JOURNAL OF MATERIALS SCIENCE 15 (1980) 3010–3016

Influence of adsorption kinetics on chemomechanically enhanced hard rock drilling

J. J. MILLS, A. R. C. WESTWOOD
Martin Marietta Laboratories, 1450 South Rolling Road, Baltimore, Maryland 21227, USA

To enhance the efficiency of diamond bit drilling into hard rocks by means of chemomechanically active additives, several not-so-obvious factors must be taken into account. These include polarity and concentration of surfactant, mode of diamond failure and rate of adsorption of the active species onto the rock under the bit. To evaluate the latter factor, Westerly granite was drilled with diamond bits ranging in size from 0.6 to 6 cm at rotational speeds ranging from 50 to 5000 rpm using aqueous concentrations of Aerosol C-61, a cationic surfactant, ranging from 10^{-4} to 10^{-2} mol l^{-1}. The results reveal that rotational speed has a strong effect on the additive-enhanced diamond life, with maxima appearing under conditions suggesting that, for higher bit speeds, the isoelectric point of the rock effectively occurs at surfactant concentrations greater than those determined under static conditions. The results also demonstrate the possibility of utilizing laboratory-scale drilling tests to inexpensively simulate field-scale tests of potentially useful, bit wear-reducing surfactants.

1. Introduction

The addition of surface-active species to circulating fluids can markedly influence the rate of drilling into hard rocks [1–10]. However, ever since Rebinder [1] published the results of his pioneering studies of such phenomena in 1944, such effects have been controversial, with conflicting results being reported by various investigators, e.g. [5, 9].

We have suggested previously [11] that this controversy has been due in part to a lack of appreciation of the number and complexity of interacting factors involved in changing drilling behaviour by this means. For example, additives can influence drilling performance through both physical and chemical effects [11]. And when changes in the chemistry of the fluid are employed to alter the near-surface flow and fracture behaviour of the rock (chemomechanical effects [5–7, 11]), numerous less-obvious factors also become relevent, e.g. the polarity and concentration of the active species [7], the type of bit, its rate of rotation and loading [4], and even the nature of the test used to reveal the environmental influence [11]. The last of these factors is important because, for example, certain surfactants can act through their indirect influence on the rate of wear of the diamonds in diamond-loaded bits [9, 11]. Consequently, tests to reveal their influence must be carried out over a significant fraction of the life of the diamonds. Short-term tests will not reveal their effects. This is a potential source of conflict in the literature.

In this paper, data are presented to clarify the role of another relevant factor when scaling up from laboratory- to field-scale, namely, the kinetics of adsorption of the active species onto the rock surface. Clearly, for an active molecule to influence rock surface properties it must first be adsorbed, a process which can be quite slow. If it is sufficiently slow that equilibrium (or appropriate) surface coverage cannot be established between impact events under the dynamic conditions of drilling, then the influence of the environment will be different from that encountered during more quiescent conditions, such as when measur-

0022–2461/80/123010–07$02.70/0

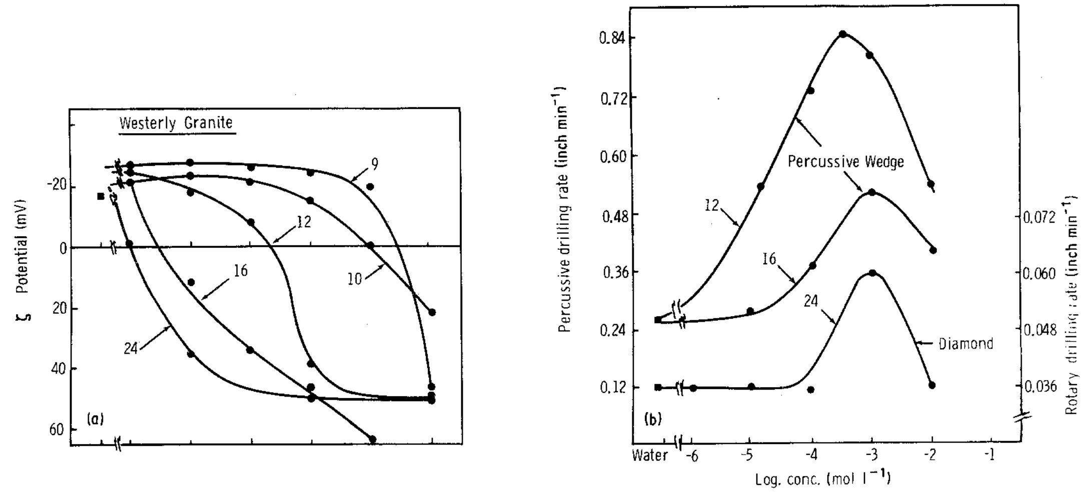

Figure 1 Effects of various aqueous surfactant-containing environments on (a) ζ-potential, and (b) rotary or percussive drilling behaviour of Westerly granite. The surfactants are: (9) nonyltrimethyl (T) ammonium (A) bromide (B); (10) decyl TAB; (12) dodecyl TAB; (16) cetyl TAB, and (24) didodecyl dimethyl TAB, from [14] (1 inch min^{-1} ≡ 2.54 cm min^{-1}).

ing the ζ-potential (see [12] for a review of the ζ-potential) or indentation hardness of the rock in the environment. Consequently, the maximum beneficial influence of the particular surfactant on drilling performance may be shifted to concentrations other than those predicted by, say, hardness tests in "static" environments [13].

To illustrate this "dynamic shift" of environmental influences, Fig. 1 presents the ζ-potential and the drilling rate, $\dot{D}(200)$*, of diamond core or percussive bits as a function of surfactant chain-, length and concentration [14]. The "ζ-correlation" [13] predicts that the maximum in $\dot{D}(200)$ should occur at the concentration producing $\zeta \simeq 0$, the isoelectric point, as it does for dodecyltrimethylammonium bromide, DTAB (Curve 12 in Fig. 1). However, the maximum in penetration rate does *not* follow the well-known shift [15] of the isoelectric point to lower concentrations for surfactants of greater molecular chain length – suggesting that some other factor has been introduced, e.g. absorption kinetics.

2. Approach

The time required to establish equilibrium between an environment containing active molecules and a clean surface, t_E, depends on such factors as the structure of the molecule and its concentration in the environment, the nature of the surface, and the strength and type of bond formed. In many practical applications, e.g. flotation, the rate of adsorption of the surfactant molecule is not critical. In drilling, however, surfaces are exposed to active fluids for only very short times (~ msec) before the next cutting edge arrives to create fresh new surface. Consequently, for a surfactant to adsorb to a preferred surface concentration, e.g. that producing $\zeta = 0$, the actual exposure time of that surface, t_A, should be at least t_E for that environment. If $t_A < t_E$, the concentration adsorbed will be non-optimum, and the influence of the adsorbate on the surficial mechanical properties of the rock, and hence on the drilling behaviour, may not be that which has been anticipated.

In principle, to determine the influence of adsorption kinetics on diamond drilling rates, t_E should first be measured independently, and then drilling conditions selected such that $t_A \geqslant t_E$. For additive concentrations producing $\zeta = 0$, drilling performance should become constant when $t_A > t_E$. For other concentrations, performance will exhibit a more complex dependence on time.

In practice, there is no simple method for measuring t_E in the millisecond range. Neither is it possible to measure t_A precisely, since it is impossible to determine the rate and manner in which individual diamonds are cutting, even for a well-characterized surface-set bit. Accordingly, to examine the role of adsorption kinetics in

---

*$\dot{D}(200)$ is defined as the rate of penetration 200 sec after starting to drill with a newly sharpened bit [5–7].

environment-assisted diamond drilling, the following approach was adopted. First, note that

$$t_A = \frac{\bar{d}}{v}, \qquad (1)$$

where $\bar{d}$ is the mean separation of the cutting diamonds in an impregnated bit, and v is the peripheral speed of the diamonds (angular velocity × bit radius). Actually, $\bar{d}$ is not a measurable parameter for any given impregnated bit, but is a relatively constant factor from dressing to dressing. Now, by changing v by altering the bit rotational speed, t_A can be varied. Then, if adsorption kinetics are important, characteristic curves should be obtained when some appropriate measure of drilling efficiency is plotted against v for bits of different diameter and a constant surfactant concentration. Further, given Equation 1, it should be possible to scale the v-axes for each bit by some empirically determined factor (proportional to $\bar{d}$) such that the data from all bits fall on the same "master" curve for a given surfactant concentration.

The issue of defining an appropriate and comparable measure of drilling efficiency can be approached as follows. First, it has been shown earlier that a plot of penetration rate, $\dot{D}(t)$, against penetration, $D(t)$, for a diamond-loaded bit into a hard rock is, after settling in, essentially linear under most conditions [11, 16, 17]. Thus

$$\dot{D}(t) = \dot{D}(0) - wD(t), \qquad (2)$$

where t is time, $\dot{D}(0)$ is the initial penetration rate, and w is the slope of a plot of $\dot{D}(t)$ against $D(t)$. w is a measure of the rate of wear of the diamonds. It has been found that, for diamond-bit drilling, active environments predominantly influence w, and have little effect on $\dot{D}(0)$ [11]. Given this information, a useful comparator of drilling performance can be defined as

$$R = \frac{w\text{ (water)}}{w\text{ (surfactant)}}. \qquad (3)$$

Since $\dot{D}(0)$ appears to be independent of environment [11], the ratio R can be defined as

$$R = \frac{L\text{ (surfactant)}}{L\text{ (water)}}, \qquad (4)$$

where $L = \dot{D}(0)/w$ is the total distance a bit can drill before it is worn out (i.e. its life). Hence R is the ratio by which a surfactant solution increases diamond life over that in water.

R can be determined in two ways. First, separate plots of $\dot{D}(t)$ against $D(t)$ can be obtained for water and the surfactant solution using bits with fresh sharp diamonds, see Fig. 2a. Then, the slopes of each curve are determined and R calculated via Equation 3. In practice, one finds that data obtained when drilling with *small, impregnated* bits (< 0.5 inch outside diameter, o.d.) exhibit variations in both $\dot{D}(0)$ and w due, presumably, to the different distributions of diamonds exposed by

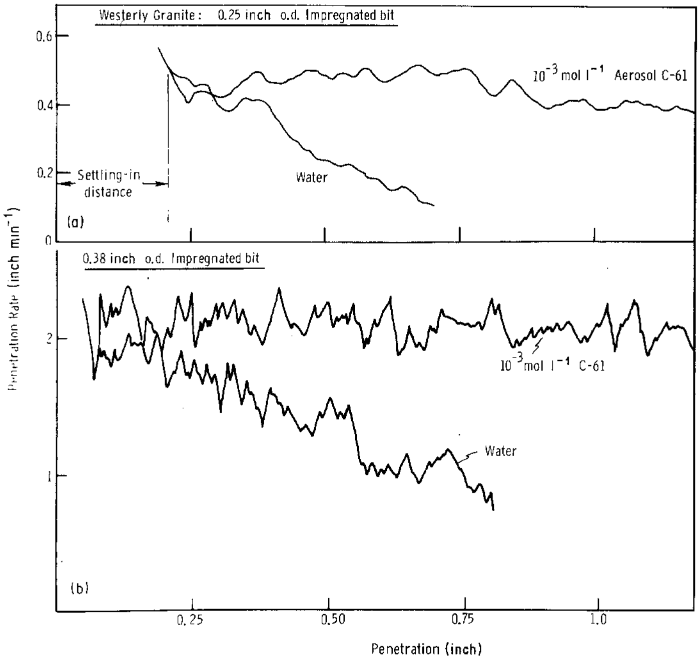

Figure 2 Penetration rate of (a) a 0.25 inch o.d. and (b) a 0.38 inch o.d. diamond-impregnated bit into Westerly granite as a function of penetration, illustrating that the wear rate induced by a 10^{-3} mol l^{-1} C-61 solution is less than that in water. Conditions were (a) 2000 rpm, 13 lb thrust and (b) 900 rpm, 13 lb thrust (1 lb ≡ 4.48 N).

redressing. In this work, therefore, R was derived using mean values from at least four experiments with each environment. For *full-size impregnated* BX bits (> 1 inch o.d.), on the other hand, w does not vary significantly between sharpenings from one similar test to another [17]. Consequently, for these bits, R can be estimated from only one set of $\dot{D}(t)$ against $D(t)$ curves (comparing water and surfactant solutions).

For *large surface set* bits (> 1 inch o.d.), neither of these approaches is practical, because both w and $\dot{D}(0)$ vary from bit to bit, and repeated tests are costly since a new bit must be used each time. It is then more convenient simply to drill with one bit in a given environment until the penetration rate has fallen to, for example, 50% of its original value, and then to change the environment; whereupon the slope of the plot of $\dot{D}(t)$ against $D(t)$ will change. R can then be computed from the ratio of the slopes of the two separate linear sections. An example of this will be presented below.

3. Experimental procedure

The various equipment employed for this work has been described previously [11]. Briefly, however, two drills were used, a precision drilling machine providing rotational speeds from 800 to 5000 rpm and thrusts to 60 lb (used for bits up to 0.5 inch o.d.); and a large, servo-controlled rig* providing rotational speeds to 500 rpm and thrusts to 10^5 lb (used for full-size bits).

The bits used on the smaller rig were 0.25 and 0.38 inch o.d., 0.03 inch kerf, diamond-impregnated coring bits†, and on the larger rig, both impregnated and surface set BX (2.38 inch o.d.) core bits‡ such as are used in mining exploration. When using the smaller rig, penetration distance was differentiated electronically to produce continuous plots of $\dot{D}(t)$ against $D(t)$. This capability was not available on the larger rig, so $\dot{D}(t)$ values were calculated over a fixed distance (typically 2 inches), and $\dot{D}(t)$ against $D(t)$ plots constructed point-by-point. Because the "lives", L, of the full-size bits were much larger than the thickness of the available rock samples, it was necessary to drill many holes to accumulate the distance required to wear out such bits.

Westerly granite was selected as the test rock. This is a fine-grained, homogeneous rock, containing approximately 40 wt% quartz, 30 wt% feldspar, 10 wt% biotite and various quantities of other minerals. Its compressive strength is ~ 30 000 psi§, and its drilling behaviour has been shown previously to be dominated by the quartz phase [6].

The surfactant chosen, Aerosol C-61¶, is water soluble, cationic, corrosion-inhibiting, biodegradable and available in commercial quantities – all attributes necessary for a practical additive. The ζ-potential against aqueous concentration relationship for Aerosol C-61 was established using fine quartz powder (Minusil No. 5) at a solids concentration of $3\,\mathrm{g\,l^{-1}}$. It was found that $\zeta \simeq 0$ at $\simeq 10^{-3.5}\,\mathrm{mol\,l^{-1}}$.

4. Results

Westerly granite was drilled under 10^{-4}, 10^{-3} and $10^{-2}\,\mathrm{mol\,l^{-1}}$ solutions of Aerosol C-61 to bracket the isoelectric concentration and provide information on the concentration dependence of kinetic effects.

Typical plots of $\dot{D}(t)$ against $D(t)$ for all three impregnated bits drilling under either water or the various C-61 solutions are presented in Figs 2a and b and 3. From such curves and others obtained at rotational speeds ranging from 50 rpm (for the 2.38 inch o.d. bit) to 5000 rpm (for the 0.25 and 0.38 inch o.d. bits), R was calculated and plotted against v, one plot for each bit at each concentration. Then, for each surfactant concentration, the v axes for the 0.38 and 2.38 inch o.d. bits were multiplied by factors of 2 and 4, respectively, to produce the "master plots" for all three concentrations (Fig. 4). The error bars in Fig. 4 represent ± the standard error on R calculated from repeated experiments.

Since the larger and more widely-spaced diamonds in a surface-set bit would give rise to a t_A value greater than that for an impregnated bit of similar diameter and rotational speed, one might expect that the R value for a 2.38 inch o.d. surface-set bit drilling into Westerly granite at peripheral speeds $> \sim 15\,\mathrm{inch\,min^{-1}}$ would be greater than that for a similar impregnated bit drilling under otherwise identical conditions. This surmize is

---

*At TerraTek, Inc., Salt Lake City, Utah, USA.

†From Felker Industries, Torrance, California, USA.

‡From Christensen Diamond Products, Salt Lake City, Utah, USA.

§$1\,\mathrm{psi} \equiv 6.89 \times 10^3\,\mathrm{Pa}$.

¶From American Cyanamid Corp., Wayne, New Jersey, USA.

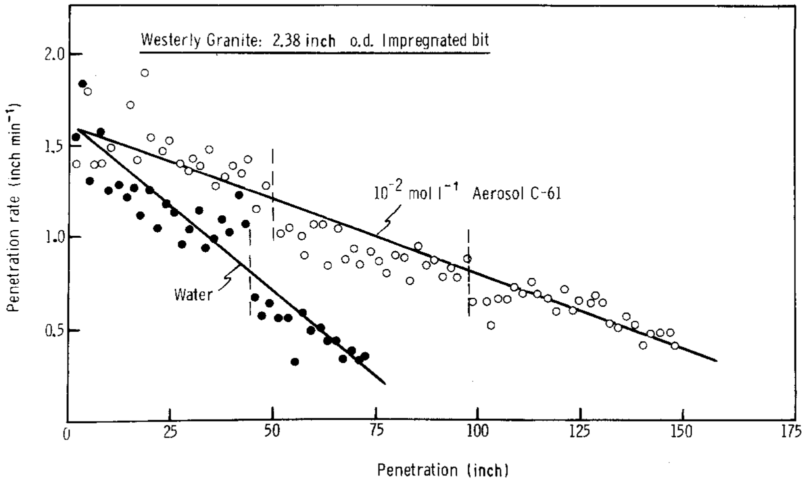

Figure 3 Influence of 10^{-2} mol l^{-1} Aerosol C-61 solution on wear rate of a BX impregnated bit rotating at 200 rpm, 3000 lb thrust. Vertical dashed lines indicate end of each hole.

correct. To illustrate: a 10^{-3} mol l^{-1} C-61 solution does not significantly influence the rate of wear of a BX impregnated bit rotating at a peripheral speed, v, of 30 inch min^{-1}; $R = 1$ for point A in Fig. 4b. However, the data for Fig. 5 show that, for a surface-set bit, there is a substantial change in slope, w, on changing from the 10^{-3} mol l^{-1} C-61 environment to water, even though this bit was run at the increased v of 45 inch min^{-1}. In this case, $R \simeq 4.5$ which, as can be seen from Fig. 4b, is close to the maximum value achievable and comparable to the value of R obtained with an impregnated bit rotating at a v of only 10 inch min^{-1}.

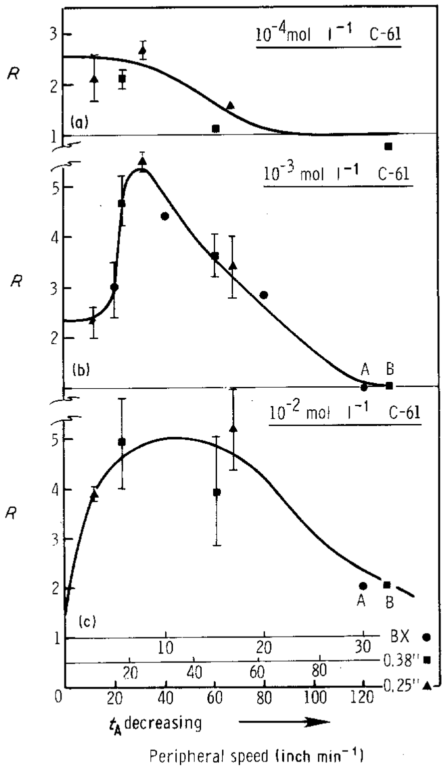

Figure 4 Variation in bit life parameter, R, for diamond bits drilling into Westerly granite as a function of bit peripheral speed under three different concentrations of Aerosol C-61.

5. Discussion

Fig. 4 reveals that bit rotational speed substantially alters the effectiveness of surfactant solutions on drilling performance. Although this influence has been noticed previously [4], the observations that master curves can be derived using concentration, independent scaling factors is new, and provides support for our view that the rate of adsorption of the active species onto the rock surface is an important factor, and one which can substantially change the optimum beneficial surfactant concentration (upwards) from that predicted by the ζ-correlation.

As surmized in Section 2 above, the shape of the master curves is quite complex, and depends on surfactant concentration. However, their likely form for any given surfactant concentration can be predicted given knowledge of the relationship between ζ-potential and surfactant concentration. For example, for granite in 10^{-4} mol l^{-1} C-61, ζ is < 0 ($\zeta \simeq 0$ at $\sim 10^{-3.5}$ mol l^{-1}), but is not as negative as it is in water. Hence, for slow drilling speeds (< 10 inch min^{-1} for the 0.25 inch o.d. bit in Fig. 4a), $R > 1$, but not as large as it would be if $\zeta = 0$. Now, as bit peripheral speed, v, increases, t_A decreases (since $t_A \propto v^{-1}$). Thus, fewer C-61 molecules can adsorb in the time available, and R decreases to its value in water, i.e. to 1.

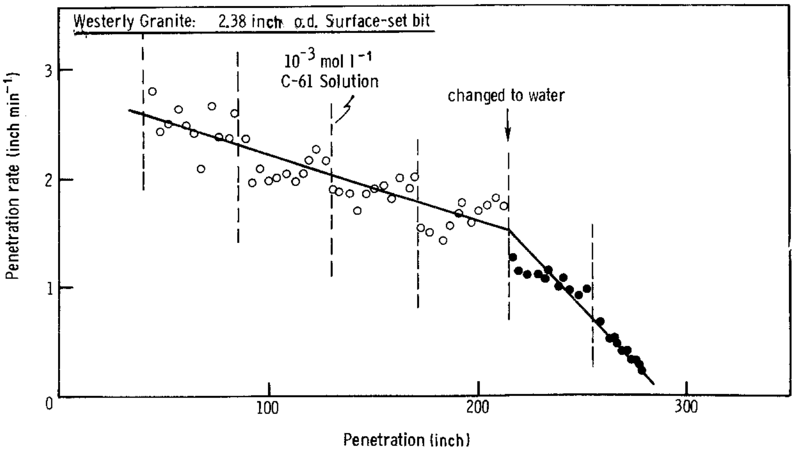

Figure 5 Plot of penetration rate of a BX surface-set diamond bit into Westerly granite as a function of penetration under 10^{-3} mol l^{-1} Aerosol C-61 solution and water; 450 rpm, 3000 lb thrust. Note the abrupt change in wear rate (i.e. slope) on changing from the C-61 solution to water. Vertical dashed lines indicate end of each hole.

For granite in 10^{-3} mol l^{-1} C-61, ζ is very slightly > 0 under equilibrium conditions, i.e. when v is low. Thus, $R > 1$ in Fig. 4b, but again this is less than it would be if $\zeta = 0$. However, as v increases and t_A decreases (moving towards the right in Fig. 4b), the number of C-61 molecules arriving in time to affect cutting behaviour decreases. In effect, the concentration of C-61 available on the rock surface decreases back to that producing $\zeta = 0$ under equilibrium conditions ($\sim 10^{-3.5}$ mol l^{-1}). For the 0.25 inch o.d. bit, this occurs when $v \simeq 30$ inch min^{-1}, and R then achieves its maximum value of ~ 5. When $v > 30$ inch min^{-1}, however, ζ again becomes < 0, and R decreases towards 1. Similar behaviour occurs for the 0.38 inch o.d. and the 2.38 inch o.d. bits except that, in these cases, the values of v producing maximum R are $\simeq 25$ inch min^{-1} and $\simeq 7$ inch min^{-1}, respectively.

For the 10^{-2} mol l^{-1} C-61 environment, $\zeta \ll 0$ when v is low, but, as with the 10^{-3} mol l^{-1} solution, the effective value of $\zeta \rightarrow 0$ as v increases (Fig. 4c), and R increases to its maximum value. The maximum appears to be located at a somewhat higher value of v than for the 10^{-3} mol l^{-1} solution, however, as might be expected in view of the greater available concentration of surfactant molecules. Finally, as v increases beyond ~ 60 inch min^{-1} for a 0.25 inch o.d. bit, ζ presumably becomes increasingly negative, and R again decreases towards unity.

The existence of "master curves" may be important from a practical viewpoint, because it implies that laboratory scale screening tests using small diameter bits may be used to simulate full-scale drilling tests in a reasonably reliable fashion. That is, surfactant solutions that meet certain criteria concerning toxicity, corrosivity and biodegradability could be rapidly and inexpensively screened in the laboratory for effectiveness in the field. The selection of the laboratory scale conditions simulating a particular bit in the field would be achieved by comparing the value of R obtained in the full-scale test with that obtained with the laboratory-size bit. When the two are comparable, as with points A and B in Fig. 4b and c, the conditions for adsorption are probably quite similar.

Given the number of factors now evidently involved in determining the influence of chemomechanical additives on drilling performance, e.g. effects related to adsorption kinetics and bit speed, and the need to perform tests of appropriate duration as well as to choose the "correct" surfactant concentration for a preferred bit speed, which will be that giving $\zeta \simeq 0$ under the specific testing conditions and not necessarily that measured under static conditions, it is not surprising that various workers using differing conditions have produced apparently conflicting or even contradictory results. Clearly, if drilling conditions and fluid composition are chosen arbitrarily ("let's add a surfactant!"), it is *unlikely* that positive influences will necessarily be observed. In contrast, a *systematic* approach, such as suggested here, involving appropriately designed laboratory screening tests, should help to identify surfactant solution compositions which are likely to provide substantial drilling benefits, e.g. improvements in bit life of up to five times, with concomitant reductions in downtime and increases in average rates of penetration.

Acknowledgements

It is a pleasure to acknowledge the assistance of the staff of the Drilling Research Laboratory of TerraTek, Inc., Salt Lake City, Utah, in obtaining the drilling data from the BX bits. Dr. Arfon Jones and Mr. Robin Reid were especially helpful. This work was performed under NSF Grant No. APR 73–07787. However, the views and opinions expressed herein are solely those of the authors.

References

1. P. A. REBINDER, L. A. SCHREINER and S. F. ZHIGACH, "Hardness Reducers in Rock Drilling" (Academy of Science, Moscow, USSR, 1944; CSIRO Translation, Melbourne, 1948).
2. A. E. LONG and W. G. AGNEW, US Bureau of Mines Report No. RI 3793 (1945).
3. A. C. T. JORIS and G. McLAREN, *Mining and Mineral Eng.* 3 (1967) 190.
4. A. A. SELIM, C. W. SCHULTZ and K. C. STREBIG, *Soc. Pet. Eng. J.* 9 (1969) 425.
5. A. R. C. WESTWOOD, *J. Mater. Sci.* 9 (1974) 106.
6. A. R. C. WESTWOOD, N. H. MACMILLAN and R. D. KALYONCU, *Trans. SME/AIME* 256 (1974) 106.
7. N. H. MACMILLAN, R. E. JACKSON, W. M. MULARIE and A. R. C. WESTWOOD, *ibid.* **258** (1975) 278.
8. W. H. ENGLEMANN, H. F. UNGER and B. S. SNOWDEN, *ibid.* **258** (1975) 185.
9. G. A. COOPER and J. BERLIE, *J. Mater. Sci.* **11** (1976) 1771.
10. W. H. ENGLEMANN, D. R. TWEETON, G. A. SAVANICK and D. I. JOHNSON, US Bureau of Mines Report No. 8186 (1970).
11. J. J. MILLS and A. R. C. WESTWOOD, *J. Mater. Sci.* **13** (1978) 2712.
12. S. M. AHMED, "Oxides and Oxide Films" Vol. 1, edited by J. W. Diggle (M. Dekker, NY, 1972) 320.
13. N. H. MACMILLAN, R. D. HUNTINGTON and A. R. C. WESTWOOD, *Phil. Mag.* **28 (4)** (1973) 923.
14. R. D. HUNTINGTON and A. R. C. WESTWOOD, Third Six-Monthly Letter Report to NSF on Grant No. GI-38114, November 1974.
15. D. W. FUERSTENAU, *J. Phys. Chem.* **60** (1956) 981.
16. C. E. TSOUTRELIS, *Trans. SME/AIME* **244** (1969) 364.
17. J. J. MILLS and A. R. C. WESTWOOD, *Industrial Diamond Review* (1977) 264.

Received 14 April and accepted 12 May 1980.