Instructions

ALKALINITY and LIME CONTENT

WATER BASED DRILLING FLUIDS

Alkalinity is the acid neutralizing power of a substance. Alkalinity measurements in drilling fluid testing may be made on the whole mud (designated with a subscript *m*) or on the filtrate (designated with a subscript *f*). The data collected can also be used to estimate the concentrations of hydroxyl (OH^-), carbonate (CO_3^{-2}) and bicarbonate (HCO_3) ions in the drilling fluid. Knowledge of the mud and filtrate alkalinity is important in many drilling operations. Mud additives, particularly some organic deflocculants, require an alkaline environment in order to function properly. Alkalinity arising from hydroxyl ions is generally accepted as being beneficial while alkalinities resulting from carbonates or bicarbonates may be detrimental to mud performance.

The ions that are primarily responsible for *filtrate* alkalinity are the hydroxyl (OH^-), carbonate (CO_3^{-2}) and bicarbonate (HCO_3^-) ions. The carbonates can change from one form to another by changing the pH of the solution. Other inorganic ions such as borate's, silicates, sulfides and phosphates may also contribute to the alkalinity. It is important to realize the following calculations are only estimates of the concentrations of the reported ionic species based on theoretical chemical equilibrium reactions. The composition of mud filtrates is often so complex that the interpretation of alkalinities may be misleading. Any particular alkalinity value represents all of the ions which will react with the acid within the pH range over which that particular value was tested. Anionic organic thinners and filtrate reducers contribute to a large portion of the M_f alkalinity value and may also mask the endpoint color change and render the test highly inaccurate in muds treated with organic thinners. For simple bentonite-based mud systems containing no organic thinners, the Phenolphthalein (P_f) and the methyl orange (M_f) alkalinities may be used as guidelines to determine the presence of carbonate/bicarbonate contamination and the treatment necessary to alleviate the problem. If organic thinners are present in large amounts, the conventional P_f/M_f test is suspect, and the P_1/P_2 method should be used instead.

Equipment - Water Based Drilling Fluids:

#147-16 Pocket pH Sensor (Optional)
#153-26 Titration Dish, Polyethylene
#153-28 Stirring Rod, Polyethylene
#153-29 Syringe, glass tip, 2 ml
#153-34 Pipette, Serological, 1 ml x 1/100 ml, glass
#153-40 Pipette, Serological, 10 ml x 1/10 ml, glass

Reagents:

#220-01 Phenolphthalein Indicator sol'n, 8 oz
#230-08 Sulfuric Acid sol'n, N/50, 8 oz
#240-02 Methyl Orange Indicator sol'n, 8 oz

Procedure - *Filtrate* Alkalinity, P_f, M_f

1. Measure one or more milliliters of filtrate into the titration dish.

2. Add two or more drops of Phenolphthalein Indicator solution. If the solution turns pink, add N/50 Sulfuric Acid, drop by drop from the pipette, while stirring, until the pink color just disappears. If the filtrate is so colored that the end point cannot be seen, use a pH meter and titrate until the pH of the solution drops to pH 8.3, and this will be the end point.

3. Report the Phenolphthalein Alkalinity of the filtrate, P_f, as the number of milliliters of N/50 Sulfuric Acid required per milliliters of filtrate.

4. To the same sample which was titrated to the P_f endpoint, add two or three drops of Methyl Orange Indicator solution. Add the N/50 Sulfuric Acid drop by drop from the pipette while stirring until the color of the indicator changes from yellow to pink. The end point may also be taken when the pH of the sample drops to pH 4.3 as measured with a pH meter (more accurate).

5. Report the Methyl Orange Alkalinity of the filtrate, M_f, as the total milliliters of N/50 Sulfuric Acid per milliliters of filtrate required to reach the Methyl-Orange end-point. This also includes the amount of acid used to reach the Phenolphthalein, P_f, end-point.

Calculation, P_f, M_f (Estimation of Hydroxide (OH^-), Carbonate (CO_3^{-2}) & Bicarbonate (HCO_3^-) ions)

Test Results	***Calculation, Concentration mg/liter***	
$P_f = 0$	$M_f \times 1220 = mg/L\ HCO_3^-$	**(Indicates Bicarbonate ion only)**
$P_f = M_f$	$P_f \times 340 = mg/L\ OH^-$	**(Indicates Hydroxide ion only)**
$2P_f < M_f$	$2P_f \times 600 = mg/L\ CO_3^{-2}$	**(Indicates Carbonate ion)**
	$(M_f - 2P_f) \times 1220 = mg/L\ HCO_3^-$	**(Indicates Bicarbonate ion)**
$2P_f = M_f$	$M_f \times 600 = mg/L\ CO_3^{-2}$	**(Indicates Carbonate ion only)**
$2P_f > M_f$	$(2P_f - M_f) \times 340 = mg/L\ OH^-$	**(Indicates Hydroxide ion)**
	$(M_f - P_f) \times 1200 = mg/L\ CO_3^{-2}$	**(Indicates Carbonate ion)**

Procedure - *Whole Mud* Alkalinity, P_m

1. Measure 1 ml of drilling mud into the titration dish and dilute with 25 to 50 ml of distilled water.

2. Add four or five drops of Phenolphthalein Indicator solution and while stirring, titrate with N/50 Sulfuric acid solution until the pink color just disappears. If the end point color change cannot be seen, it can be taken when the pH drops to pH 8.3 as measured on a pH meter. If cement contamination is suspected, the titration must be performed as rapidly as possible and the end-point is reported as the first disappearance of the pink color.

3. Report the Phenolphthalein alkalinity of the whole mud, P_m, as the number of milliliters of N/50 Sulfuric acid required per milliliter of mud.

Procedure - Lime Content, Estimated

1. Determine the P_f and P_m of the filtrate and whole mud as described in the Alkalinity test.
2. Determine the volume fraction of water F_w, using the percent of water from the liquid and solids as determined in a Retort analysis.

$$F_w = \frac{\text{\% Water by Volume}}{100}$$

3. Report the Lime Content of the Fluid:

$$\textit{Estimated Lime, lb/bbl} = 0.26\ (P_m - F_w \times P_f)$$

$$\textit{Estimated Lime, kg/m}^3 = 0.742\ (P_m - F_w \times P_f)$$

Alternate Alkalinity Procedure

The P1/P2 Back Titration method is used to overcome some limitations of the P_f/M_f alkalinity method. A serious problem arises with anionic organic thinners, filtrate reducers and their degradation products which may contribute to a large portion of the alkalinity value, as well as masking the end point color change. These organic materials make a particularly large contribution to the M_f alkalinity and thus render the test highly inaccurate in treated with organic thinners. If organic thinners are present in large amounts, the P1/P2 method should be used, but it also has its limitations. See the table below:

Method	Advantages	Disadvantages
P_f/M_f	Traditional Method	Interference with the M_f titration
	2 Titrations, 1 Sample	Bicarbonate result normally too high
P1/P2	Eliminates interference in M_f titrations	3 Titrations with 3 samples Caustic measurement critical Uses a toxic material - $BaCl_2$

Equipment - P1/P2 Alkalinity Method

#147-16 Pocket pH Meter (Optional)
#147-54 pH paper strips, range 7 - 14 pH
#153-16 Graduate Cylinder, 25 ml x 2/10 ml, glass
#153-18 Graduate Cylinder, 10 ml x 2/10 ml, glass
#153-20 Graduate Cylinder, 5 ml x 1/10 ml, glass
#153-26 Titration Dish, polyethylene
#153-34 Pipette, 1 ml x 1/100 ml, glass
#153-36 Pipette, 2 ml x 1/100 ml, glass
#168-05 Stirring Rod, polyethylene

Reagents:

#206-02 Distilled Water, 16 oz
#220-00 Phenolphthalein Indicator sol'n, 2 oz
#260-01 Sodium Hydroxide sol'n, 16 oz
#275-04 Hydrochloric Acid sol'n, 0.02N, 8 oz
#285-07 Barium Chloride, 10 % sol'n, 8 oz

Procedure - P1/P2 Alkalinity

1. Determine the P_f alkalinity as described above.

2. Measure and add 1.0 ml of *Filtrate* to the titration dish, then add 25 ml of distilled water.

3. Using a pipette add 2.0 ml of Sodium Hydroxide, 0.1N and stir well.

4. Measure the pH of the solution with the pH paper or the pH meter.
   If the pH is 11.4 or greater proceed to the next step.
   If the pH is less than 11.4 add 2.0 ml more of 0.1N Sodium Hydroxide solution and then proceed. Exact measurements of Sodium Hydroxide is necessary to avoid serious errors.
5. Using the 5 ml Graduate Cylinder, measure 3 ml of Barium Chloride and add to the titration dish.
   Caution: Do not use your mouth to pipette Barium Chloride as it is <u>extremely poisonous.</u>

6. Add 2 to 4 drops of Phenolphthalein Indicator solution while stirring.

7. Immediately titrate the mixture with the standard 0.02 normal Hydrochloric Acid to the first disappearance of the pink color - or to a pH of 8.3 with a pH meter. The color may reappear after a short time but do not continue the titration.

8. Report the Alternate Alkalinity, P1, as the total ml of 0.02 normal Hydrochloric acid required to reach the phenolphthalein end point.

9. Determine the Blank Alkalinity, P2. Omit the *Filtrate*, but repeat the above procedure from item 1 through 8 for determining the P1. Use <u>*exactly*</u> the same quantities of water and reagents in preparing the sample.

10. Report the Blank Alkalinity, P2, as the total ml of 0.02 normal Hydrochloric acid required to titrate the reagent mixture to the phenolphthalein end point.

Calculation - P1/P2 Alkalinity Method

When P1 > P2:

$$\mathbf{OH^-, mg/L = 340\ (P1 - P2)}$$
$$\mathbf{CO_3^{-2}, mg/L = 1200\ [P_f - (P1 - P2)]}$$

When P1 < P2:

$$\mathbf{HCO_3^-, mg/L = 1220\ (P2 - P1)}$$
$$\mathbf{CO_3^{-2}, mg/L = 1200\ P_f}$$

WHOLE MUD ALKALINITY - <u>OIL</u> BASED DRILLING FLUID

Procedure:

1. Add 100 ml of Arcosolv PNP solvent to the 400 ml beaker

2. Fill the 5 ml syringe with at least 3 ml of whole mud and discharge 2 ml into the beaker. Swirl the mixture until it is homogenous.

3. Add 200 ml of distilled water.

4. Add 15 drops of Phenolphthalein Indicator solution.

5. While stirring with the magnetic stirrer, slowly titrate with N/10 Sulfuric Acid until the pink color just disappears. Continue stirring for one more minute, and if no pink color reappears, discontinue stirring. It may be necessary to stop the stirring to allow separation of the two phases in order to more clearly see the color in the aqueous phase.

6. Let the sample stand for 5 minutes and if no pink color reappears, the Alkalinity end point has been reached. If the pink color returns, titrate a second time with the Sulfuric Acid solution. If the pink color still returns titrate a third time, but if the color returns after this third titration, call this the end point.

7. Use the total ml of N/10 Sulfuric acid solution required to reach the end point to calculate the whole mud Alkalinity, V_{sa}.

Calculation:

$$\textit{Alkalinity (Whole Mud), } V_{sa} = \frac{\textit{N/10 Sulfuric Acid, ml}}{\textit{Mud Sample, ml}}$$

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