

The Effect of Temperature on Polyacrylate-and CMC-Treated Drilling Muds

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Synopsis

Viscometric and filtration properties have been studied at 80°F. and at elevated temperature for a saturated gypsum mud and a 20,000 ppm sodium chloride mud, treated with an acrylate-acrylamide copolymer (0.62 mole fraction sodium acrylate) and with sodium carboxymethyl cellulose (CMC). In the muds containing CMC and also for the acrylic polymer in the sodium system, the observed plastic viscosity decrease (at 175°F.) and the API filter loss increase (at 200°F.) were about what one would predict from the change in the viscosity of water with temperature. In contrast, the polyacrylate-treated gypsum mud showed a viscosity increase, rather than a decrease, at the elevated temperature, and the API filter loss increased to a level substantially greater than would have been predicted on the basis of the change in the viscosity of water. This anomalous behavior of the acrylate-treated system is interpreted as evidence of polymer-calcium ion-clay interaction. Data are presented to illustrate the extent of degradation of the acrylic polymer and CMC in a gypsum mud when heated for 16 hr. at 350°F. under a nitrogen atmosphere. The room temperature filter loss of the acrylate-treated mud was scarcely changed after this treatment, while the filter loss of the CMC-treated system was comparable to that of the blank mud. These results show that, from an operational point of view, CMC was completely degraded. Despite the apparent stability of the acrylic polymer, its usefulness is severely restricted by the high viscosities and filtration rates observed at elevated temperatures in the presence of calcium ions.

INTRODUCTION

The control of the flow properties and the filtration rate of drilling fluids in deep drilling operations are important aspects of drilling fluid technology. Low viscosities are desirable in the interest of efficient hydraulic horsepower utilization; low filtration rates imply thin filter cakes, which are desirable in order that the annular clearances between the drill pipe and the well bore be restricted to a minimal extent. It is perhaps not sufficiently well recognized that room temperature measurements do not necessarily give an indication of mud properties at elevated temperatures. Not only can degradation processes alter the performance of additives, but also the colloidal stability of the system may be upset by temperature-induced effects, such as changes in adsorption phenomena and solubilities.

This study compares the room temperature and elevated temperature viscometric and filtration properties of a gypsum mud and a sodium chloride

mud treated with sodium carboxymethyl cellulose (CMC) and with a sodium acrylate-acrylamide copolymer. The susceptibility of these polymers to degradation is inferred from the increase in the API filter loss¹ following exposure of the treated muds to 350°F.

THEORETICAL

There are many empirical equations that have been used to express the viscosity of suspensions.² One of these, the Arrhenius equation, states that the plastic viscosity of the suspension μ increases exponentially with the solids concentration c

$$\mu = \eta e^{kc} \quad (1)$$

where η is the viscosity of the suspending liquid and k is a constant, called the "shape factor," which is characteristic of the solids in a particular environment. Our concern here is to note that if k is really constant, the ratio μ/η should be independent of temperature,

$$\left(\frac{\mu}{\eta}\right)_{T_2} = \left(\frac{\mu}{\eta}\right)_{T_1} \quad (2)$$

which is to say that the plastic viscosity at temperature T_2 can be calculated from a knowledge of the plastic viscosity at T_1 and the known viscosities of water:

$$\mu_{T_2} = \mu_{T_1} \frac{(\eta)_{T_2}}{(\eta)_{T_1}} \quad (3)$$

It is one of the purposes of this paper to compare the observed and calculated viscosities of the polymer-treated muds at elevated temperature.

It can be shown³ that, for a constant-pressure, uniform-cake filtration process in which the resistance of the septum is negligible, the product of the API filter loss F and the square root of the viscosity of the filtrate is independent of temperature:

$$(F\eta^{1/2})_{T_2} = (F\eta^{1/2})_{T_1} \quad (4)$$

that is, the filter loss at elevated temperature can be calculated:

$$F_{T_2} = F_{T_1} \left(\frac{\eta_{T_1}}{\eta_{T_2}}\right)^{1/2} \quad (5)$$

Again, it will be of interest to compare the observed with the calculated filter loss at elevated temperature for the systems at hand.

EXPERIMENTAL

A laboratory barrel-equivalent (350 cc.) of the gypsum mud had the composition shown:

Water.....	324.2 g.
Clay mix*.....	49.1
Gypsum.....	11.8
	<hr/> 385.1

The clays were added with agitation to the water, stirred for 30 min., after which the gypsum was added and mixing continued for 2 hr. The batch was sealed and aged under static conditions for 48 hr. at 175°F. After cooling, the slurry was stirred for 2 hr.; any evaporation loss was compensated by water addition. Polymer additions (CMC or acrylate-acrylamide copolymer) were made to 350 cc. aliquots while shearing for 5 min. on a Waring Blendor, after which the samples were sealed in containers and heat-aged in a roller oven for 16 hr., at 175°F. Following aging, the samples were cooled, sheared three minutes on a Waring Blendor, allowed to stand for about an hour, and stirred 5 min. with a moderate speed mixer. Properties were then measured.

The 20,000 ppm sodium chloride mud contained, in order of addition, 350 g. water, 0.25 g. sodium carbonate, 10 g. clay mix, 7.0 g. sodium chloride, and 30 g. clay mix. Thus, one-fourth of the clay was prehydrated before the salt was added. Polymer additions were made to 350 cc. aliquots using the same mixing and aging procedure as outlined above.

The CMC used was a medium viscosity grade with degree of etherification (by titration of the acid) 0.7. The composition of the copolymer was 0.62 mole fraction sodium acrylate and 0.38 mole fraction acrylamide.

A model 35 Fann viscometer (Fann Instrument Corporation, Houston, Texas) with a water-jacketed cup was used to measure the rheological properties. Standard drilling mud filtration equipment was used. Corrections for surge loss and cell holdup were applied to the filtration data.

RESULTS AND DISCUSSION

In Table I are listed the rheological properties of the muds at 80° and 175°F. The higher yield points and gel strengths observed at the higher temperature indicate increased attractive forces (or decreased repulsive forces) between the particles. Only in the case of the CMC-treated gypsum mud was this apparently greater particle association lacking. The plastic viscosities decreased on heating, except in the case of the gypsum mud treated with the acrylate-acrylamide copolymer.

Table II compares the plastic viscosities in more detail. Values of plastic viscosity at 175°F. calculated from the values at 80°F. and the viscosity of water at the two temperatures [eq. (3)] are shown under the heading "Calc. μ_{175} ." The ratio of the viscosity observed at 175°F. to that calculated is given in column six. It is noted that all of the samples had ratios

* The clay mix contained 17.3% Aquagel, Wyoming bentonite from the Baroid Division, National Lead Company, Houston; 58.7% Xact Clay, a Texas sub-bentonite from Magnet Cove Barium Corporation, Houston; and 24.0% Mojave Rotary Clay, a nonswelling clay from Brown Mud Company, Los Angeles.

TABLE I. Effect of Temperature on Rheological Properties

Sample identification	80°F.				175°F.			
	Conc. of additive lb./bbl.	Plastic viscosity cps.	Yield point	Gel strength lb./100 sq. ft.	Plastic viscosity cps.	Yield point	Gel strength lb./100 sq. ft.	Gel strength 10 min.
Gypsum mud, blank	none	4.9	10.0	8.0	24.0	13.7	17.0	48.0
Gypsum mud, CMG	2.0	6.1	0.0	1.0	2.0	0.5	1.0	2.0
Gypsum mud, acrylate	2.0	5.6	4.7	2.0	16.0	11.4	6.0	51.0
NaCl mud	none	5.1	33.0	28.0	68.0	28.7	51.0	>100.0
NaCl mud, CMG (tech)	3.0	13.8	6.9	2.1	23.0	10.1	6.1	33.0
NaCl mud, acrylate	1.0	7.3	2.3	1.0	4.0	4.4	1.2	29.0

TABLE II. Calculated and Observed Viscosities at 175°F.

Sample identification	Observed			
	Conc. of additive lb./bbl.	Plastic Viscosity (μ)		Obs. μ_{175}
		at 80°F.	at 175°F.	
Sample identification	Conc. of additive lb./bbl.	Observed Plastic Viscosity (μ)		Obs. μ_{175}
		Observed Plastic Viscosity cps.	Calculated Plastic Viscosity cps. eq. (3)	
Water	—	0.852	0.360	1.0
Gypsum mud, blank	none	4.9	2.7	1.30
Gypsum mud, CMG	2.0	6.1	3.0	1.16
Gypsum mud, acrylate	2.0	5.6	8.1	3.43
NaCl mud, blank	none	5.1	3.1	1.42
NaCl mud, CMG (tech)	3.0	13.8	6.7	1.15
NaCl mud, acrylate	1.0	7.3	4.4	1.43
				(Obs. μ /Calc. μ) _{blank}

greater than one. In other words, the viscosity decrease on heating was less than would have been anticipated from the change in the viscosity of water. The higher than anticipated viscosity implies an increased degree of asymmetry for the kinetic unit. This would be compatible with the association of particles into threadlike structures characteristic of the higher gel strengths observed. The above ratios (observed to calculated) relative to the ratio for the blank muds are shown in the last column. Values less than one indicate that particle association increased on heating to a lesser extent than in the untreated muds. Such was the case in the samples containing CMC. Particularly noteworthy is the marked increase in association, compared with the blank, indicated in the case of the polyacrylate-treated gypsum mud. However, in the sodium chloride system (that is, in the absence of calcium ions) the rheological behavior of the polyacrylate-treated mud was the same as the blank.

Filter loss data at 80° and 200°F. are given in Table III. Calculated values of the filter loss at 200°, based on the filter loss at 80° and the viscosity of water at the two temperatures [eq. (5)], are listed in column five. A comparison with the observed filter loss at 200° is made in column six, which gives the ratio of the observed to the calculated value. The ratios are normalized or expressed relative to the blank muds in the last column. Of the gypsum muds only the sample treated with CMC had a predictable filter loss at 200°. The filter loss of the blank gypsum mud increased more than was calculated, and the relative increase for the polyacrylate-treated sample was significantly greater than for the blank. On the other hand, the high temperature filtration behavior of the sodium chloride muds was in reasonably good agreement with the theoretical. The formation at elevated temperature of an association complex between clay and calcium polyacrylate, thus decreasing the effective concentration of the polymer in the liquid phase, is consistent with the observed filtration behavior. As pointed out above, the rheological data also support the interpretation of increased particle association to form more asymmetric units at elevated temperature.

Table IV compares the room temperature properties of gypsum mud samples aged 16 hr. at 175°F. with those aged 16 hr. at 350°F. The most striking result was the increase in the filter loss of the CMC-treated sample after aging at the higher temperature. A value higher than the filter loss of the blank mud was measured. The plastic viscosity of the sample also decreased. These results are evidence of extensive degradation of the polymer. It will be noted that the filter loss of the polyacrylate-treated mud increased after 350°F. aging only to the extent shown by the blank.

All of the samples in Table IV had higher gel strengths after exposure to the higher temperature. The 10-min. gel strength of the CMC-treated sample increased to the same level as the blank mud, consistent with the degradation of the polymer. No explanation is offered for the high value shown by the polyacrylate-treated sample.

CONCLUSIONS

(1) The formation at elevated temperature of a complex involving clay, calcium ions, and polyacrylate ions is suggested by the following: (a) The polyacrylate-treated gypsum mud showed a viscosity rise when heated, in contrast to the decrease in viscosity observed on heating the untreated gypsum mud, the CMC-treated gypsum mud, and the polyacrylate-treated and CMC-treated sodium chloride mud; (b) The high temperature filter loss of the polyacrylate-treated gypsum mud was anomalous, increasing significantly above the value expected from the change in the viscosity of water. This anomaly was not observed when CMC replaced the acrylic copolymer or in the sodium chloride system. (2) The deviations in viscosity and filtration rate shown by the acrylate-treated gypsum system are not in a desirable direction from the standpoint of drilling fluid technology. (3) Room temperature filter losses of treated gypsum muds before and after aging at 350°F. indicated extensive degradation of CMC. The filter loss of the polyacrylate-treated mud was notably stable.

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Résumé

On a étudié à 80°F et à une température élevée les propriétés de viscosité et de filtration d'une boue saturée de gypse et une boue avec 20.000 ppm de chlorure de sodium, traitées par un copolymère acrylate-acrylamide, (fraction molaire d'acrylate: 0,62 et par la carboxycellulose (CMC). Dans le boues, contenant de la CMC, et aussi pour le polymère acrylique dans le système à chlorure de sodium, on a observé une diminution de la viscosité plastique (à 175°F) et une augmentation de la perte de filtration API (à 200°F) qui correspondent environ à ce que l'on peut prédire en se basant sur le changement de la viscosité de l'eau sous l'influence de la température. Par contre, la viscosité de la boue, contenant du gypse et traitée par le polyacrylate, augmentait au lieu de diminuer à cette température élevée. La perte de filtration API augmentant beaucoup plus que l'on aurait du prévoir d'après de changement de la viscosité de l'eau. Le comportement anormal du système traité par l'acrylate est une preuve des interactions entre le polymère, les ions calciques et l'argile. On présente des données expérimentales qui illustrent le taux de dégradation du polymère acrylique et de la CMC dans la boue à gypse, quand on la chauffe pendant 16 H à 350°F, sous atmosphère d'azote. La perte de filtration à température ambiante, de la boue traitée par l'acrylate, avait peu changée après le traitement, tandis que la perte de filtration du système traité par la CMC était comparable à celle de la boue seule. Ces résultats démontrent que, du point de vue opérationnel, la CMC était complètement dégradée. Malgré la stabilité apparente du polymère acrylique, il n'est pas très utile en raison de sa haute viscosité, et de la vitesse de filtration observée à température élevée en présence d'ions calciques.

Zusammenfassung

Viskositäts- und Filtrationseigenschaften eines gesättigten Gipsschlammes und eines 20.000 ppm Natriumchloridschlammes wurden bei 80°F und bei erhöhter Temperatur nach Behandlung mit einem Acrylat-Acrylamidcopolymeren (Molenbruch Natriumacrylat 0,62) und mit Natrium-carboxymethylcellulose (CMC) untersucht. Bei dem CMC-haltigen Schlamm und auch bei dem Acrylpolymeren im Natriumsystem entsprach die beobachtete Abnahme der plastischen Viskosität (bei 175°C) und die Zunahme des API-Filterverlustes (bei 200°F) ungefähr den aus der Temperatur-abhängigkeit des Wassers zu erwartenden Werten. Im Gegensatz dazu zeigte der polyacrylat-behandelte Gipsschlamm bei erhöhter Temperatur eine Viskositätszunahme an Stelle einer Abnahme und der API-Filterverlust erreichte ein wesentlich grösseres Ausmass, als auf Grund der Viskositätsänderung des Wassers zu erwarten war. Dieses anomale Verhalten der acrylat-behandelten Systeme wird als Beweis für eine Wechselwirkung Polymeres-Calciumion-Schlamm betrachtet. Ergebnisse zur Illustrierung des Ausmasses des Abbaus von Acrylpolymerem und CMC in einem Gipsschlamm beim Erhitzen durch 16 Stunden auf 350°F in einer Stickstoffatmosphäre werden mitgeteilt. Der Filterverlust bei Raumtemperatur änderte sich beim acrylat-behandelten Schlamm nach dieser Behandlung kaum, während der Filterverlust des CMC-behandelten Systems dem des ursprünglichen Schlammes vergleichbar war. Diese Ergebnisse zeigen, dass, vom Verarbeitungsgesichtspunkt aus, CMC vollständig abgebaut wurde. Ungeachtet der scheinbaren Stabilität des Acrylpolymeren, wird aber seine Verwendbarkeit durch die hohe Viskosität und die bei erhöhter Temperatur in Gegenwart von Calciumionen auftretende Filtrationsgeschwindigkeit stark beschränkt.

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