiver reservoir and maintain the desired pressure on the cell with the hydraulic pump. The pressure will decrease during the filtration of the mud so additional pressure will be applied to the cell in order to maintain a constant pressure. Maintain the pressure on the cell for 30 min occasionally bleeding of the liquid collected in the reservoir. After 30 min are completed, record the total amount of liquid recovered (excluding the spurt loss). Close the drain valve and open the pressure release valve on the pump. While the back pressure is still applied, opening the pressure release valve on the pump will push the floating piston to the bottom of the cell and allow for recovering of the hydraulic oil back into the pump. Turn off the power to the heating jacket.
10. After the oil has been recovered in the pump, close the safety valve. Remove the hydraulic quick connect from the cell. Close the back pressure source valve and then bleed off the back pressure from the receiver. After the pressure has been completely removed from

the reservoir, remove the safety retaining pin and remove the back pressure device from the reservoir.

11. Either allow the cell to cool while still in the heating jacket or carefully remove the cell from the heating jacket and allow to cool by allowing to come to room temperature or place the cell in the sink and cool off with water. After the cell has completely cooled off, hold the cell such that the safety valve stem is not pointing toward yourself or others. Slowly open the safety valve to remove any trapped pressure in the cell. Repeat this process several times to ensure that all pressure has been released. Remove the top cell cap of the cell and then turn the cell upside down in the sink. Remove the hydraulic end cap (bottom cell cap) to expose the floating piston. Screw the T-bar wrench into the piston and push down to force out the mud and the disk out the opposite end of the cell.

    NOTE: This should be done carefully as too much applied pressure will cause the mud to splatter out. Completely disassemble the cell and clean and dry the entire apparatus.

12. Recover the disk and filter cake and wash off same very lightly with freshwater or base oil if an oil mud is tested and measure the filter-cake thickness in 32nd of an inch. The total fluid loss is calculated as follows:

Total fluid loss (ml) = spurt loss (ml) + 2 x (30 min fluid recovery (ml))

Figure 19: Permeability plugging apparatus.

Section 13. Brookfield Viscometer Used to Obtain Low-Shear-Rate Viscosity (LSRV)

The following standardized procedures are recommended when measuring LSRV of a FLO-PRO fluid. These procedures are designed to allow accurate measurement of the unique viscosity profile provided by a FLO-PRO fluid. Every effort should be made to use these procedures in order to make valid comparisons between wells.

Equipment

Testing will be made using the **Brookfield LVDV-II+ or LVDV-III** digital viscometer with guard leg and cylindrical spindles (#1 through 4). The LVDV-II+ is the most widely used viscometer. The LVDV-III model has a wider speed selection and also has a programmable feature neither of which is necessary for FLO-PRO applications. The spindle viscosity ranges at 0.3 RPM using the LVDV-II+ or LVDV-III are: #1 to 20,000 cP, #2 to 100,000 cP, #3 to 400,000 cP and #4 to 2,000,000 cP.

When ordering a Brookfield viscometer specify LVDV-II+ or LVDV-III with cylindrical spindles #1 through 4. The

LV prefix designates the proper spring torque for the viscosity ranges M-I desires. Also Input voltage and frequency should be indicated when ordering. The units are available in 115, 220 or 230 volts AC and 50 or 60 cycle frequency.

Other necessary equipment includes the large heating cup (3.25 in. diameter by 4 in. deep) and a mixing device to heat the fluid sample evenly.

Location

Locate the Brookfield where a stable power supply is available. It should be located where vibrations from the rig are minimal. Rig vibrations may contribute to inaccurately low LSRV measurements. Dust may damage the electronics or the bearings so a dust-free atmosphere should be located.

Setup

Remove the viscometer from the case. Install gear assembly on stand with rack and insert Brookfield viscometer post in assembly and tighten clamp screw. Level viscometer by rotating it slightly on the stand and/or by adjusting feet. Use the bubble level on the top as a guide.

Plug the temperature probe into the receptacle on the back of the viscometer. Make sure the power switch on the rear of the viscometer is OFF. Plug the power cord into the receptacle on the back of the viscometer and plug into appropriate AC socket. *"The AC input voltage and frequency must be within the appropriate as shown on the name plate of the Viscometer." NOTE: The LVDV-II+ must be earth grounded to ensure against electronic failure!*

This is a delicate electronic instrument. Care should be taken to avoid power surges and frequency variations. Disconnect the viscometer when not in use.

Pour the FLO-PRO fluid to be tested to within a ½ in. of the top of the heating cup and heat to desired temperature. The fluid sample should be tested at the same temperature as the other rheological properties. Stir the sample while heating to equalize the temperature throughout the sample. A Hamilton Beach-type mixer with a rheostat may be used. Stir at a slow rate to avoid overshearing the fluid which may result in polymer degradation. Avoid entrapping air while stirring. Entrapped air will result in erroneous readings.

Initializing the Viscometer

While heating the sample, remove the rubber band holding the viscometer shaft in place. The viscometer uses a gem bearing and calibrated spring. Avoid impact and twisting of the shaft. Always replace the rubber band when not using the viscometer.

Turn on the viscometer. The digital screen will display the operations as the viscometer autozeroes itself. The following screen descriptions are for the LVDV-II+ viscometer, the most widely used model.

When the power is on the screen will flash "Brookfield DV-II+ LV Viscometer," then "Version 3.0." The screen then automatically changes to "Remove spindle Press any key." Press any of the yellow keys and the display changes to "Autozeroing Viscometer." After autozeroing the screen will display "Replace spindle press any key." Select the appropriate cylindrical spindle for the desired viscosity. Most applications will use the Number 2 spindle. Note that the spindles are marked on the neck.

Attach the spindle by threading it onto the shaft. These are left-handed threads. Hold the shaft in one hand to prevent damage to the spring and bearing while tightening the spindle. After tightening the spindle, press one of the yellow buttons on the key pad. The default display will appear on the screen.

Viscometer display

The screen will look something like this:

```
% 0. 0          S 62
0.0 RPM         70.5°F
```

Values may vary according to what was last tested.

The upper left corner displays viscometer readings. These may be in the following units:

% viscometer torque (%)
cP viscosity (cP or mPa)
SR — Shear Rate (always 0 due to spindle configuration)
SS — Shear Stress (always 0 due to spindle configuration)

The default units for the LVDV-II+ is %. The value in the upper left corner should be ~ +1.0% when not in use. A value greater may indicate damage to the bearing or spring.

M-I is using viscosity in cP (centipoise) as the standard reading. To select the appropriate units, press the Select Display key until the cP value appears. The SI unit mPa is equivalent to cP (40,000 cP = 40,000 mPa).

The upper right-hand value is the spindle code. The code allows the viscometer to correctly calculate viscosity for a given spindle geometry. **The code for the #2 spindle is S62** and for the #3 spindle it is S63. If the correct code is not on the screen, press **"Select Spindle"** key. The S will blink. Use the orange up and down arrow keys to search for the correct spindle code. When the correct code is found, press the **Select Spindle** key and this code will become the default code.

This viscometer can test viscosity at 0.3, 0.5, 0.6, 1.0, 1.5, 2.0, 2.5, 3.0, 6.0, 10.0, 12.0, 20.0, 30.0, 50.0, 60.0 and 100.0 RPM. To set the speed, press the orange arrow keys until the desired speed appears to the right of RPM. *M-I is doing all testing at 0.3 RPM.* When the proper value appears, press the set speed key. NOTE: **The viscometer is now running, press the MOTOR ON/OFF key to stop the viscometer, but hold the desired speed in memory.** The value in the lower right is temperature as noted by the temperature probe.

The viscometer is now ready for running a test.

NOTE: In order to have SI units displayed, hold the AUTO RANGE key while turning on the viscometer. To get temperature in °C hold the Select Display key while turning on the power.

Testing

After setting up the viscometer and heating the sample to test temperature, a test can be performed. Centralize the heating cup beneath the viscometer. Boundary effects caused by eccentric placement may alter LSRV readings. **Make sure the guard leg is in place to avoid damage to the spindle, bearings and spring.** Lower the viscometer until the recess in the spindle shaft is at the top of the fluid. While lowering the viscometer hold it under the front to prevent excessive vibration.

Set a timer for 3 min and turn on the viscometer motor with the MOTOR ON/OFF button. Take viscosity readings at 1, 2 and 3 min while the viscometer is running. These values should be labeled LSRV1, LSRV2 and LSRV3, respectively. Part of the first min will involve torquing the spring. Generally the fluid will reach its maximum viscosity within the three min time. The 3-min reading may actually be less than the 2-min reading. If the 3-min reading is less than the 2-min reading the spindle is probably slipping as it "drills a holes in the fluid."

After the test, turn off the viscometer and raise the spindle above the fluid.

Clean up

Turn off the viscometer. Remove the spindle, then the guard leg. Wash them thoroughly. Replace the guard leg and reinstall the rubber band on the shaft. Keep the viscometer away from water and dust and unplug it when not in use to avoid power surges.

Calibration

Calibration fluids are available from Brookfield and their agents. The viscometer should be calibrated regularly. The procedures are outlined in the Brookfield Digital Viscometer Operating Instructions Manual, which is included with the viscometer. This manual also contains more detailed information not discussed here.

Address:
Brookfield Engineering
  Laboratories, Inc.
240 Cushing Street
Stoughton, MA 02072, USA
Tel: 617-344-4310
Fax: 617-344-7141

Figure 20: Brookfield viscometer and thermocup.

Section 14. Drill Pipe Corrosion Ring Coupons

Drill pipe Corrosion Ring Coupons that are placed in the drillstring is one technique for monitoring the drilling fluid corrosion rate. The removal and examination of rings after a period of approximately 100 hr exposure downhole can be highly informative. The cause of corrosion, and type of corrosion may possibly be determined by this technique.

The examination of the scale, if any, will indicate the dissolved gas that is causing the damage. If the source is known, the type of chemical treatment may be more effectively selected for better control.

The circular-ring-type corrosion coupon, or “corrosion ring” as it is called, should fit properly in the tool joint box. Ideally, the ring should be made from steel identical to that of the tool joint, to avoid galvanic corrosion. This is usually impractical so a steel similar to the drill pipe is used. Usually AISI 4130 is used with no difficulty noted. If any steel other than the 4130 is used, it should be noted on the ring package/report form. The rings are machined from cold drawn seamless tubing, and usually are not quenched and tempered.

There are plastic encapsulated coupons that are available in limited areas for use in the drillstring. Each operation should compare the results, and experimentally determine the proper correlation that would be desired. Do not assume they are interchangeable in results.

The plastic encapsulated coupons have a preweighed metal ring that is heat sealed similar to a specimen in metallography. The overall dimensions of the coupon are similar to the steel coupon to ensure a proper fit. Proper care in placement is necessary. There can be a coating fracture then the chips could plug the bit nozzles.

To process the plastic encapsulated ring, the plastic is broken away using a vise or other technique that will allow no damage to the metal band. The scale, if any, is observed and tested. The coupon then is cleaned just as a steel coupon would be. The "K"-factor calculations are different for each of the plastic encapsulated coupons. The calculation of the corrosion rate is performed in the same manner as with the steel coupons.

A) RING COUPON MONITORING PROCEDURE

1. Drill pipe corrosion coupon rings should be kept in the drillstring for a minimum of 40 hr. Exposures of less than 40 hr should not be used because the initial corrosion rates are unusually high and can give misleading data. It is normal to run the coupons for approximately 100 hr. The rings are run in pairs. The first in the Kelly Saver Sub, and the one downhole in the last joint of drill pipe above the collars. The rings are left in the string for more than one bit run if necessary. The total time in the string is recorded, not just rotating hours.

   Care should be taken to ensure that the recess space in the box joint is clean to prevent an interference with tool joint makeup, and mechanical damage to the ring. During the installation, it has been suggested that a clean dry glove be used to place the coupon ring in the tool joint.
2. The drill pipe corrosion ring form or envelope should be filled out completely. The information should include the operator, well name, location and person with address/fax/phone number to contact with results. The type of drilling fluid, location of rings in the string, type of metallurgy if not AISI 4130, date in and date pulled from the string is also desired. The total hours run, and the depth in and depth out can be recorded. The chemical treatments used could also be noted and copies of the daily mud check enclosed.
3. Following the test period, remove the coupon ring, and wipe off all of the drilling fluid residue with a cloth. The ring should be examined visually for the severity of corrosion and for any mechanical damage. If the ring looks "like-new," then the rate is probably low. If severe corrosion is evident, the cause of the corrosion should be determined promptly so remedial action can be performed quickly. After the ring is dry, it is suggested that it be replaced in the vapor inhibited paper, then in the mailing envelope. The API RP 13B-1 supplement now states that oil or grease is NOT to be put on the coupon before sending to the lab. For many years they said to put oil on them. The oil or grease can interfere with the scale identification in the laboratory, and is a nuisance to the lab when trying to clean the coupon.

B) LABORATORY COUPON ANALYSIS

1. Before proceeding with a quantitative evaluation of the corrosion rate of the ring, the ring should be rinsed with a suitable solvent. This will remove any oily residue that may have been added. Verify that the coupon number agrees with the number on the shipping package. If it does not, proper communications should be set up to resolve the discrepancy. If a number can not be seen clearly, or with the aid of a

scope, note this. Do not report a coupon ring number on the report if it can not be verified. Prior to cleaning and weighing, determine the nature of the scale, if any. A magnet will indicate an oxide, and possibly oxygen corrosion. With the dropwise addition of the Iron Sulfide Test Solution, effervescence could indicate the presence of carbonates from the dissolved acid gas, carbon dioxide.

The presence of iron sulfide is also noted during this same test. A yellow precipitate of arsenic sulfide would appear as “miniature scrambled eggs” in nature. The mere presence of a yellow color just may indicate some of the steel is dissolving from the coupon, and without the yellow/green precipitate, no sulfide should be noted on the report.

2. The ring should be cleaned with a detergent solution and a stiff bristle brush or equivalent. It may be necessary to dip the ring in inhibited 15% hydrochloric acid one or more times to aid in removal of the corrosion products. The ring should be scrubbed with detergent after each acid dip. When the ring is clean, rinse with clear water and then anhydrous acetone or methyl alcohol to allow the ring to dry. (Always maintain proper safety precautions when handling chemicals.)
3. After the ring has been properly processed, then it should be reweighed at least to the nearest milligram. The weight loss can be calculated. If there is significant loss of metal due to mechanical damage, it is recommended that Mechanical Damage (MD) be noted, and all of the calculations be shown at the bottom of the ring report. The weight loss in g multiplied by the “K”-factor, divided by the total hours in the string yields the corrosion rate.

Visual inspection

If corrosion is evident when the coupon is removed from the string, it may be due to either a pitting or a generalized attack. The corrosion rates determined by the weight loss method assume a generalized attack. Pitting rates from the corrosion ring can not be made. Mechanical damage to the ring can be seen if the metal has cuts, dents or metal moved from the surface. In some cases, the ring will exhibit a series of worn spots, indicating considerable movement of the ring in the box recess area. Just being bent may not cause a high rate to be determined.

Since the corrosion ring is exposed to the mud pumped down the drill pipe, the weight loss of the metal will include that removed by corrosion and also erosion.

Examination of the ring may reveal deep pitting with a relatively low weight loss. This condition would indicate a more severe corrosion problem than if it were all generalized corrosion.

The pH and Pf should be at the optimum for each water-base system. CONQOR 404 should be considered if the rate is higher than desired. Any bacteria problem should be addressed, and treated, as this can cause serious problems in the system also.

The normally accepted value for corrosion rates of freshwater muds is 2 lb/ft^2-y or less with no pitting noted. Values near the top of this range should be evaluated for the addition of proper chemical treatments and possible mechanical alterations to the rig equipment.

C) CALCULATION OF CORROSION RATES

Corrosion ring coupons are available from drilling fluid service and supply companies. The coupons are usually supplied numbered, preweighed, wrapped in a vapor inhibited wrapper along with a shipping envelope. The coupon number is also recorded on the package along with a calculation factor called “K”-factor. In the USA, most factors are offered to obtain the corrosion rate in lb/ft^2-y. This value may be changed into other units if desired with the aid of tables or other equations. The difference in the weight of the cleaned coupon before and after the test period is determined by weighing. This weight loss multiplied by the “K”-factor divided by the total hours will yield the corrosion rate.

It is possible to have other laboratories recalculate corrosion rates by reweighing the coupon at another facility. Always take extreme care in weighing and recording the proper data to ensure excellent integrity.

1. The corrosion rate in pounds per square foot per year (lb/ft^2-y) could be calculated by the following formula if a “K”-factor was not supplied:

$$\text{lb/ft}^2\text{-y} = \frac{\text{wt loss (mg)} \times 144 \times 365}{453{,}600 \times \text{*area (in}^2\text{.)} \times \text{days exposed**}}$$

$$\text{or} = \frac{\text{wt loss (mg)} \times 2{,}781}{\text{*area (in}^2\text{.)} \times \text{hours exposed**}}$$

$$\text{kg/m}^2\text{-y} = \frac{\text{wt loss (mg)} \times 10{,}000 \times 365}{1{,}000{,}000 \times \text{area (cm}^2\text{)} \times \text{days exposed**}}$$

$$\text{or} = \frac{\text{wt loss (mg)} \times 87.60}{\text{*area (cm}^2\text{)} \times \text{hours exposed**}}$$

* The total surface area of the ring is used in these calculations.

** Time used based on total time in the drillstring.

2. Following are the conversion rates between the various units for steel coupons:

mpy = 24.62 x lb/ft^2-y
mpy = 5.03 x kg/m^2-y
lb/ft^2-y = 0.04 x mpy
lb/ft^2-y = 0.20 x kg/m^2-y
kg/m^2-y = 0.20 x mpy
kg/m^2-y = 4.90 x lb/ft^2-y

Oil-Mud Testing (Including Diesel Oil, Mineral Oil and Synthetic Fluids)

Section 1. Aniline Point Determination

This test determines the aniline point of an oil. When diesel oil was popular as an additive in muds, a high number near 150°F was preferred. A lower number could indicate a potential for attack of the rubber/elastomer compounds in contact with the drilling fluid. Aniline is an aromatic organic chemical, and oils similar in nature would have a low (undesirable) aniline point.

The oil and fresh (pure) aniline are mixed in equal amounts, and temperature increased until they are miscible, and clear in a tube. The temperature (°F) at which this happens, is the aniline point.

Equipment

1. Aniline reagent, pure.
2. Pyrex glass test tube.
3. Coiled wire through stopper for stirring.
4. Thermometer, 0 to 220°F.
5. Heat source.

Procedure

1. Into the clean and dry test tube, add equal volumes of oil and aniline.
2. Place the stopper with stirrer and thermometer into the neck of the tube.
3. While stirring, warm the mixture until it changes from cloudy to a miscible/clear phase.
4. Remove the heat source, and continue until the mixture becomes trace cloudy. Read the thermometer at that point, and record as the aniline point.

   CAUTION: The aniline is a poison chemical, and extreme care is suggested in handling it. Keep the chemical off body, hands, etc., and clothes. In case of serious contact, flush with water about 15 min, while a physician is called for guidance.

Section 2. Density (Mud Weight)

Equipment

1. Density may be expressed as pounds per gallon (lb/gal), pounds per cubic foot (lb/ft^3), g per cubic centimeter (g/cm^3), Specific Gravity (SG) or pressure gradient. Any instrument of sufficient accuracy to permit measurements within ±0.1 lb/gal or ±0.5 lb/ft^3 (±0.01 g/cm^3) may be used. The mud balance is the instrument generally used. The weight of a mud cup attached to one end of the beam is balanced on the other end by a fixed counterweight and a rider free to move along a graduated scale. A level bubble is mounted on the beam. Attachments for extending the range of the balance may be used.
2. Thermometer.

Procedure

1. The instrument base should be set up approximately level.
2. Measure and record the temperature of the mud. Fill the clean, dry cup with mud to be tested; put on and rotate the cap until firmly seated. Make sure some of the mud is expelled through the hole in the cap to free trapped air or gas.
3. Wash with base oil or wipe the mud from the outside of the cup.

4. Place the beam on the support and balance it by moving the rider along the graduated scale. The beam is balanced when the bubble is on the center line.
5. Read the density at the side of the rider toward the knife edge. Make appropriate corrections when a range extender is used.
6. Report the density to the nearest 0.1 lb/gal or 0.5 lb/ft^3 (0.01 g/cm^3).
7. To convert to other units, use the following relationships:

Specific gravity or g/cm^3 =

$$\frac{lb/ft^3}{62.3} \text{ or } \frac{lb/gal}{8.345}$$

Mud gradient in psi/ft =

$$\frac{lb/ft^3}{144} \text{ or } \frac{lb/gal}{19.25} \text{ or } \frac{g/cm^3}{2.31}$$

Calibration

The instrument should be calibrated frequently with freshwater. Freshwater should give a reading of 8.33 lb/gal or 62.3 lb/ft^3 (1.0 g/cm^3) at 70°F (21°C). 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.

Section 3. Viscosity and Gel Strength

Equipment

The following instruments are used to measure the viscosity and/or gel strength of drilling fluids:

1. Marsh funnel — a simple device for routine measurement of viscosity.
2. Direct-indicating viscometer — used for measurement of plastic viscosity, yield point and gel strength.
3. Thermometer.

A) MARSH FUNNEL

Description

The Marsh funnel is dimensioned so that, by following standard procedures, the outflow time of 1 qt (946 cm^3) of freshwater at a temperature of 70±5°F (21±3°C) is 26±0.5 sec. A graduated cup or 1-quart vessel is used as a receiver.

Procedure

1. Cover the orifice with a finger and pour a freshly taken mud sample through the screen into the clean, dry, upright funnel until the liquid level reaches the bottom of the screen (1,500 ml).
2. Quickly remove the finger and measure the time required for the mud to fill the receiving vessel to the 1-qt (946-ml) mark.
3. Report the result to the nearest second as Marsh funnel viscosity. Report the temperature of the sample in °F or °C.

B) ROTATIONAL VISCOMETER

Description

Direct-indicating viscometers are rotational-type instruments powered by means of an electric motor or a hand crank. Mud is contained in the annular space between two cylinders. The outer cylinder or rotor sleeve is driven at a constant rotational velocity. The rotation of the rotor sleeve in the mud produces a torque on the inner cylinder or bob. A torsion spring restrains the movement. A dial attached to the bob indicates displacement of the bob. Instrument constants have been so adjusted that plastic viscosity and yield point are obtained by using readings from rotor sleeve speeds of 600 and 300 RPM. The apparent viscosity in centipoise equals the 600-RPM reading divided by 2.

CAUTION: These Direct-Indicating Viscometers are designed for a maximum temperature of 200°F (93°C) in unpressurized fluids. If fluids above 200°F (93°C) are to be tested, the operator should use a solid metal bob. Liquid trapped inside a hollow bob may vaporize and cause the bob to explode when immersed in high-temperature fluid.

1) PROCEDURE: PLASTIC VISCOSITY, YIELD POINT AND APPARENT VISCOSITY

1. Place a sample of mud in a thermal cup and immerse the rotor sleeve exactly to the scribed line. Measurements should be made with a minimum delay from the time of sampling. Tests should be conducted at either 120±2°F (50±1°C) or 150±2°F (65±1°C). (Operators may require testing at additional temperatures.)
2. Heat or cool the mud sample to the selected temperature. The sample should be sheared at 300 RPM while heating or cooling to ensure a uniform sample temperature. Record the temperature of the sample.
3. With the sleeve rotating at 600 RPM, wait for the dial reading to reach a steady value (the time required is dependent on the mud characteristics). Record the dial reading for 600 RPM.
4. Shift to 300 RPM and wait for the dial reading to come to a steady value. Record the dial reading for 300 RPM.
5. The Plastic Viscosity (PV) in centipoise equals the 600-RPM reading minus the 300-RPM reading. The Yield Point (YP) in lb/100 ft^2 equals the 300-RPM reading minus the plastic viscosity. Report the temperature of the sample in °F or °C. The Apparent Viscosity (AV) in centipoise equals the 600-RPM reading divided by 2.

2) PROCEDURE: GEL STRENGTH

1. Place the mud sample in position as above. Stir at high speed for 10 sec.
2. Allow the mud to stand undisturbed for 10 sec with the motor off. With the clutch in neutral, slowly and steadily turn the handwheel in a counterclockwise direction to produce a positive dial reading. The maximum reading is the initial gel strength in lb/100 ft^2. For instruments having a 3-RPM speed, the maximum reading attained after starting rotation at 3 RPM is the initial gel strength. Report the temperature of the sample in °F or °C.
3. Restir the mud at high speed for 10 sec and then wait 10 min. Repeat the measurement as before and report the maximum reading as the 10-min gel strength in lb/100 ft^2. Report the temperature of the sample in °F or °C.
4. In some instances, a 30-min gel strength measurement may also be required. To conduct the 30-min gel strength, repeat the 10-min gel strength procedure as above but allow the fluid to stand undisturbed for 30 min.

Calibration

Operation of the instrument as a direct-indicating viscometer depends upon maintenance of the correct spring tension and the correct speed of sleeve rotation. Procedures are available from the manufacturer to test spring tension and speed. Generally, however, a simpler test of reliability of the instrument can be made by measuring a Newtonian liquid of known viscosity (e.g. silicone liquids, sugar solutions or petroleum oils of known viscosities at specified temperatures).

Section 4. Filtration

HIGH-TEMPERATURE, HIGH-PRESSURE TEST

Equipment

CAUTION: Carefully observe the recommendations of the manufacturer on limitations on sample volume and pressure for the temperature to be used.

The instruments consist essentially of a controlled pressure source, a cell designed to withstand a working pressure of at least 1,000 psi (70.3 kg/cm^2), a system for heating the cell, and a suitable frame to hold the cell and heating system. For filtration tests at temperatures above 200°F (93.4°C), a pressurized collection cell should be designed to withstand a working back pressure of at least 500 psi (35.3 kg/cm^2) to avoid flashing or evaporation of the filtrate at high temperatures.

The filter cell is equipped with a thermocouple or thermometer, thermometer well, oil-resistant gaskets, and support for the filter medium. For temperatures to 350°F (149°C) use filter paper (Whatman No. 50 or equivalent). For temperatures above 350°F (149°C) use a Dynalloy disc for each test. API currently does not have a recommended procedure for temperatures above 400°F. A non-hazardous gas such as nitrogen (preferred) or carbon dioxide should be used for the pressure source. Above 300°F, only nitrogen should be used. *WARNING: Do not use N_2O for this test, as the cartridges may allow the cell to explode. The API warns against this usage.*

For stirring a sample, if possible use a high-speed mixer, 11,000 to 17,000 RPM under load, with single, corrugated impeller approximately 1 in. (25 mm) in diameter (e.g. Multimixer or Hamilton Beach) and a container such as Hamilton Beach mixer cup No. M 110-D.

NOTE: Each filter or fiber glass backed filter can be used only ONCE!

Due to the expansion of the fluid while heating it is necessary to leave space in the heating cell to prevent over pressurization.

Recommended head gaps.

Temperature (°F)	Empty Space (in.)
Up to 300	1
300 - 400	1.5 - 2
400 - 500	2.5 - 3

It is also necessary to apply pressure to the filtrate receiver to prevent boiling the filtrate. The recommended back-pressures for various temperatures are as follows (the top pressure must be adjusted to maintain the proper differential):

Temperature (°F)	Bottom Pressure (psi)
Up to 300	100
300 - 400	200
400 - 500	300

Procedure for temperatures not above 300°F (149°C)

1. Connect the heating jacket to the correct voltage for the unit before the test is to be made. Place a thermometer in the thermometer well. Preheat the heating jacket to 10°F above selected test temperature. Adjust the thermostat in order to maintain the desired temperature.
2. Stir the mud sample for 5 min. Prepare the cell with the mud sample then filter paper, taking care not to fill the cell closer than 1 in. (2.5 cm) from the top to allow for expansion.
3. Place the cell into the heating jacket with both top and bottom valves closed. Transfer the thermometer to the cell thermometer well.
4. Place the pressure unit on the top valve and lock in place. Lock the bottom pressure receiver to the bottom valve. Apply 200 psi (1,380 kPa) to

the top pressure unit and 100 psi (690 kPa) to the bottom pressure unit while keeping the valves closed. Open the top valve and apply 200 psi (1,380 kPa) to the mud while heating to the selected temperature.

5. When the sample reaches the selected temperature, increase the pressure of the top pressure unit to 600 psi (42.18 kg/cm^2) and open the bottom valve to start filtration. Collect the filtrate for 30 min maintaining the elected temperature within ±5°F. If back pressure rises above 100 psi (7.03 kg/cm^2) during the test, cautiously reduce the pressure by drawing off a portion of the filtrate. Record the total volume.
6. The filtrate volume should be corrected to a filter area of 7.1 in.^{2} (45.8 cm^2). If the filter area is 3.5 in.^{2} (22.6 cm^2), double the filtrate volume and report.
7. At the end of the test, close both valves. Back the T-screw off and bleed pressure from both regulators.

   CAUTION: Pressure in the filter cell will still be approximately 500 psi (35 kg/cm^2). Maintain cell in upright position and cool to room temperature before disassembling.

Procedure for temperatures between 350 to 400°F (149 to 204°C)

1. Connect the heating jacket to the correct voltage for the unit before the test is made. Place a thermometer in the thermometer well. Preheat the heating jacket to 10°F above the selected test temperature. Adjust the thermostat to maintain the desired temperature.
2. Stir the mud sample for 10 min.
3. Prepare the cell with the stirred mud sample taking care not to fill the cell closer than 1½ in. (38 mm) from the top to allow for expansion, then place the appropriate filtration medium.
4. Place the cell into the heating jacket with both top and bottom valves closed. Transfer the thermometer to the cell thermometer-well.
5. Place the pressure unit on the top valve and lock in place. Lock the bottom pressure receiver to the bottom valve. For testing at temperatures from 300 to 400°F (149 to 204°C) apply 300 psi (21.1 kg/cm^2) to both pressure units with the valves closed. Open the top valve and apply 300 psi (21.1 kg/cm^2) to the mud while heating.
6. When the temperature of the sample reaches the selected test temperature, increase the pressure of the top pressure unit to 800 psi (56.2 kg/cm^2) and open the bottom valve to start filtration. Collect the filtrate for 30 min, maintaining the test temperature at ±5°F. Maintain the initial back pressure during the test; cautiously reduce the pressure by drawing off a portion of the filtrate. Allow sufficient time for all filtrate to drain from the receiver, and record the total volume. Time of heating of the sample in the filter cell should not exceed one hour.

   CAUTION: Testing at high temperatures and high pressures will call for added safety precautions. Pressuring systems and filtrate receivers should be equipped with suitable safety relief valves. Heating jackets should be equipped with both an overheat safety fuse and thermostatic cutoff. Vapor pressure of the liquid phase of muds becomes an increasingly critical design factor as test temperatures are raised.

   CAUTION: Pressure in the filter cell will still be approximately 500 psi (35 kg/cm^2). Maintain cell in upright position and cool to room temperature, bleed all pressure before disassembling.

Section 5. Activity

The equation for the activity curve using calcium chloride salt is:

$$A_W = 1.003 + [(4.66079 \times 10^{-3}) \times (\% \text{ by wt } CaCl_2)] - [(7.2903 \times 10^{-4}) \times (\% \text{ by wt } CaCl_2)^2] + [(5.6323 \times 10^{-6}) \times (\% \text{ by wt } CaCl_2)^3]$$

Section 6. Electrical Stability

1. An electrical stability meter is used to measure the relative stability of a water-in-oil emulsion. This measurement is made using a pair of accurately and permanently spaced electrode plates which are immersed in a fluid sample. A DC power source is used to provide an AC voltage which is applied to the electrode at a constant rate of voltage increase. The voltage at which the emulsion becomes conductive is indicated by current flow between the electrode plates, completing the circuit will (1) illuminate the indicator bulb when using a manual dial meter or (2) cause the numerical reading to stabilize when using a direct reading meter.
2. Thermometer.

Procedure

1. Place a sample which has been passed through a 12 mesh screen (Marsh Funnel Screen) in a container assuring that the fluid has been stirred well.
2. Heat or cool the sample to 120±5°F (50±2°C). Record the temperature at which the electrical stability reading was taken.
3. After inspecting cleanliness of the electrode, immerse the electrode into the mud. Hand stir the sample with the electrode for approximately 10 sec. Hold the electrode motionless and do not allow the electrode to touch the sides or bottom of the container when taking a reading.
4. There are two types of stability meters available. The newer, most recent meter uses an automatic direct reading. The older manual type requires that the power source button is depressed manually and held during the entire test while a dial is turned. Do NOT move the electrode during measurements.

Figure 21: Electrical stability meter.

5. a) If using the newer style direct reading electrical stability meter, depress and hold down button until displayed value stabilizes. Record the displayed value as the electrical stability (volts).
   b) If using the older style manual dial electrical stability meter, depress and hold down red button while starting from a zero reading, increase the voltage by moving the dial in a clockwise direction at a rate of 100 to 200 volts per second. Continue increasing the voltage until the indicator light illuminates. When the indicator light illuminates, the voltage ramp has ended.

Calculation for the older style manual dial electrical stability meter:

Electrical stability (volts) = dial reading x 2

6. Clean electrical probe and repeat test. The two readings should not differ by more than 5%. If the readings differ by more than 5%, check meter and electrical probe for malfunctions.
7. Record the average of the two measurements as the electrical stability.

Section 7. Liquid and Solids

Equipment

1. A retort is used to determine the quantity of liquids and solids in the drilling fluid. Mud is placed in a steel container and heated until the liquid components have been vaporized. The vapors are passed through a condenser and collected in a graduated cylinder, and the volume of liquid is measured. Solids, both suspended and dissolved, are determined by difference. A 10, 20 or 50 ml retort may be used in determining the liquid and solids content. To reduce the amount of error associated with entrained air, a 20 or 50 ml retort is recommended.

Procedure

1. Be sure the retort, condenser and liquid receiver are clean, dry and cooled from the previous use.
2. Collect a sample of mud and allow it to cool to approximately 75±2°F (24±1.4°C) or ambient temperature. Screen the sample through a 12 mesh screen to remove lost-circulation material and large cuttings.
3. If the mud contains gas or air, slowly stir 2 to 3 min to remove the gas.
4. Lubricate the threads on the sample cup and condenser tube with a light coating of Never-Seez (this is the only material to be used according to API procedures). This prevents vapor loss through the threads.
5. Lightly pack a ring of steel wool into the retort chamber above the sample cup. Liquid steel wool is NOT approved by API.
6. Fill the retort sample cup with gas-free oil mud.
7. Place the lid on the sample cup and allow the mud overflow to pass through the hole in the lid. To ensure a correct volume of sample, some mud must flow through the hole.
8. Wipe the overflow from the sample cup and lid.
9. Place a clean, dry receiver under the condenser discharge.
10. Heat the retort, continuing for 10 min beyond the time that no more condensate is being discharged from the condenser.
11. Remove the liquid receiver from the retort. Note the total volume of liquid recovered. If solids are present in the liquid, whole mud has boiled over and the procedure MUST be repeated.
12. Record the volumes of oil and water in the liquid receiver after it has cooled to 75±2.5°F (24±1.4°C) or ambient temperature.
13. From the volumes of oil and water collected and the volume of the original mud sample, calculate the percent by volume oil, water and solids of the mud.
14. All solids — both suspended and in solution — will be retained in the retort. For muds containing substantial quantities of salt, calculations of suspended solids content will be in error unless corrections are made for the dissolved salt.

Section 8. Chemical Analysis of Oil-Base Drilling Muds

A) ALKALINITY (P_{om}) (V_{SA}•API)

The alkalinity of an oil mud is determined by breaking the emulsion and titrating the mixture rapidly to the first color change or endpoint. The number of ml of 0.1 N sulfuric acid used in the titration per ml of mud is reported as the alkalinity of the mud or P_{OM}.

Two testing procedures will be discussed which use different solvents. Procedure #1 is an effective test for an oil-base fluid using either barite or hematite as the weighting material. Procedure #2 is not as effective because of the difficulty with detecting the end point when used for the testing of an oil-base fluid which uses hematite as the weighting material.

Equipment and reagents

1. Titrating assembly (magnetic stirrer or Hamilton Beach stirrer).
2. 5-ml pipette.
3. 16-oz Mason jar, 500-ml beaker or equivalent.
4. Xylene-isopropyl alcohol mixture (50:50) or Propyl Propasol.
5. Phenolphthalein Indicator.
6. Sulfuric acid solution, 0.1N H_2SO_4.

Procedure

1. When using Testing Procedure #1, put 100 ml of Xylene/IPA blend or 75 ml of Propyl Propasol in glass jar. Fill a 5-ml syringe with whole mud to past the 3-ml mark.
2. Disperse 2 ml of oil mud into the solvent and add 200 ml of distilled water.
3. Add 15 drops of phenolphthalein.
4. Stir rapidly with a magnetic stirrer, Hamilton Beach stirrer or equivalent.
5. While stirring, slowly titrate with 0.1N H_2SO_4 until the pink color just disappears. Continue stirring and if no pink color reappears within one min, stop stirring. It may be necessary to stop stirring and allow the mixture to separate into two phases to more clearly see the color in the aqueous phase.
6. Let the sample stand for 5 min. If no pink color reappears, the end point has been reached. If the pink color returns titrate a second time with sulfuric acid. If pink color returns a third time titrate again. Do not titrate after the third time.
7. P_{om} = ml of 0.1 N H_2SO_4 per ml mud.
8. Excess lime (lb/bbl) = P_{om} x 1.295.

B) SALINITY — CHLORIDES IN THE WHOLE MUD

Reagents

- Potassium Chromate Indicator.
- 0.282N AgNO3 solution.

The chloride titration is a continuation of the alkalinity measurement. To the sample that has just been checked for alkalinity, add 10 to 15 drops of potassium chromate indicator. Titrate with 0.282N $AgNO_3$ while stirring until the first color change occurs. This is the endpoint. Do NOT titrate to “brick red.”

API requires the salt content to be expressed as total chlorides in the mud phase calculated as below:

Total Cl^- in mud (mg/l) = ml of 0.282 N $AgNO_3$ x 10,000 per ml mud

The chloride content can also be expressed in other units depending on the operating company, the information desired and the mud system.

Two salt systems ($CaCl_2$/NaCl)

In two salt or binary salt systems, it is necessary to test the mud for the calcium chloride concentration by the calcium titration procedure described below. This measurement is required along with the previous titration for salt content to determine the amounts of NaCl and $CaCl_2$ present in the system.

Equipment

1. Titrating assembly (magnetic stirrer with stirring bar or Hamilton Beach mixer stirrer).
2. 5-ml pipette.
3. 6-oz Mason jar with cap.
4. Xylene-isopropyl alcohol mixture (50:50) or Propyl Propasol.
5. Calver II Indicator powder.
6. 8N sodium hydroxide buffer solution.
7. 5-ml syringe.
8. Deionized water.
9. EDTA solution (Strong Versenate or equivalent) 0.1 molar, 1 ml = 4,000 mg/l calcium), also known as “x 10 strong.”

Procedure

1. Add 100 ml of 50/50 xylene/isopropanol solvent or 75 ml of Propyl Proposal to jar.
2. Fill 5-ml syringe with whole oil mud past the 3-ml mark.
3. Displace 2 ml of oil mud into the jar.
4. Cap the jar tightly and shake for 1 min.
5. Add 200 ml deionized water to the jar.
6. Add 3 ml 1N sodium hydroxide buffer solution.
7. Add 0.1 to 0.25 g Calver II Indicator powder.
8. Recap the jar and shake again for 2 min. Set jar aside for 15 to 30 sec to allow the two phases to separate. If a reddish color appears in the aqueous (lower) phase, this indicates that calcium is present.
9. Place jar on the magnetic stirrer or Hamilton Beach mixer. Stir only fast enough to agitate the aqueous phase without remixing the upper and lower phases.
10. Titrate very slowly with 0.1 molar EDTA or Strong Versenate solution. A very distinct color change from the reddish color to a blue-green color indicates the end point has been reached.

C) WHOLE MUD CALCIUM CALCULATION

Nomenclature

P_{om} = Whole mud alkalinity
Ca^{2+} mud = Whole mud calcium
Cl^- mud = Whole mud chlorides
Vo = % by volume oil
Vw = % by volume water

Example

P_{om} = 3.0 cm^3
Ca^{2+} mud = 33,600 mg/l
Cl^- mud = 100,000 mg/l
Vo = 59.5%
Vw = 25.0%

D) SULFIDES

This procedure is used to measure the active soluble sulfides concentration in an oil-base mud.

Equipment

1. Complete Garrett Gas Train (GGT).
2. H_2S Dräger tubes (low range and high range).
3. Flowmeter.
4. Flexible tubing made of Latex rubber or Tygon (plastic or equivalent).
5. Magnetic stirrer.
6. Magnetic stirring bar (¼ in. x 1 in.).
7. Hypodermic syringe: 10-ml glass or plastic.
8. 2 molar citric acid/isopropyl alcohol/demulsifier solution.
   a. 420 g ($C_6H_8O_7H_2O$) citric acid dissolved into 1,000 ml deionized water.

   b. To this solution add 25 ml of Dowell W-35 demulsifier from Fann Instrument or equivalent (an asphalt dispersant chemical).
   c. To this solution add 200 ml of isopropyl alcohol.
9. Defoamer: octanol (CAS # 111-87-5).
10. 25-ml graduated cylinder.
11. Carrier gas — CO_2 cartridges, or preferably, nitrogen. Do Not use N_2O.
12. Sample injection tube: 6-in. (15.2-mm) long PTFE (Teflon or equivalent) needle or equivalent.

Procedure

1. Start with a clean, dry Garrett Gas Train.
2. Modify the Garrett Gas Train by inserting the sample injection tube through the rubber septum so that the bottom end of the dip tube is approximately ½ in. from the bottom of chamber 1. The dip tube is used so that the mud sample can be injected directly into the citric acid solution.
3. Arrange the magnetic stirrer and stirring bar (in chamber 1) so that the bar will rotate freely.
4. Install CO_2 cartridge.
5. Add 20 ml of 2 molar citric acid/isopropyl/demulsifier solution to chamber 1.
6. Add 10 drops of octanol defoamer to chamber 1.
7. Break tips of H_2S Dräger tube and insert into the Garrett Gas Train holder on the extreme right side. The arrow indicating the gas flow should be pointing down. Place an O-ring on the Dräger tube.
8. Insert the flowmeter in the other holder with the air flow arrow pointing up. Place an O-ring on the flowmeter.
9. Install the top of the Garrett Gas Train and tighten all screws to seal.
10. Adjust the dispersion tube so that the tube is positioned above the liquid level.
11. Connect the rubber hose from the regulator to the dispersion tube. Connect the rubber hose from chamber 3 to the Dräger tube. *DO NOT START GAS.*
12. Draw into the syringe the whole mud sample volume plus 0.5 ml of excess mud. The excess mud compensates for the hold-up volume inside the injection tube.
13. Insert the syringe into the dip tube, and using a rubber band, secure the syringe plunger to the dip tube. This will prevent the citric acid-defoamer mixture from traveling up the dip tube when pressure is applied.
14. Gently flow gas through the dispersion tube for 10 to 15 sec to purge air from the GGT. Regulate the flow of gas to avoid frothing of the solution in chamber 1. Check for leaks and for proper operation of the flowmeter.
15. Turn on the magnetic stirrer. Adjust speed so that a vortex is formed. Carefully lower the dispersion tube into the liquid to a point just above the stirring bar.
16. Lower the injection tube so that the bottom is slightly below the dispersion tube. This will allow the oil mud to be injected into the vortex.
17. Slowly inject a measured amount** (see Table 6 on page 3.38) of oil-base mud into chamber 1 through the injection tube. Increase the speed of the stirring bar to improve dispersion and to prevent oil mud from sticking to the walls. Continue to stir for 1 min.

18. Use a rubber band to secure the plunger of the syringe in place. Restart gas flow. Adjust the rate so that the flowmeter shows between 200 and 400 ml/min by keeping the flowmeter ball between the red marks on the flowmeter.
19. Observe changes in appearance of the Dräger tube. Note and record the maximum distinct darkened length (in units marked on the tube) before the front starts to "feather" or smear. Continue flowing for a total of 15 min, a second gas cartridge may be required.
20. Clean the GGT immediately after use to minimize deterioration of the plastic. Clean the chambers and passages with warm water and a mild detergent. Wash the dispersion tube and injection tube with an organic solvent such as acetone and then with water. Occasionally, the dispersion tube may require soaking in an acid to remove calcium carbonate deposits. The organic solvents can crack the lucite body of the GGT.

Using the sample volume, the Dräger tube darkened length, and the Dräger tube factor, calculate sulfides in the sample.

$$\text{GGT sulfides (mg/l)} = \frac{\text{darkened length x tube factor}}{\text{sample volume (ml)}}$$

Pilot Testing

In drilling fluid engineering work, calculations are based upon the oilfield barrel. The oilfield barrel contains 42 U.S. gal. Mud treatments are generally made by adding a certain number of pounds (or fractions of a pound) of material to the oilfield barrel of mud.

For pilot test and laboratory work, an oilfield barrel would be difficult to handle. It is much more convenient to work with a much smaller sample of fluid. Instead of working with a barrel of fluid one works with a "barrel equivalent." A barrel equivalent contains 350 ml of fluid. This representative amount for one barrel is obtained as follows:

An oilfield barrel has a volume of 42 U.S. gal. It would hold 350 pounds of fresh water. Three hundred and fifty g of water would occupy a volume of 350 ml in the metric system. Thus, 350 ml can represent the 42 U.S. gal, or oilfield barrel. If 1 g of a material is added to this barrel equivalent, this would be the same as adding 1 lb of material to an oilfield barrel. If a liquid is added to the final barrel, then the specific gravity of the fluid must be taken into account. For example, if a fluid has a specific gravity of 1.2, then only 0.83 ml will be needed for 1 g or 1 lb/bbl. The specific gravities of most materials are contained either in Product Bulletins or the Material Safety Data Sheets.

Purpose

By using these reduced quantities of materials several possible treatments can be tested economically prior to treating the mud system as a whole. This procedure is useful not only when contamination arises, but also to evaluate treatments when an alteration of fluid properties is planned. It should be noted chemical solubility and effectiveness may be enhanced by actual circulation conditions, i.e. temperature and pressure. Therefore, it is advisable to stage the addition of chemical treatment over two or more circulations to avoid over-treatment. For example, 60 to 70% of the planned addition can be made on one circulation and adjustments to the total amounts made prior to adding the remaining chemicals. Additions of lime to a clay-base mud are an example of a treatment difficult to pilot test without heat aging to simulate downhole conditions.

Equipment

1. Balance accurate to 0.1 g.
2. Hamilton Beach-type mixer or equivalent.
3. Samples of chemicals to be tested (preferably obtained at the rig site).
4. Equipment to perform mud check.
5. Roller oven complete with aging cells if the sample is to be heat aged.

Procedure

A sample of the fluid to be tested is collected and a base mud check run and recorded. Based on the properties recorded a judgement is made as to the type and amounts of treatment chemicals necessary to achieve the desired results.

Since the agitation imparted to the mud sample during the addition of treating chemicals can by itself alter the fluids properties, a "control" sample should be stirred for an equivalent amount of time and the properties recorded for comparison.

Careful notation of the order of addition of all treatments should be kept. The reasoning for this is most evident by the example of the properties displayed by fluid samples containing water, bentonite and NaCl. If the salt is added first hydration of the bentonite is suppressed and the fluid properties are markedly different. Whether the chemicals are added “dry” or in solution will also effect results. For this reason chemicals used in pilot testing should be added in their normal order of addition to the mud system and in the same physical state.

Which additives to test is governed by the following criteria:

1. Availability.
2. Suitability for existing mud system and hole conditions, i.e. temperature and salinity.
3. Effectiveness relative to cost.

To more closely simulate bottom-hole conditions samples are frequently heat aged at bottom-hole temperatures and for time periods equivalent to anticipated periods of no circulation. Most ovens used for this procedure allow the cell to remain either static, roll or rotate during aging. If the sample is to be heat aged certain safety precautions must be observed (some guidelines taken from API Recommended Practice 13I, Fifth Edition, Supplement 1, July 1996).

1. Use only cells constructed of stainless steel (303, 304 or 316, but not 314) unless testing for prolonged periods of time at elevated salinities. In that case the use of premium metal cells is advised, i.e. Iconel® 600, Hastalloy® C or Incolloy® 825. These types of cells do have a lower strength rating than the stainless cells. Any aging cell used must be constructed to exceed the temperature and pressure requirements of the test.
2. A major consideration is not to overfill the aging cells. When filling the cells an adequate space must be left to allow expansion of the test fluid. In general no more than 1 bbl equivalent should be added to an individual cell. This will generally leave a gap of ±2 in.
3. Upon the cells removal from the oven the cell should be allowed to cool to room temperature. If you cannot touch the cell barehanded it is not cool enough, even when cool to the touch the interior may still be hot. *REMEMBER: THE CELL CONTAINS PRESSURE GENERATED BY THE VOLUME EXPANSION OF THE FLUID!*
4. After cooling, the top of the cell can be SLOWLY unscrewed, be sure any remaining pressure is released prior to the final turns. If you can safely wiggle the top without hearing an escape of pressure you are probably safe, however NEVER lean over the top of a cell while opening. Any remaining pressure can propel the top at gun-barrel speeds and with the same effects.

Figure 22: Hot roll oven.

The M-I program MUDCALC generates a list showing the quantities of materials needed to mix pilot tests at specified concentrations. The specific gravities of many products are contained within the program. You will need to have the specific gravity of any product not listed.

To assist in pilot testing some approximate spoon weights for common oilfield products are listed (see Table 7). It is preferred to accurately weigh the products to 0.10 g whenever possible. The spoon weights can be inaccurate depending on the physical condition of the sample.

Product	Specific Gravity	¼ Teaspoon	½ Teaspoon	1 Teaspoon	1 Tablespoon
Benex	1.2	0.90	1.80	3.60	10.80
Caustic soda	2.13	1.25	2.50	5.00	15.00
CMC	1.60	0.50	1.10	2.30	6.60
Desco	1.60	0.75	1.50	3.00	9.60
Diaseal M	>2.0	0.80	1.60	3.20	12.60
Drispac	1.50-1.60	0.60	1.20	2.40	7.60
DUO-VIS	1.5	0.75	1.50	3.00	10.00
FLOXIT	1.4	0.40	1.00	2.00	6.50
GELEX	1.2	1.00	1.75	3.50	11.00
Gypsum	2.32	1.30	2.30	4.90	12.60
Ironite sponge	4.30	1.50	3.50	8.00	25.00
KOH	2.04	1.00	2.50	5.00	15.00
KWIK-THIK	2.3-2.6	1.00	2.00	4.00	12.00
Lime	2.20	0.60	1.30	2.40	7.70
Lo Loss	1.5	0.50	1.50	3.00	9.00
LO-WATE	2.8	1.00	2.25	4.50	13.00
MF-1	1.2	0.50	1.50	3.00	10.00
M-I BAR	4.20	2.08	4.17	8.33	25.00
Mica	2.75	0.50	0.80	2.00	5.80
Mixical	2.70	1.00	2.50	5.00	15.00
M-I GEL	2.30-2.60	0.98	1.95	2.90	6.70
MY-LO-JEL	1.45	0.63	1.25	2.50	7.50
Phos	2.5	1.00	3.00	6.00	20.00
POLYPAC	1.5-1.6	0.50	1.00	2.00	8.00
Potassium chloride	1.98	1.90	3.10	6.10	19.10
Quebracho	1.10-1.40	1.00	2.00	4.00	12.00
RESINEX	1.65	0.75	1.50	3.00	10.50
Salt	2.16	1.50	3.00	6.00	18.00
SALT GEL	2.20-2.40	0.70	1.50	3.00	8.80
SAPP	1.90	1.15	2.30	4.60	13.80
Soda ash	2.51	1.60	3.00	6.00	17.80
Sodium bicarbonate	2.16	0.72	1.45	2.90	8.70
Soltex	1.2-1.5	0.50	1.00	2.00	6.00
SP-101	1.05	0.75	1.50	3.00	10.00
SPERSENE	1.20	0.50	1.00	2.00	6.00
Starch	1.50	0.60	1.00	2.00	5.80
TANNATHIN	1.60	0.85	1.70	3.40	10.20
THERMPAC	1.50	0.50	1.00	2.00	8.00
VG-69	1.57	1.00	2.00	3.00	9.00
XCD polymer	1.5	1.00	1.90	3.60	10.70
XP-20	1.83	1.17	2.33	4.67	14.00

Table 7: Approximate spoon weights for common oilfield products.