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Influence of Surface-Active Chemicals on Drilling and Fracturing Rock

UNITED STATES DEPARTMENT OF THE INTERIOR

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Influence of Surface-Active Chemicals on Drilling and Fracturing Rock

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INFLUENCE OF SURFACE-ACTIVE CHEMICALS ON DRILLING AND FRACTURING ROCK

by

Daryl R. Tweeton,[1] William H. Engelmann,[2] George A. Savanick,[3]
and Donald I. Johnson[3]

ABSTRACT

The Bureau of Mines compared the effects of surface-active chemicals with those of pure water on core-drilling rock and quartz and on fracturing quartz. The objectives were to determine if these chemicals assist drilling and fracturing rock and if zeta potential control was worth pursuing as an aid to full-scale drilling. All tests were performed in the laboratory.

No significant increases in drilling rates were observed for 1 to 10,000 ppm Al (as $AlCl_3$) in flushing water when drilling microcline or serpentine, nor for 1 to 10,000 ppm Mg (as $MgCl_2$) when drilling microcline or marble. Concentrations near those giving a zero zeta potential were used with microcline and marble. A 50-pct rate increase was observed for drilling quartz in 0.7 ppm oleylammonium acetate, which gave a zero zeta potential. No other concentrations were used. No effect on the tensile strength of quartz thread in 0.05 ppm Al (as $AlCl_3$), which gave a zero zeta potential, was observed. Heptanol, reported to give a zero zeta potential on quartz, did not reduce the bending strength of small quartz bars below that in water.

These generally negative findings raise doubt about the usefulness of zeta potential control in full-scale drilling. The results, combined with previous studies, suggest that controlling physical properties of drilling fluids, such as viscosity, is more useful than altering chemical properties.

INTRODUCTION

Fragmentation of rocks and minerals can be accomplished or aided by mechanical, explosive, thermal, hydraulic, or chemical means. Data from chemically augmented fragmentation research performed and published by the Bureau of Mines have sometimes been at variance with other workers' results, and other discrepancies abound throughout the literature. The Bureau has reported (15)[4] that drilling rate increases of about 30 pct can be achieved

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[1] Research physicist.
[2] Research chemist.
[3] Physicist.
[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

by drilling with chemical agents rather than with water alone. The Soviet literature (9) reports twice as large a percentage increase, whereas another U.S. group (20) claims a tenfold increase. Accordingly, further work was undertaken by the Bureau on the effect of chemical agents on drilling and other fragmentation schemes. Previous research is reviewed in the following paragraphs.

Chemical solutions have been used in rock fragmentation processes for over 50 years. Rehbinder (7) claimed in 1928 that adsorbable compounds in a fluid medium accelerated the mechanical failure of certain crystals. He published further work (8) where he explained that the hardness level of minerals is connected with a decrease in free surface energy and decreases to its lowest level at saturation of the mineral surfaces with oriented, polar molecules. In a homologous series of organic acids, the hardness-reduction effect rises with the orientation ability of the molecule, which increases as a function of molecular weight. Rehbinder attempted to relate the hardness-reduction effect with easier microcrack formation when the mineral is under stress, and reference 9 reviews all the Soviet work on chemical hardness reducers since 1928. Because of Rehbinder's extensive work, introduction of chemical reagents in many rock fragmentation systems and the observation of lessened energy requirements for breakage have come to be loosely defined as Rehbinder effects.

The following discussion of the Soviet work is based on a review of chemical fragmentation by Engelmann (3): Rehbinder and his school (9) noted that drilling rates were greatly increased when chemical solutions were applied to a system that used a fast rotary-percussive rate. The chemical effect ahead of the bit essentially forms a region of predestruction under the drill bit. Adsorbed molecules apparently affect the rehealing of the microcracks, which occur in the short interval between impacts. Experiments showed that at 70 impacts/min, aluminum chloride ($AlCl_3$) solutions (0.01 to 0.1 pct) produced a 10-pct increase in drilling rate over that of water alone (9). At 1,600 to 2,000 impacts/min, drilling rate was raised 60 to 70 pct. Aluminum chloride solutions had almost no effect on percussive drilling of hard quartzite with a sharp bit. In 1941, Schreiner, Rossmit, and Demin (10) showed that while the optimum $AlCl_3$ concentration was 0.05 pct in a crimson quartzite (Shokshinsk bed) the efficiency of the additive depends upon the dullness of the bit crown and on the attendant, related decrease of the coefficient of work. At a thrust of 30 kg, the effect of $AlCl_3$ solution remained the same as that of water for the first 10 cm of penetration. At 30 cm, the $AlCl_3$ promoted a 50-pct rate increase over water, but the bit became dulled. Schreiner's conclusion was that, when the bit was sharp, the coefficient of useful work was high, and the fragmentation or cutting action caused little formation of a predestruction zone. The absence of such a zone, with its chemically sensitive microcracks, permitted little interaction with the $AlCl_3$ solution and thereby gave a drilling rate comparable to that of water.

Schreiner, Rossmit, and Demin (10) also found that by lowering the thrust from 30 kg to about 10 to 20 kg, the drilling rate with $AlCl_3$ solution increased 10 to 50 pct over that with water, depending on the pressure. At the end of the hole, the increase was over 100 pct. Therefore, for lower thrusts and a sharp bit, much of the energy of the impact forms a predestruction zone, but the coefficient of useful work is less than its maximum. Fragmentation within the zone is at a peak when the coefficient of useful work drops to minimum. The wear rate of the bit varies indirectly with increased speed of drilling and can decrease by as much as 35 pct.

Rehbinder (8) classified hardness reducers into two groups according to the chemical character of the adsorbed layers on the rock and the traits of hardness reduction that depend on solution strength. The first group contained the inorganic compounds NaCl, $MgCl_2$, $CaCl_2$, $AlCl_3$, NaOH, and Na_2CO_3. As hardness reducers, their effect increased rapidly with addition level but reached its maximum at fairly low levels. Optimum solution strength ranges for quartzite rocks are 0.01 to 0.05 pct for $AlCl_3$, 0.1 to 0.2 pct for $MgCl_2$, and 0.5 to 1.0 pct for NaCl. The effect of these narrow concentration ranges is ascribed to the responsive change in the size of the ionic double layer which adheres to all mineral surfaces. Inorganic compounds that do not adsorb on the surface, such as chloride salts on limestones, do not reduce hardness.

In 1954-55, drilling and fragmentation studies in the United Kingdom, using additives including $AlCl_3$, were published by Shepherd (11-12). He reported that in rotary drilling of rock, chemical softeners (as he termed them) increase the drilling rate; a maximum rate occurred for an optimum concentration. Only relatively weak (approximately 0.01 pct) solutions of $AlCl_3$ enhanced drilling rates in rotary drilling of quartz-containing rocks. Shepherd (12) isolated two main factors which apparently control the action of inorganic chemical softeners (including $AlCl_3$): viscosity and pH level. He ran viscosity measurements using $AlCl_3$ solutions at 0.01, 0.02, 0.03, 0.04, and 0.05 pct (by weight). Plotting viscosity as a function of solution strength gave a minimum viscosity for $AlCl_3$ solution at about the 0.01-pct level.

In 1962, Boozer, Hiller, and Serdengecti (1) presented the results of a comprehensive study of the effects of pore fluids on the deformation behavior of rock under various triaxial compression loads. The deformation of Indiana limestone and Navajo Sandstone was affected by fluids that were strongly adsorbed on the surfaces of the rock grains. The major effects of the pore-saturating and adsorbed liquids, oleic acid and oleylamine, were (1) a decrease in the ultimate strength of the Navajo Sandstone, and (2) a decrease in the yield stress of Indiana limestone, which deformed in a ductile manner.

In more recent work on hardness reducers, Vutukuri (16) reported in 1972 that the tensile strength of quartzie is lowest (11.1-pct reduction) when the rock is immersed in $AlCl_3$ solution of about 0.06 pct concentration. However, the data are questionable, since the standard deviation is 30 pct for the 20-sample experiment.

An excellent overall review by Somasundaran and Lin (13) (165 references) on how chemical environments affect all types of fragmentation processes was also published in 1972.

In the early 1960's Westwood and others at the Research Institute for Advanced Studies (RIAS) began investigations into Rehbinder-type effects. Since the early 1970's, this group has added greatly to the literature, publishing now under the name of Martin Marietta Laboratories, located in Baltimore.

In 1960, Westwood (17) published on the Rehbinder effect and the "adsorption-locking" of dislocations in nonmetals. In lithium fluoride crystals, he explained, the adsorption of polar molecules from solution is likely to occur preferentially at such active or high-energy sites as the points of emergence of dislocations and at kink sites. If adsorption occurs at dislocations, subsequent motion of the dislocation may be temporarily pinned at the surface. This restraining has been termed "adsorption-locking." Since this phenomenon affects surface sources of dislocations, it also affects yields and flows. This adsorption-locking hypothesis predicts an increase in the yield stress of crystals which are deformed in surface-active environments. In 1968, Westwood (18) extended his hypothesis to other nonmetals, and to silver chloride, magnesium oxide, and germanium crystals. Microhardness and dislocation mobilities either increased or decreased, depending on the nature of the environment and the crystal system.

In 1967, Engelmann, Terichow, and Selim (4) described the zeta potential (ξ) control of a mineral's environmental fluid and how this changed the hardness of granite immersed in the test fluid. The hardness was measured with a pendulum sclerometer. With this device, they found that the mineral was most easily penetrated when the zeta potential was nearly zero.

The zeta potential is defined as that potential that occurs across the diffuse double layer that forms when most minerals are immersed in ionic fluids (fig. 1). Under the diffuse layer is a monolayer of tightly adsorbed ions. Examination of charges, starting from the mineral surface, typically shows the following: Mineral surfaces are anionic and therefore adsorb cations tightly to help screen the mineral's highly negative surface. In dilute solutions, negative counterions will predominate within the second diffuse layer. The diffuse layer has one type of ion predominating, and the bulk of the solution, much farther away from the mineral surface, being electroneutral, gives rise to the zeta potential (fig. 1). When the bulk solution is relatively concentrated, the source of ions for the double layer is plentiful, and the double layer transfers some ions into the first layer. At a critical bulk concentration level, the first layer is fully compensated or electrically neutral. This is the isoelectric point, where the zeta potential is zero ($\zeta = 0$).

Several years after reference 4 appeared, Westwood and his group began examining the zeta potential control of mineral hardness. In more recent publications, Westwood and his group have revised their mechanism-supporting theories, and today they strongly endorse the zeta potential control of rock or mineral hardness. A 1973 paper (6) describes the relationship between zeta potentials and dislocation mobilities. For magnesium oxide crystals, the dislocation mobilities were the lowest--and the microindentation hardness was the greatest--when the zeta potential at the mineral-solution interface was

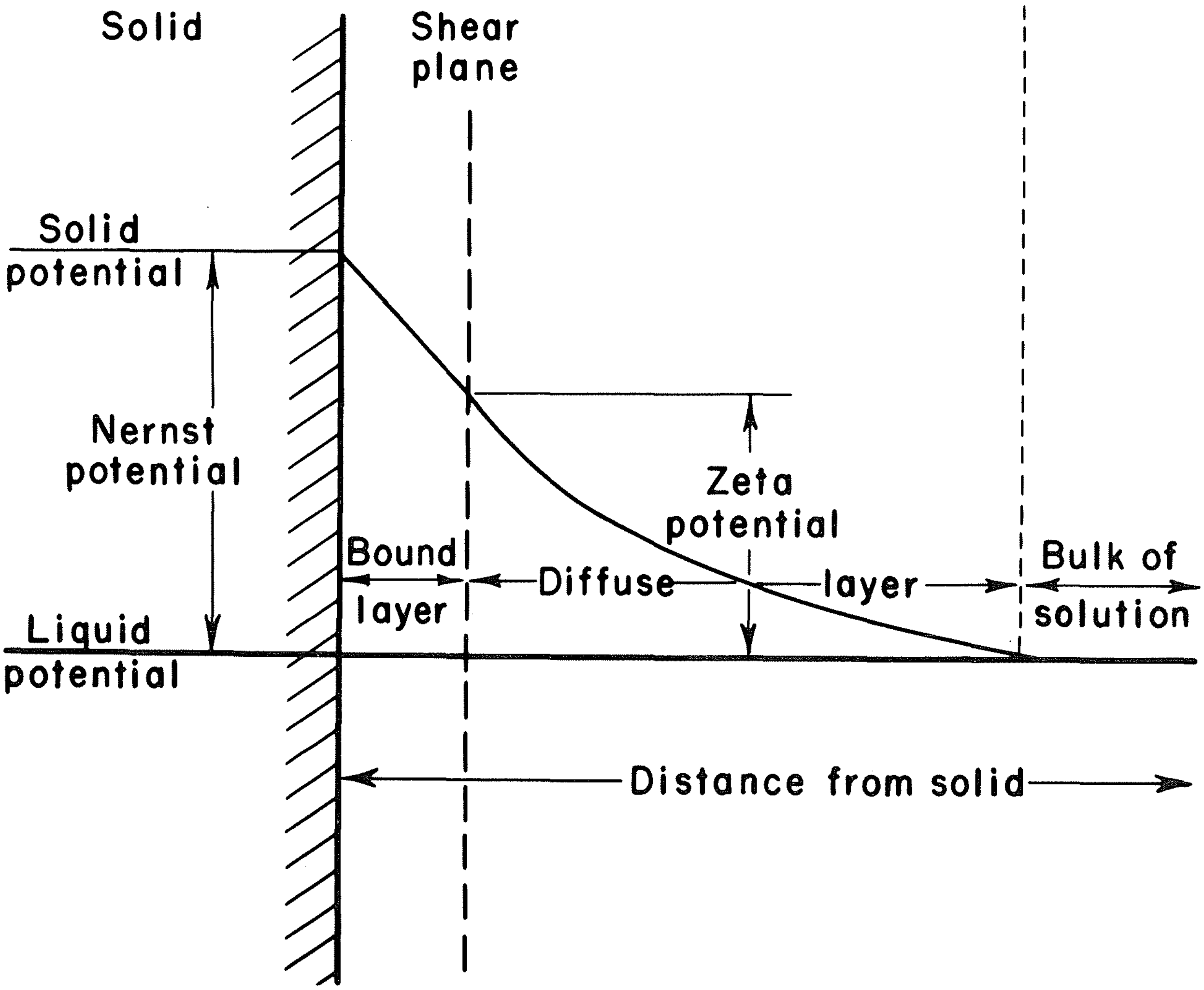

FIGURE 1. - Diagram illustrating zeta potential.

zero. In a 1974 paper, Westwood, Macmillan, and Kalyoncu (20) describe laboratory-scale experiments where quartz was drilled 13 times faster than in water, under chemical control with the zeta potential at zero. Quartz was about 20 pct harder, as measured by pendulum hardness, at zero potential than at other zeta potential values. This points to an embrittlement of the mineral lattice at zero zeta potential, which lead to increased drilling rates for the particular type of diamond-studded bit used by Westwood and coworkers. The large (thirteenfold) increase in drilling rate through chemical additives and zeta potential control reported by Westwood, however, is difficult to reconcile in view of other much lower changes reported in the literature.

Westwood (19) published work in 1975 that described an unexpected "absence of an effect." Drilling into a Texas granite with a 5-3/4-inch-diameter tricone bit with a zeta-potential-controlling surfactant solution produced no significant change in rate. He found that the same surfactant solution tripled the penetration rate when a diamond-loaded coring bit was drilled into soda-lime glass. When the bit was changed to a spade type, with no change in fluid nor drilling substrata, there was no chemical enhancement of penetration rate over that of water. Westwood therefore concluded that the cutting action of the 5-3/4-inch-diameter tricone bit was similar to that of a spade-type drill. The present authors do not agree with Westwood's conclusion. We assert that a tricone bit is more related in action to a diamond-loaded bit. This presently leaves no explanation for the "absence of an effect" when drilling is performed by the tricone bit under zeta-potential-modifying solutions. Westwood and Mills (21) in a 1975 paper put forward a warning that opposing results are easily obtained from the same environmental fluid and same material when different drill bit types are used. Skepticism as to the reality of chemical enhancement or chemical retardation could easily arise, with two separate researchers, each using the different bit types, reporting their contradictory effects.

The problem is twofold: First, no clearly understood theory exists today to explain what occurs at the mineral-solution interface. Workers have proposed several explanatory mechanisms and argued about them for years. Second, workers in mineral "hardness" research (drillability, microindentation hardness, pendulum hardness, and others) report changes from about 10 pct to over 1,000 pct, depending on experimental conditions. Workers seldom duplicate each others' results.

Accordingly, the present research sought to measure the chemically induced effects on drilling and fracturing rock, and to clarify somewhat the interesting, yet controversial, effects of surface-active chemicals. This work was performed under the Bureau of Mines program on Improving Extraction Technology (Advanced Fragmentation Techniques).

ACKNOWLEDGMENTS

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EFFECT ON DRILLING RATES

Drilling Microcline, Marble, and Serpentine

Equipment and Procedure

Tests were conducted to determine if $MgCl_2$ or $AlCl_3$ increased core-drilling rates when added to the flushing water. A small drill press turned a 4.8-mm-OD diamond-tipped coring bit at about 500 rpm, which gave a bit edge speed of 0.13 m/sec. The load was 2.50 kg. The vertical position of the bit was indicated by a linear variable differential transformer (LVDT) with a digital readout, which allowed the penetration to be calculated. The rock samples were blocks several centimeters across and 1 to 3 cm thick. They had been set in melted paraffin wax in shallow cans, and so were held by the solidified wax. The cans were clamped to the drill base with magnets. The apparatus is shown in figure 2.

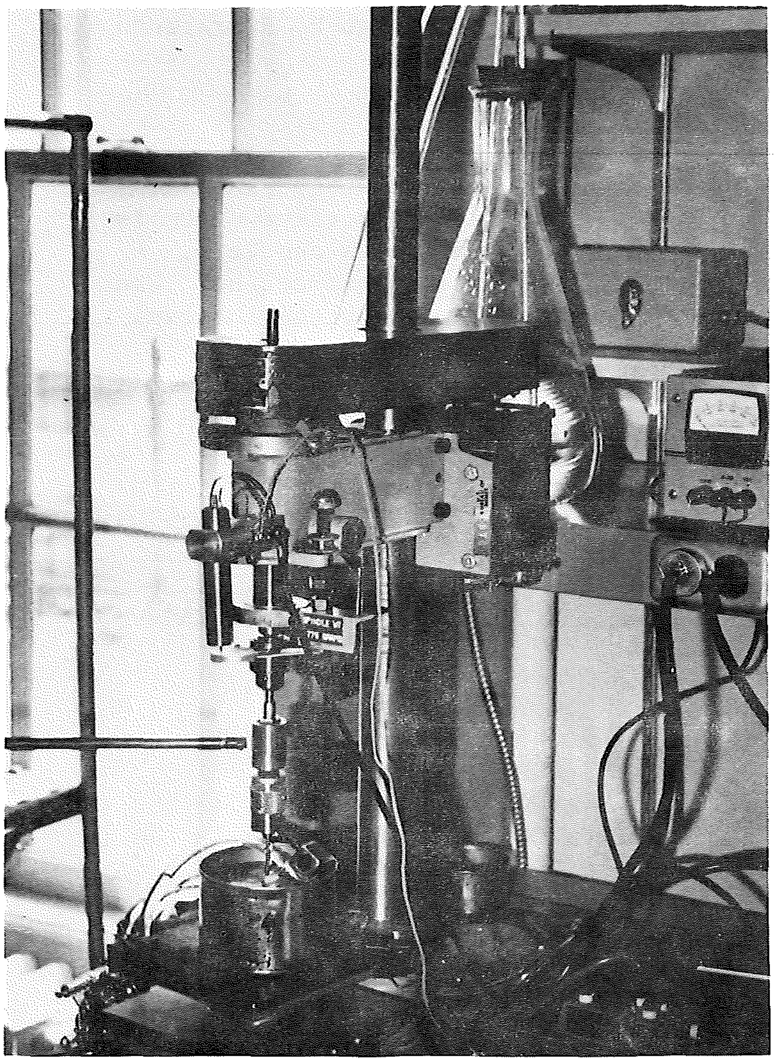

FIGURE 2. - Laboratory core-drilling equipment.

The bit was gently lowered onto the rock by hand. The voltage output of the LVDT was recorded after 10 sec of drilling. The bit was then raised for 10 sec, and the cycle was repeated. This procedure was followed because continuous drilling quickly ruined a bit, apparently from overheating.

The flushing fluid flowed from the can holding the sample into a flask and was then pumped back through the bit. About 3 liters of fluid was prepared for each test. The flushing fluids were aqueous $MgCl_2$ for drilling microcline and marble and aqueous $AlCl_3$ for drilling microcline and serpentine. The concentrations were 1 to 10,000 ppm Mg or Al, in decade steps. Distilled water was also used.

The concentrations making $\zeta = 0$ were not determined until after this drilling was completed because no attempt to relate this drilling to zeta potential had originally been planned. Later, however, literature claiming large increases in drilling rates with $\zeta = 0$ generated considerable interest. Therefore, streaming potential measurements were made to determine if any of the concentrations used were near those making $\zeta = 0$. (A zero streaming potential implies $\zeta = 0$.)

For the zeta potential tests rock samples left from the drilling tests were crushed and sieved. The microcline measurements were done with minus 28- plus 48-mesh material. There was less marble and serpentine from the drilling tests, so they were done with minus 16- plus 65-mesh material. The crushed rock was washed several times in distilled water. No acid was used in cleaning. No pH buffer was used in the streaming potential measurements or in the drilling. For each sample, the streaming potential was measured first in distilled water. The concentration of $MgCl_2$ or $AlCl_3$ was then increased until the streaming potential reversed sign. Graphical interpolation was used to determine the concentration giving a zero streaming potential. The streaming potential cell, based on a design by Fuerstenau (5), is fully described by Engelmann, Terichow, and Selim (4).

Results

The penetration rates after 70 sec of core-drilling microcline and marble in $MgCl_2$ solution are listed in table 1. Each microcline datum is the average of five tests, but each marble datum represents one test. A test in marble was done before each set of five tests in microcline. The penetration rate at 70 sec was taken to be the average over the interval from 50 to 90 sec.

TABLE 1. - Penetration rates at 70 sec for drilling microcline and marble using magnesium chloride ($MgCl_2$) as a drilling fluid

Magnesium, ppm	Penetration rate, µm/sec		Magnesium, ppm	Penetration rate, µm/sec	
	Microcline	Marble		Microcline	Marble
0	4.4	17	300	4.4	11
0	3.8	18	300	6.2	12
0	3.8	20	1,000	4.4	11
0	3.8	14	1,000	5.6	11
1	2.5	16	1,000	6.2	11
1	3.1	20	1,000	5.6	15
1	3.8	14	10,000	6.2	14
1	3.1	12	10,000	8.8	13
10	3.8	13	10,000	8.8	12
10	5.0	11	10,000	9.4	14
10	3.1	11	0	8.8	17
10	6.2	11	0	8.8	16
100	4.4	12	0	8.8	16
100	8.1	11	0	8.1	16
100	6.2	15	1	8.8	16
100	5.0	14	1	9.4	16
300	6.9	12	1	9.4	16
300	5.6	13	1	10.0	18

NOTE.--Tests are listed in chronological order.

The table shows no evidence that $MgCl_2$ increased the drilling rate in microcline. The increase in the average penetration rate when the magnesium concentration was increased from 1,000 to 10,000 ppm should not be attributed to the magnesium, because the rate stayed high after the magnesium concentration was lowered to 0 and 1 ppm.

The table suggests that $MgCl_2$ actually reduced the marble penetration rate. The average marble penetration rate was 16.4 µm/sec with 0 and with 1 ppm magnesium, but was 12.4 µm/sec with 10 to 10,000 ppm. A t-test indicated that this difference was significant at the 99-pct confidence level.

Table 1, when combined with the streaming potential measurements, shows that concentrations near those making $\zeta = 0$ did not increase the penetration rate. The ζ potentials calculated from the streaming potential measurements are shown in figures 3-4. The concentrations of magnesium which made $\zeta = 0$ on microcline and on marble were between 1.2 and 1.9 ppm and between 2.0 and 2.9 ppm, respectively. Greater accuracy was not needed because the effects are not sharp functions of concentration. Engelmann, Terichow, and Selim (4) found that an effect on pendulum hardness extended at least over the range from one-third to three times the concentration making $\zeta = 0$. It is reasonable to suppose that the same is true for drilling. Thus the concentrations of magnesium making $\zeta = 0$ were close enough to 1 ppm so that an increase in drilling rate should have been observed if lowering ζ to about zero aids drilling.

Table 2 shows the penetration rates after 70 sec of core drilling in microcline and in serpentine using $AlCl_3$ solution as a drilling fluid. The rates were calculated by the same method as for table 1. Each microline datum is the average of five tests, but each serpentine datum represents one test.

TABLE 2. - Penetration rates at 70 sec for drilling microcline and serpentine using aluminum chloride ($AlCl_3$) as a drilling fluid

Aluminum, ppm	Penetration rate, µm/sec		Aluminum, ppm	Penetration rate, µm/sec	
	Microcline	Serpentine		Microcline	Serpentine
0	13.0	42	300	6.0	18
0	7.0	28	300	5.0	19
0	6.0	19	1,000	5.0	22
0	5.5	16	1,000	5.5	17
1	6.5	14	1,000	5.0	16
1	5.5	10	1,000	5.5	19
1	5.5	14	10,000	5.5	14
1	4.5	16	10,000	5.0	15
10	5.0	12	10,000	5.0	16
10	5.0	12	10,000	5.0	18
10	5.5	14	0	5.0	15
10	5.0	16	0	5.0	16
100	6.0	20	0	5.0	18
100	5.5	16	0	4.5	21
100	5.5	14	1	4.0	28
100	5.5	12	1	5.0	17
300	5.5	16	1	6.0	16
300	6.0	13	1	5.0	14

NOTE.--Tests are listed in chronological order.

The concentration of aluminum did not significantly affect the penetration rate in microcline or serpentine. The high penetration rate for the first tests resulted from beginning this series of tests with a new bit.

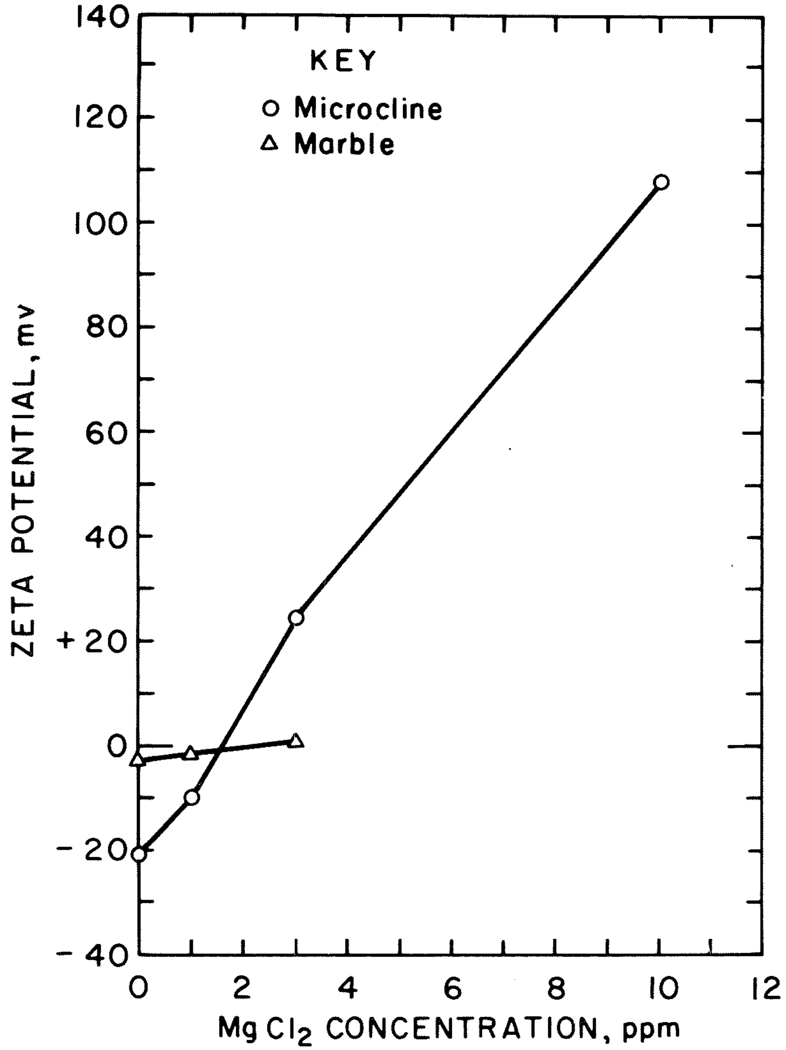

FIGURE 3. - Zeta potentials in magnesium chloride.

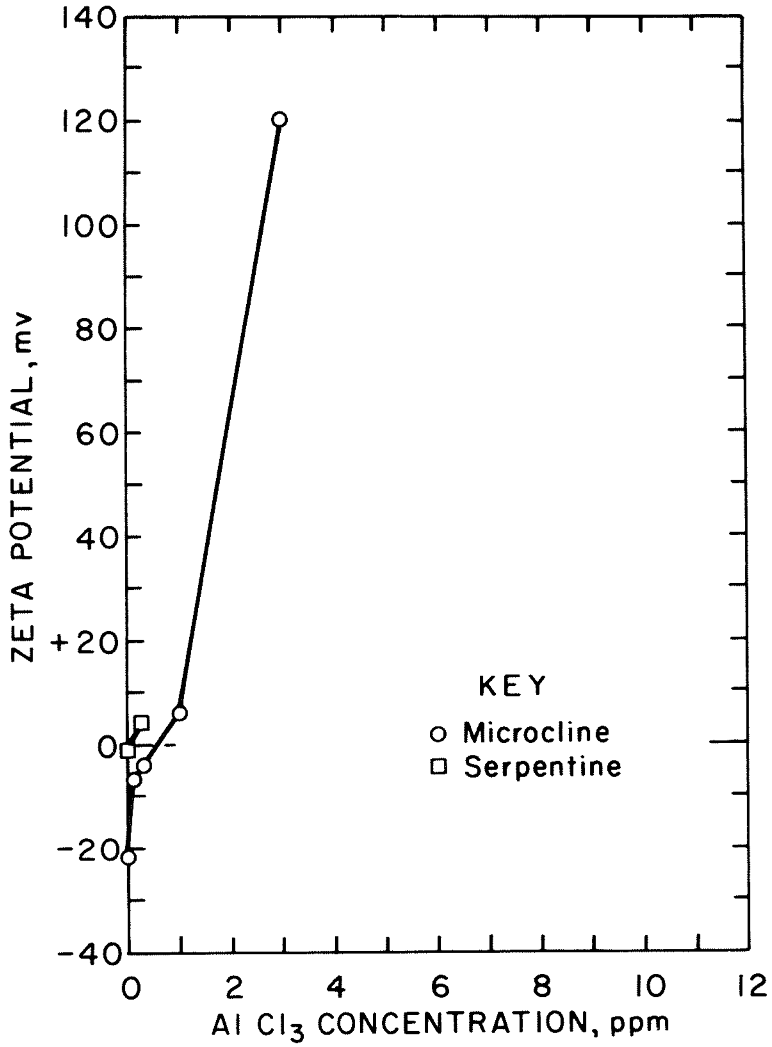

FIGURE 4. - Zeta potentials in aluminum chloride.

As before, reducing ζ did not enhance the penetration rate in microcline. Based on streaming potential measurements, the concentration of aluminum that made $\zeta = 0$ on microcline was between 0.5 and 0.9 ppm (fig. 4). This was close enough to 1 ppm that an effect should have been seen if reducing the zeta potential were effective.

No conclusion regarding the effect of ζ on drilling in serpentine can be made. The concentration of aluminum which made $\zeta = 0$ on serpentine was well under 0.2 ppm (fig. 4). This is far enough below 1 ppm that an effect with $\zeta = 0$ would not necessarily be observed with 1 ppm aluminum.

The concentrations making $\zeta = 0$ were surprisingly close for magnesium and aluminum on microcline. A trivalent ion such as aluminum would be expected to make $\zeta = 0$ at 1/10 to 1/100 the concentration of a bivalent ion such as magnesium. Accordingly, checks of possible errors were made. Two tests with each ion on microcline had been run, and the tests were consistent within the errors stated previously. The concentration of the chemical standards were cross-checked with atomic absorption (AA) spectroscopy against two standards made by other workers. No inconsistencies were found. Another source of possible error was the chance that aluminum was adsorbed on the microcline in the streaming potential apparatus. Such adsorption could make the effective aluminum concentration less than the concentration was at the time it was put in the apparatus. However, AA spectroscopy measurements showed that aluminum adsorption on microcline was negligible. After reviewing this work, J. L. Huiatt, Bureau of Mines, Salt Lake City Metallurgy Research Center, suggested that part of the aluminum may have been adsorbed as complex ions having a valence less than three.

Drilling Quartz

Equipment and Procedure

Tests were conducted to determine if oleylammonium acetate increased core-drilling rates in fused quartz when added to the flushing water in a concentration making $\zeta = 0$. This concentration was 0.7 ppm (2×10^{-6} $\underline{M}$), found in previous streaming potential measurements (14) conducted as described in the preceding section.

The equipment was similar to that used for microcline, marble, and serpentine, except that the bit was 3.2 mm OD and was turned at 2,480 rpm which gave a bit edge speed of 0.42 m/sec. The quartz blocks, 4 mm thick, were drilled on a 7- by 40-mm face. A block was held in the inverted cap of a Nalgene[5] plastic bottle by the lip of the bottle neck, which was cut from the bottle. This allowed a block to be removed by unscrewing the neck from the cover. The cover was set in melted paraffin and so was held by the solidified wax. Before being drilled, the quartz blocks were cleaned twice in methanol in an ultrasonic cleaner for one-half hour, then baked for 16 hours at 100° C and stored in a desiccator until used.

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[5] Reference to specific brands does not imply endorsement by the Bureau of Mines.

Two different methods were used to compare the effectiveness of the oleylammonium acetate with that of pure water as a drilling fluid. In the first method, each hole was drilled using both fluids. First one fluid was used while a hole was drilled for several hundred seconds, until a steady penetration rate was obtained. (The rate was always higher close to the surface.) Then the system was drained and flushed and refilled with the other fluid, and drilling was resumed in the same hole. Two tests were started with water, and two with oleylammonium acetate solution. The penetration rates just before and 60 sec after changing the fluid were compared. In the second method, a pair of holes, one hole with each fluid, was drilled in each block. It was desired to average out the effect of bit wear, which could make the first hole in each block have a higher penetration rate. Therefore, the fluid used in the first hole of each block was alternated, using water for the first hole in six blocks and oleylammonium acetate for the first hole in six other blocks. The penetration rates after 150 sec of drilling were compared.

These procedures were followed so that a paired t-test could be used because variations in penetration rates due to random variations among blocks, as well as the changing conditions of the bit, might mask any systematic effect of the chemical environment if an unpaired t-test were used. Even though the bit was dressed by drilling several holes in sandstone between each pair of holes in quartz, the drilling rates with the same fluid varied significantly.

For all quartz drilling, the bit was alternately lowered and raised for 10 sec each, as described in the preceding section.

Results

The penetration rates obtained with oleylammonium acetate solution and with pure water are compared in table 3. A paired t-test showed that the oleylammonium acetate was effective at the 95-pct confidence level.

Large variations in drilling rates for the same drilling fluid are apparent in table 3. Combining all data for each fluid, the average penetration rates and the standard deviations were 0.76 μm/sec ±0.48 for oleylammonium acetate and 0.51 μm/sec ±0.27 for water. With such large standard deviations, an unpaired t-test would not have indicated a significant difference.

TABLE 3. - Drilling rates in quartz as a function of drilling fluid

Test pair	Drilling rate, μm/sec	
	Oleylammonium acetate ($\zeta = 0$)	Water
Pair of tests in each hole:		
1......................	0.26	0.29
2......................	.30	.22
3......................	.57	.32
4......................	.31	.28
Pair of tests in each block but in separate holes:		
1......................	.50	.56
2......................	.56	.62
3......................	.33	.18
4......................	1.18	.23
5......................	.40	.42
6......................	1.46	.72
7......................	1.09	.99
8......................	1.40	.94
9......................	.51	.80
10......................	.47	.33
11......................	1.08	.53
12......................	1.73	.80
Average............	0.76±0.48	0.51±0.27

NOTE.--For paired t-test, t = 2.63.

EFFECT ON STRENGTH AND ELASTIC MODULUS

Bending Quartz Bars

Equipment and Procedure

Small fused-quartz bars, 7.6 mm wide and 3.9 mm thick, were broken in water and in heptanol to determine if heptanol reduced the strength or elastic modulus. Heptanol appears to make $\zeta = 0$ on quartz (20).

A bar was held between four half-cylinders as shown in figure 5. The half-cylinders were supported by roller and ball bearings as shown in the figure so that the bar was not twisted as the upper half-cylinders were forced down. This device, which will be called the four-point breaker, provided a uniform bending moment between the two inner (lower) half-cylinders. If a three-point breaker were used, the bending moment would be greatest at the center point. This would make the measured strength of a bar very sensitive to its position on the breaker, unless the bar were completely homogeneous.

Before use, bars were cleaned three times in methanol in an ultrasonic cleaner, dried 16 hours in an oven at 100° C, and stored in a desiccator until used.

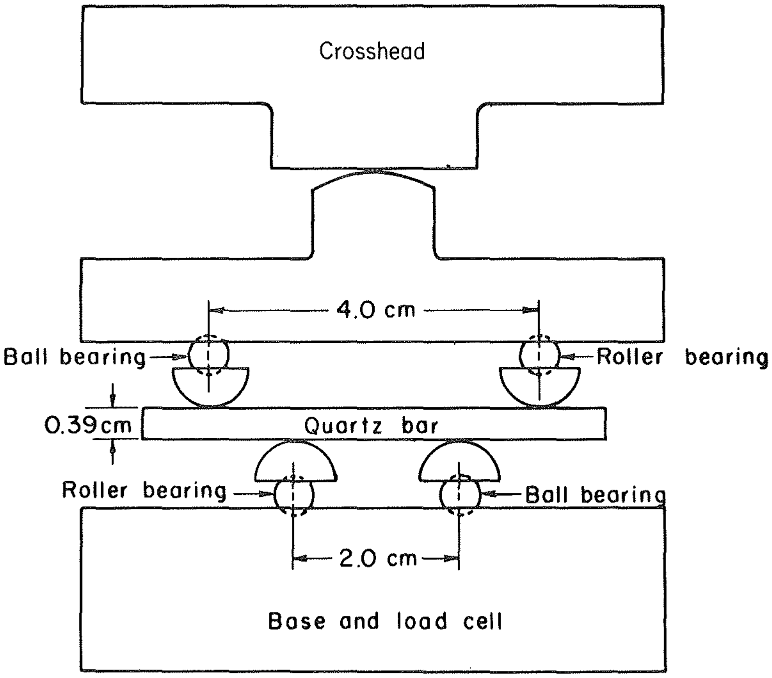

FIGURE 5. - Four-point breaker.

For each test, a bar was placed on the two lower half-cylinders. Then the top side, which was under tension during breaking, was covered with water or heptanol. The liquid was left on the bar for 1 minute before each test. To test the effect of length of time of soaking, some bars were soaked overnight, but no difference was observed.

An Instron model TM-M materials-testing machine powered the four-point breaker. The top part of the breaker was first gently lowered by hand onto the bar. Next, the Instron crosshead was lowered to just above the breaker. The speed of the crosshead was then set, usually to 0.5 mm/min, but some tests were run at 0.05 mm/min to check the effect of the slower speed. No difference was observed.

The force exerted by the crosshead was measured by a calibrated load cell and recorded as a function of time on a chart recorder. The load cell was calibrated with a weight.

The breaking force was taken as the maximum force applied by the crosshead plus the weight of the top part of the breaker. The ratio of crosshead travel to applied force represented the average vertical travel of the crosshead per Newton (N) of applied force. This was found from the force versus time chart, using the known speed of the crosshead.

To determine whether the crosshead travel really represented the bending of the quartz, or if it was due mostly to deforming the tester, two checks were made. The first check consisted of putting three bars on the breaker at once, and comparing the crosshead travel per unit of applied force to what had been obtained with one bar. If all the crosshead travel were due to bending the quartz, then the travel per unit force with three bars would be one-third of the travel per unit force with one bar. If all the travel were due to deforming the breaker, then the travel per unit force with three bars would be the same as with one. The measured values for travel per unit force showed that the ratio of crosshead travel due to bending quartz to crosshead travel due to deforming tester was 1.2. In other words, the quartz bent more than the breaker.

The second check consisted of calculating the expected crosshead travel per unit of applied force due to the quartz bending, and comparing it with what was observed. With a four-point breaker of the dimensions shown in figure 5, bending a quartz bar 7.6 mm wide and 3.9 mm thick having Young's modulus $E = 7.2 \times 10^{10}$ N/sq m, the expected travel per unit force is 0.49 µm/N. This is close to what was usually observed. Thus, both checks indicated that most of the crosshead travel was due to the bending of the quartz.

Results

The results shown in table 4 indicated that heptanol did not greatly alter the breaking force or the ratio of crosshead travel to applied force from that in water. The data are listed in order of increasing breaking force in water. The sensitivity of the test was reduced by random variations among the bars, especially in breaking force.

TABLE 4. - Breaking force and ratio of crosshead travel to applied force for small quartz bars broken with four-point breaker in water and in heptanol

Breaking force, N		Crosshead travel to applied force, µm/N	
Water	Heptanol	Water	Heptanol
133	145	0.53	0.74
(141)	(153)	(.58)	(.85)
147	165	.61	.75
160	(181)	.47	(.58)
161	183	.52	.62
(170)	191	(.82)	.54
173	192	.49	.55
178	(195)	.69	(.50)
180	203	.55	.51
183	203	.68	.58
187	205	.70	.73
(190)	(206)	(.56)	.51
(193)	219	(.50)	.52
278	228	.49	.54
349	231	.41	.54
357	250	.42	.60
385	261	.44	.53
395	273	.41	.51
426	469	.39	.43
(441)	-	(.39)	-
Av = 244	Av = 219	Av = .53	Av = .59
SD = 107	SD = 70	SD = .12	SD = .11
t = 0.79, not significant		t = 1.49, not significant at 90-pct confidence level.	

NOTE.--Tests in parentheses were at 0.05 mm/min; others were at 0.5 mm/min.

Stretching Quartz Threads

Equipment and Procedure

Tests were conducted to determine if the tensile strength or the elastic modulus of quartz thread was smaller in 0.05 ppm Al (2 × 10^{-6} $\underline{M}$ $AlCl_3$) than in water. This concentration of $AlCl_3$ made $\zeta = 0$ on quartz, according to earlier streaming tests (14).

The thread was furnished by the General Electric Co. It consisted of many fibers of fused quartz spun to give a thread 0.7 mm thick. Each fiber was 10 µm thick, as determined with a measuring microscope. The fine threads gave a large surface area for the liquids to act on.

Nine centimeters of thread were stretched at 0.5 mm/min by an Instron model TM-M materials-testing machine. It was held in jaws faced with thin rubber. Eight centimeters of the thread were in $AlCl_3$ solution or in water. The liquid was held by a small plastic bottle with a hole in the bottom for the thread to pass through. The hole was sealed with stopcock grease applied to the bottom of the bottle. To avoid contaminating thread with grease, the grease was wiped off and the hole was cleaned after each test. Also, the thread was put through the hole from the top side, so only the part of the thread that was going to be below the bottle went through the hole.

The tension on the thread was measured with a load cell which indicated the pulling force on the upper jaws. The load cell was calibrated with a weight each day. The tension was recorded as a function of time by a chart recorder. Using the speed of the crosshead and the speed of the chart, the ratio of crosshead travel to increase in tension was calculated. This ratio was calculated for 10 to 60 N, and also for 10 to 40 N and 40 to 60 N in case the effect of the $AlCl_3$ was greatest near the beginning or near the limit of the stretching. Preliminary tests had shown that the tensile strength was about 70 N.

Results

No significant differences were observed between tests in water and those in 0.05 ppm Al. This showed that the $AlCl_3$ did not greatly alter the tensile strength or the prefracture stretching of the quartz thread. The thread usually broke near one of the jaws rather than in the liquid, so this was not a sensitive test of strength. However, the rubber-covered jaws did not lower the tensile strength very much, as shown by the fact that no greater tensile strength was measured when using holders made from rubber disks, with the thread merely wrapped around them to reduce pinching. (The rubber disks were not adopted because the thread could slide a little on them, making them unsuitable for measuring the stretch of the thread.)

The average tensions required to break the thread using water and $AlCl_3$ solution were 72 N ±6 and 71 N ±6, respectively. Crosshead travel per tension in water and in $AlCl_3$ solution was 16.8 µm/N ±0.4 and 16.7 µm/N ±0.7, respectively, for 10 to 60 N of force. The values for 10 to 40 N and 40 to 60 N were similar.

DISCUSSION

The difference between the drilling results of the Bureau and of Westwood was surprising. The difference is not due to one group drilling just into the surface (Beilby layer). Westwood used the drilling rate after 200 sec of drilling, and the Bureau used the rate after 70 sec in microcline, marble, and serpentine, and 150 sec in quartz. Neither group used the total depth of penetration, because that would have been undesirably sensitive to the initial condition of the surface.

One difference in experimental technique was that at the Bureau the flushing fluid was pumped through the drill and forced against the material while drilling, whereas in Westwood's work the material was immersed but fluid was not pumped through the drill. The fluid may have made better contact during drilling using the Bureau technique. If this difference in technique caused a difference in results, the Bureau experiment should have been more sensitive to an effect by the fluid. As reported, however, the Bureau's results indicated less effect. Thus the difference remains unexplained.

The lack of an effect on the strength and elastic modulus was also unexpected. The purpose of this part of the study was to investigate two possible ways by which the efficiency of fracturing could be increased. The possible factors were--

A. Decrease the fracture strength so that less force is required to initiate and propagate cracks.

B. Decrease the prefracture deformation; that is, the total deformation the material can withstand before fracturing. The maximum force required could remain the same, but if the displacement over which the force had to be applied were reduced, the energy required would also be reduced.

The second factor could be more important than the first. In grinding, for example, most of the energy is wasted in prefracture deformation (2, p. 5). Thus, measuring the fracture strength alone would not be sufficient to determine whether making $\zeta = 0$ improved the efficiency of fracturing.

The lack of an effect of heptanol on the bending strength or prefracture deformation of the quartz bars suggests that making $\zeta = 0$ would not make comminution more efficient. The sensitivity of the test may have been reduced because the bar was exposed to normal air for a short time before being covered with heptanol, and would have adsorbed water vapor. An alternate test would be to have the bars in a vacuum and let in heptanol vapor without exposing the bars to air. However, if samples have to be prepared in this way before a ζ-related effect can be seen, the practical applications are limited.

It is likely that making $\zeta = 0$ affects only the near-surface region, and it is possible that the heptanol (or any liquid) cannot follow a rapidly propagating crack. Therefore, tests with the quartz thread were performed to give a much greater surface area. Unfortunately, this was the most inconclusive part of the study. Because the threads broke at a holder instead of in the liquid, all that can be concluded is that making $\zeta = 0$ with $AlCl_3$ did not greatly lower the tensile strength or the prefracture stretching.

CONCLUSIONS

1. No significant increases in core-drilling rates were observed for 1 to 10,000 ppm Al (as $AlCl_3$) in flushing water when drilling microcline or serpentine, nor for 1 to 10,000 ppm Mg (as $MgCl_2$) on microcline or marble. These concentrations included those reducing ζ to near zero on microcline and marble.

2. A statistically significant increase in core-drilling rates was observed for 0.7 ppm oleylammonium acetate in flushing water when drilling quartz. This concentration made $\zeta = 0$. No other concentration was used. The average increase over pure water was 50 pct. This increase was small compared to the several hundred percent increases reported by Westwood (20).

3. Heptanol, which appeared to make $\zeta = 0$ on quartz (20), did not reduce the bending strength of small fused-quartz bars below the strength in water. Similarly, no effect on the tensile strength of fused-quartz thread in 0.05 ppm Al (as $AlCl_3$), which made $\zeta = 0$, was observed.

4. Because of the generally negative findings of this study, we recommend that field tests of enhancement of drilling by making $\zeta = 0$ not be conducted unless the effect is confirmed on rock at more than one laboratory. Since only one laboratory has reported a strong correlation between ζ being zero and drilling rate, and since the Bureau did not find such a correlation, the present evidence should be regarded as contradictory. The cost of full-scale field tests with adequate control of variables is great enough that they would not be warranted without further laboratory evidence. Because of the difference between the results of the Bureau and of Westwood, new evidence of an effect would be more convincing if it came from some other laboratory. The evidence should include work with natural rock which has not been artificially prepared.

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