pH CONTROL OF ROTARY DRILLING FLUIDS.

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Introduction.

The hydraulic rotary system of drilling oil well bores consists in circulating mud-laden fluid with a rotary drill. For this purpose the viscosity should lie between certain limits, sufficient to carry up the cutting and yet not too high to require excessive power for drilling and also cause undue wear and tear.

The viscosity of rotary drilling fluid is greatly reduced by addition of small quantities of reagents like sodium hydroxide, sodium silicate and sodium tannate. The viscosity falls to a minimum with the addition of 0.1 to 0.2 per cent. of the reagent and increases with large quantities. The range of concentration over which the minimum persists varies with the clay, and the reagent used is an important factor in practice, a sharp minimum being undesirable as it necessitates a close control of the quantity of the reagent.

Watson, Narayana and Govinda Rau, in their unpublished paper, have investigated the effect of such agents as myrobalan extract and alkali on the viscosity of muds from Burma oil-fields. They obtained a minimum in the viscosity curve with gradual addition of caustic soda while the myrobalan extract gave a constant value with larger additions. The purpose of this investigation is to study the corresponding effect of successive addition of these reagents on the pH of the clays. Experiments were also done with addition of hydrochloric acid and these brought out the remarkable behaviour near the isoelectric point (8.7 pH) of the mud examined.

EXPERIMENTAL.

A special form of the calomel electrode was prepared according to Randolph and Dormanwirth (*Jour. Amer. Ceram. Soc.*, 1926, 9, 541, see Fig. 2). The contact is made through a porous cup that prevents contamination of the cell by fine particles of clay. The potassium chloride in the porous cup was renewed easily. The other electrode was a Hildebrand type of hydrogen electrode. The E.M.F. measurements were taken on the valve electrometer potentiometer described previously (*Proc. Ind. Acad. Sci.*, 1934, **1A**, 390). The advantages of the electrometer were shown by quick attainment of equilibrium as shown by the following sample readings. With capillary electrometer it took 12 hours to attain any sort of equilibrium.

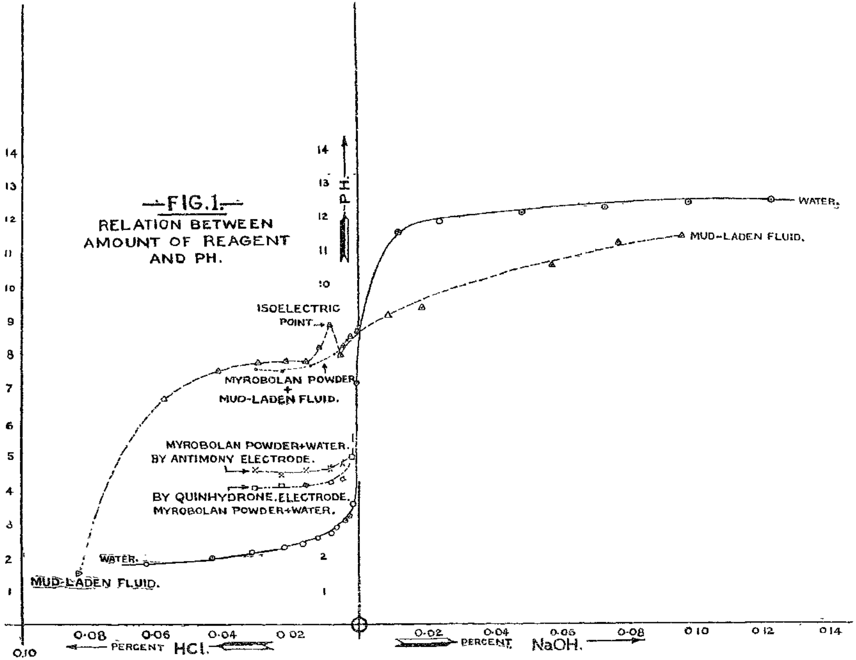

FIG. 1.
RELATION BETWEEN AMOUNT OF REAGENT AND PH.
P.H.
ISOELECTRIC POINT
MYROBOLAN POWDER + MUD-LADEN FLUID.
MYROBOLAN POWDER+WATER. BY ANTIMONY ELECTRODE.
BY QUINHYDRONE ELECTRODE. MYROBOLAN POWDER+WATER.
WATER.
MUD-LADEN FLUID.
PERCENT HCl.
PERCENT NaOH.

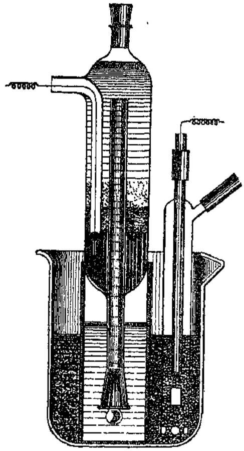

FIG. 2.
—Cell Pt.H_2 | Mud ‖ Sat. KCl, Hg_2 Cl_2 | Hg.—

	E. M. F. observed	Time
Mud laden fluid	0.7498 volt	2.30 P.M.
	0.7486 ,,	3.0 P.M.
	0.7478 ,,	3.30 P.M.
	0.7467 ,,	4.0 P.M.
	0.7459 ,,	4.30 P.M.
Mean	0.7477 ,,	

The mud used was supplied by the Burma Oil Company and had a density of 1.34 and initial pH of 8.5.

The myrobalan powder was analysed for its tannin content by the method recommended by American Leather Chemists Association. The sample contained 43.5 per cent. of tannins and 10.3 per cent. non-tannins. The tannic and elagitannic acids in the myrobalan extract were estimated by electrometric titration to be equivalent to 0.002 mols. per gram of the powder.

The pH values of tannin solutions are shown in Table I.

The values obtained with antimony electrode were higher than those determined by quinhydrone electrode. The results of calibration of antimony and bismuth electrodes are being published separately.

The pH of clays with addition of myrobalan powder was investigated next, hydrogen electrode being used. The results are as follows:

TABLE I.

Temp.	Percentage of myrobalan powder	Amount of HCl equivalent to the % myrobalan	E. M. F. observed			pH		
			Quinhydrone	Antimony	Bismuth	Quinhydrone	Antimony	Bismuth
29.62°	0.0196	0.0015	0.1619	0.2695		4.83	4.70	
25.10°	0.0502	0.0037	0.2043	0.2476		4.20	4.68	
26.61°	0.1014	0.0076	0.2065	0.2449		4.13	4.51	
27.00°	0.2002	0.0149	0.2110	0.2401		4.06	4.42	
25.00°	0.2992	0.0223	0.2155	0.2238		4.01	4.29	
23.65°	0.3980	0.0300	0.2216	0.2262		3.93	4.43	
26.80°	0.4594		0.2473		0.0415	3.44		4.28
30.26°	0.0498		0.2090		0.0677	4.40		4.71

TABLE II.

Cell Hg | Hg_2Cl_2 | KCl || mud + tannin | H_2Pt 25°–26°C.

Percentage of myrobalan powder added	Amount of HCl equivalent to the % myrobalan	E. M. F. volt	pH
0.00	0.00	0.748	8.48
0.019	0.0014	0.740	8.36
0.051	0.0038	0.728	8.10
0.093	0.0069	0.710	7.81
0.201	0.0149	0.688	7.49
0.311	0.0232	0.680	7.31
0.402	0.0299	0.680	7.34

In the following table the pH of the mud with addition of varying amounts of hydrochloric acid is given.

TABLE III.

Cell Hg | Hg_2Cl_2 | KCl || mud + HCl | H_2Pt at temperature 28°–29°C.

Amount of HCl%	E. M. F.	pH
0.002	0.742	8.37
0.003	0.737	8.24
0.005	0.714	7.83
0.008	0.766	8.71
0.011	0.729	8.06
0.015	0.702	7.66
0.021	0.703	7.67
0.029	0.701	7.62
0.041	0.684	7.34
0.057	0.637	6.56
0.082	0.337	1.53

In the following table the pH of mud with addition of different percentages of sodium hydroxide is given:—

TABLE IV.

% NaOH	E. M. F.	pH
0.011	0.780	8.98
0.019	0.792	9.24
0.039	0.838	10.00
0.058	0.865	10.50
0.077	0.905	11.17
0.096	0.920	11.40

DISCUSSION OF RESULTS.

The values obtained in all the Tables I–IV are shown graphically (Fig. 1), the values of myrobalans were reduced to their equivalent of hydrochloric acid to show the comparison.

The pH curve for the aqueous solution of the corresponding amounts of acid and alkali is also shown in the figure (1) and brings out the difference in adsorptive power of the clay for acid and alkali.

The addition of myrobalan powder changed the pH of the mud in a manner analogous to the effect on viscosity; the range of constant viscosity corresponding to 7.5 pH.

The effect of addition of hydrochloric acid was to decrease the pH at first until it reached 7.83 pH. Further addition increased the pH to 8.71 owing to the bound alkali solution being forced out owing to coagulation. Further addition of acid did not materially change the pH. It will be noticed that the flat region of pH is 7.5 for both hydrochloric acid and equivalent quantities of myrobalan.

The addition of caustic soda increases the pH approximately the same way as the increase in viscosity, the effect of adsorption being shown by the lower position with respect to that of water.

Hall (*Jour. Amer. Ceram. Soc.*, 1923, **6** (9), 989) has examined the effect of changes in hydrogen ion concentrations on the flocculation and deflocculation of clays. He concluded that the effect was a physical one until a pH of 12 was reached, after which a chemical action set in. According to him, for every clay water electrolyte mixture there exists a certain pH (the isoelectric point) at which the rate of settling of the clay is a maximum and a pH at which the rate of settling was a minimum (a point of maximum deflocculation). Neither of these two points was sharp owing to his clay being a mixture of colloids.

In the mud examined by the authors, the isoelectric point is 8.71, the viscosity increasing on both sides of the pH. Curiously enough Ambrose and Loomis (*Ind. Eng. Chem.*, 1933, **25**, 1019) obtained exactly this value for the Baroid, a mixture of barytes stabilised with bentonite prepared for the same purpose as discussed in the introduction.

Gieber and Caldwell (*Jour. Amer. Ceram. Soc.*, 1921, **4** (6), 479) made a study of the action of alkali on clay. They found that alkali was adsorbed by the clay. Salter and Morgan (*J. Phys. Chem.*, 1923, **27**, 117) believed that the lower pH value was due to preferential adsorption of the hydroxyl ions by the clay. This preferential adsorption of the hydroxyl ions, according to them, caused a lowering of the viscosity. It must, however, be pointed out that the rise or fall in viscosity due to small quantities of reagents depends upon the distance of the actual pH of the clay from its isoelectric point. Thus, Navias

(*Colloid Chemistry* by Alexander, 3, 313) cites the case of a Canadian ball clay of high pH, *viz.*, 8.0, as against 5.5 to 6.5, which is usual, for deflocculating which an exceptional procedure of adding an acid was adopted.

The marked change of aggregation of the clay particles at the isoelectric point described above, which corresponds to a considerable fall in the viscosity of the mud would point to a pH control of the deflocculating agents. The case of sodium tannate, which is used in Burma and Assam, is worth mentioning. The curve obtained by Narayana, Govinda Rau and Watson for this substance shows a minimum similar to that observed in the case of caustic soda. Analysis of the sodium tannate used by them showed that it contained 25 per cent. tannin and the rest alkali.

Another important point is the unreliability of the usual method of determining viscosity in spite of complicated apparatus and time spent in measurements due to the thixotropic property of the clay. The medium becomes very viscous when in a static condition and is quite fluid when the suspension is in motion. The formation of such a light gel is highly helpful in boring oil wells inasmuch as it prevents the heavy particles from settling. The laboratory conditions favouring, this would be thought useless in virtue of high viscosity.

SUMMARY.

1. The effect of adding acid, alkali and tannin extract on the pH of rotary drilling muds has been measured by an improved valve potentiometer using antimony, bismuth, hydrogen and quinhydrone electrodes.

2. As the rise or fall in viscosity, due to the addition of acid or alkaline reagents, depends on the distance of the actual pH of the mud from its isoelectric point, the most rational and convenient method of dealing with the problem of drilling muds is through pH measurements.

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