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Zeta Potential Control for Simultaneous Enhancement of Penetration Rates and Bit Life in Rock Drilling

By William H. Engelmann, Pamela J. Watson, Patrick A. Tuzinski,
and John E. Pahlman



UNITED STATES DEPARTMENT OF THE INTERIOR



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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Å	Angstrom	µm	micrometer
cm	centimeter	µmho/cm	micromho per centimeter
dB	decibel	mm/min	millimeter per minute
g	gram	µm/s	micrometer per second
kg	kilogram	mol/L	mole per liter
kg/mm ²	kilogram per square millimeter	mV	millivolt
kW	kilowatt	pct	percent
m	meter	r/min	revolution per minute
min	minute	V/cm	volt per centimeter
mL	milliliter	V dc	volt, direct current
mm	millimeter	yr	year

Factors for Conversion of Metric to U.S. Customary Units

Unit of measure	To convert to--	Multiply by--
Centimeter	inches	0.3937
Kilogram	pounds	2.2046
Kilogram per square millimeter	pounds per square inch	14.2233
Kilowatt	horsepower	1.3410
Millimeter	inches	.0394

ZETA POTENTIAL CONTROL FOR SIMULTANEOUS ENHANCEMENT OF PENETRATION RATES AND BIT LIFE IN ROCK DRILLING

By William H. Engelmann,¹ Pamela J. Watson,² Patrick A. Tuzinski,³ and John E. Pahlman⁴

ABSTRACT

In pursuit of innovative methods to improve mining productivity, the Bureau of Mines is investigating the use of inorganic salts as drilling fluid additives for penetration enhancement. Laboratory diamond drilling tests were performed on Westerly Granite with aluminum chloride solutions and on Sioux Quartzite with aluminum nitrate and aluminum, calcium, sodium, and zirconium chloride solutions as drilling fluid additives. These drilling results were compared with the average drilling performance using distilled, deionized water on Sioux Quartzite (12 replicate tests) and Westerly Granite (3 replicate tests). Maximum increases in penetration per given time and bit life were obtained when drilling with zero point of charge (ZPC) concentration solutions of each additive. For Sioux Quartzite, maximum increases in penetration and bit life ranged from 96 to 115 pct and 64 to 99 pct, respectively. For Westerly Granite, maximum increases in penetration of 155 and 165 pct and bit life of 109 and 136 pct were obtained at or near ZPC aluminum chloride concentrations of quartz (7.3×10^{-7} mol/L AlCl_3) and alkali feldspars (1.1 to 1.5×10^{-6} mol/L AlCl_3), respectively. This simultaneous increase in penetration per time together with extended bit life should result in increased productivity and reduced bit costs.

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INTRODUCTION

The results of an extensive literature survey of the past work on uses of chemical additives in various phases of mining and mineral processing operations have been summarized in a Bureau of Mines Information Circular (1).⁵ In this survey it was found that chemical solutions have been tested in rock fragmentation processes for over 50 yr. Several researchers reported greatly enhanced drilling performance when using various chemical additives (2-5), while others reported no beneficial effect whatsoever (6-8). Some researchers have also reported added benefits when drilling with concentrations of additive solutions that give rise to a zero point of charge (ZPC) on the surface of the rock or mineral being drilled (5-6, 9).

Rehbinder (2) in 1944 first reported aluminum chloride (AlCl_3) to be a "hardness reducer" in Soviet rock drilling tests. Ten years later, Shepherd (3) also reported the use of AlCl_3 as a "rock softener" in rotary shothole drilling in British mining operations. Concentrations of AlCl_3 employed in these two investigations ranged from 0.01 to 0.15 pct (0.0075 to 0.11 mol/L). Increases in drilling performance of less than 40 pct were reported by Shepherd and about 60 pct by Rehbinder. Drilling with ZPC concentrations of AlCl_3 was not investigated by either researcher.

In 1967 Engelmann (10) reported maximum penetration of charcoal granite (produced by chemically induced embrittlement) using an oscillating pendulum with sharp diamond points impinging on the rock surface under the zero point of charge (ZPC) concentration of 3×10^{-6} mol/L AlCl_3 . In the 1970's Westwood (7-9) further investigated the zeta potential effect in rock and mineral drilling and fracture

and termed it "zeta correlation." In 1981, Appl (11) reported minimum diamond wear at 3×10^{-6} mol/L AlCl_3 , the ZPC concentration for AlCl_3 contacting Georgia granite. This concurs with the findings of Engelmann (10). When the ZPC condition exists, rock hardness is supposedly maximized and failure tends to be more brittle, requiring less work to cut the rock (5, 7-8). This, in turn, means that the diamonds do less work, and the cutting surface temperature is apparently reduced. Lower surface temperatures result in decreased rates of diamond wear (11).

Results in the literature for drillability, cuttability, and hardness tests, respectively, on the same mineral or rock type, with the same solution, vary widely from one researcher to another depending upon experimental approach and conditions. Because of such disparities the Bureau began its present laboratory-scale drilling research investigation, which involves determining the fundamentals of chemically enhanced drilling and the conditions for optimum penetration effect. Through this research, possible explanations for past disparities may be forthcoming.

The objectives of this research are (1) to evaluate the effect on drilling performance of ZPC drilling performance concentrations of inorganic chemical compounds or salts of varying cationic valences, (2) to determine the boundary conditions for enhanced drilling performance, (3) to determine the mechanics that control such improved drilling performance, and (4) to determine the applicability of the mechanistic theory or model to drilling of rock types commonly encountered in drilling operations, using typical drilling fluids and drill bits. This report describes the results of the investigation associated with the first research objective.

⁵Underlined numbers in parentheses refer to items in the list of references at the end of this report.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Kent S. Roessler for his invaluable help in designing the computer programs that made the recording and analysis of the drilling data more

efficient. The authors also would like to thank Chester Grozdanich for his help in modifying and/or creating various specialized mechanical components for the drilling system.

DESCRIPTION OF ROCK MATERIALS DRILLED

Sioux Quartzite and Westerly Granite were employed in the present drilling research work. Both were chosen for their homogeneous, fine-grained, equigranular textures, and the fact that they are found massive in nature (quarried as dimension stone) and relatively free of fractures. To date, none of the prepared cubes of either rock type has shown any noticeable fractures or inhomogeneities that would affect the results of the tests; therefore, there is very little waste in preparing test samples from these rock types. Furthermore, both of these rock types are essentially impermeable to water, i.e., below the permeability detection limit of $1 \times 10^{-4} \mu\text{m/s}$ (12). This means that there should be no loss of the drill fluid into pores and very low probability of fluids traveling through the rock to precontaminate other undrilled areas of the rock. Perhaps most importantly, in the development of a mechanistic model to explain the drilling results, the impermeable condition of these rocks dictates that all chemical and electrochemical reactions occur at the rock mineral-fluid interface, i.e., on or very near the rock surface at the point of drilling action. Since the silica in Sioux Quartzite is almost totally quartz, results from drilling this rock type can be related to a pure quartz-water-additive system. Westerly Granite has only about one-fourth as much free silica (as the quartz phase) as does Sioux Quartzite. From this, deductions can be made as to how drilling performance with zeta-potential-controlling

fluids varies with quartz content and how drilling performance varies with two dominant feldspar phases also present in granite. Chemical analyses of major oxides present in Sioux Quartzite and Westerly Granite are presented in table 1 along with published chemical analysis results of other researchers.

SIOUX QUARTZITE

Cubes of Sioux Quartzite, approximately 15 cm on each edge, were obtained from the Jasper Stone Co. quarry near Jasper, MN. This sedimentary rock, which is also known commercially as Adamant silica, Jasper stone, or Jasper quartzite, consists primarily of compacted, fine-grained quartz sand particles cemented together with silica as the binding agent. Trace iron as hematite coats the quartz sand grains and gives the rock its characteristic pink color. Its composition of quartz sand and silica cement gives the rock its hardness, impermeability, homogeneity, and purity (>98 pct SiO_2). Trace impurities exist as hematite, magnetite, zircon, rutile, amphibole, and/or potassium feldspar (table 2).

WESTERLY GRANITE

Westerly Granite is actually a light-gray, fine-grained, equigranular granodiorite, containing about 65 pct feldspars, 25 pct quartz, 9 pct micas, and about 1 to 2 pct accessory minerals. Historically, samples of Westerly Granite

TABLE 1. - Whole-rock analyses of Sioux Quartzite and Westerly Granite, percent

Mineral	Sioux Quartzite		Westerly Granite		
	JSC ¹	Bureau of Mines ²	USGS Standards (13)		Bureau of Mines ³
			G-1	G-2	
SiO ₂	98.68	98.41	72.64	69.11	69.96
Al ₂ O ₃66	.76	14.04	15.40	14.57
Fe ₂ O ₃16	.19	.87	1.08	1.77
FeO.....	.13	ND	.96	1.45	ND
MgO.....	Trace	Trace	.38	.76	.75
CaO.....	.00	.69	1.39	1.94	3.31
Na ₂ O.....	.01	.09	3.32	4.07	4.15
K ₂ O.....	.05	Trace	5.48	4.51	4.59
H ₂ O ⁺10	Trace	.34	.55	Trace
H ₂ O ⁻00	ND	.06	.11	ND
TiO ₂05	Trace	.26	.50	.59
P ₂ O ₅01	Trace	.09	.14	.31
MnO.....	.00	Trace	.03	.03	Trace
CO ₂	ND	ND	.07	.08	ND
Total.....	99.85	100.14	99.93	99.73	100.00

ND Not detected.

¹Data furnished by Jasper Stone Co., Golden CO.

²In-house analysis at Twin Cities Research Center, Minneapolis, MN, May 24, 1985.

³In-house analysis at Twin Cities Research Center, Minneapolis, MN, Mar. 6, 1986.

TABLE 2. - Petrographic modal analyses of Sioux Quartzite and Westerly Granite, percent

Mineral	Sioux Quartzite [Krech (12)]	Westerly Granite		
		G-1 (14)	G-2 (15)	Krech (12)
Quartz.....	99+	27.5	21.4	24.6
Hematite.....	Trace	ND	ND	ND
Magnetite.....	Trace	.8	.7	.9
Zircon.....	Trace	.4	.8	1.0
Rutile.....	Trace	ND	ND	ND
Amphibole.....	Trace	ND	ND	ND
Potassium feldspar.	Trace	35.4	27.0	22.0
Plagioclase.....	ND	31.4	43.4	43.0
Biotite.....	ND	3.2	6.2	6.9
Muscovite.....	ND	1.3	.5	2.0

ND Not detected.

have been used by the U.S. Geological Survey (USGS) as geochemical rock standards G-1 and G-2 for almost 40 yr. G-1 was sampled in 1947 at the Smith Granite Co. quarry in Westerly, RI (14). G-2 was sampled in 1962 from the Sullivan Quarry of Bradford, RI, about 3 miles east of the site where sample G-1 was collected (16). The Westerly Granite employed in this research was obtained in May 1985 as

a single 1,500-lb slab from a newer, active hole in Bradford, RI, about 400 m east of the Sullivan Quarry; this hole is being quarried by the Bonner Monument Co. of Ashaway, RI. Cubes of Westerly Granite (15 cm on each edge) employed in the drilling research were cut from the large slab. Rock chips from the slab were crushed and ground to minus 100 mesh, and total chemical analysis was determined.

These chemical analysis values and those published for USGS standards G-1 and G-2 are given in table 1 for comparison.

Petrographic modal analysis results for Westerly Granite are compared in table 2.

LABORATORY DRILLING APPARATUS AND PROCEDURE

DRILLING APPARATUS

Mechanical

Drilling tests were performed in the laboratory using a modified 1.12-kW Powermatic Houdaille⁶ drill press (fig. 1). The drill press quill was designed to accept tooling with a No. 3 Morse taper. A No. 3 to No. 2 Morse taper nylon adapter was inserted into the quill, and a water swivel was fitted into the nylon adapter. To accommodate drill bits, the water swivel was machined to industry standard 5/8-in pin with 11 threads per inch.

For all tests performed, 16-mm-OD, diamond-impregnated core drilling bits were used. The bits used were of the series III (red-color-coded) high-diamond-content variety, manufactured by the Longyear Co.

Downward thrust on the drill bit during tests was achieved with constant air pressure using an Ortman pneumatic cylinder, which has an 83-mm-diam bore and a 152-mm stroke. The cylinder pressed onto a heavy steel plate attached to the drill press quill. The air pressure was set at 0.028 kg/mm², gauge for all tests; the resulting total thrust was 150 kg.

The drill was rotated using a dc motor driven by a solid-state speed control incorporating electronic feedback. This allowed the rotational speed to be varied from 0 to 720 r/min, while still providing full torque at any speed. The solid-state speed control provided exceptional speed stability, and the 100-r/min rotational speed of the drill was held constant to within ± 1 pct with full thrust, as measured by a hand-held, light-reflecting tachometer.

⁶Reference to specific products does not imply endorsement by the Bureau of Mines.

In the drilling tests 15-cm cubes of either Sioux Quartzite or Westerly Granite were placed into a clear acrylic plastic (Plexiglas acrylic sheet) sample-holding box 16.5 cm on a side with a wall thickness of 19 mm (fig. 1). This box was mounted onto a larger dimensioned 19-mm-thick acrylic plastic "baseplate," which in turn was tightly dimensioned to set into a larger box, made of the same 19-mm acrylic plastic, with inside dimensions of 42.0 by 30.5 cm. All joints were sealed to provide water tightness

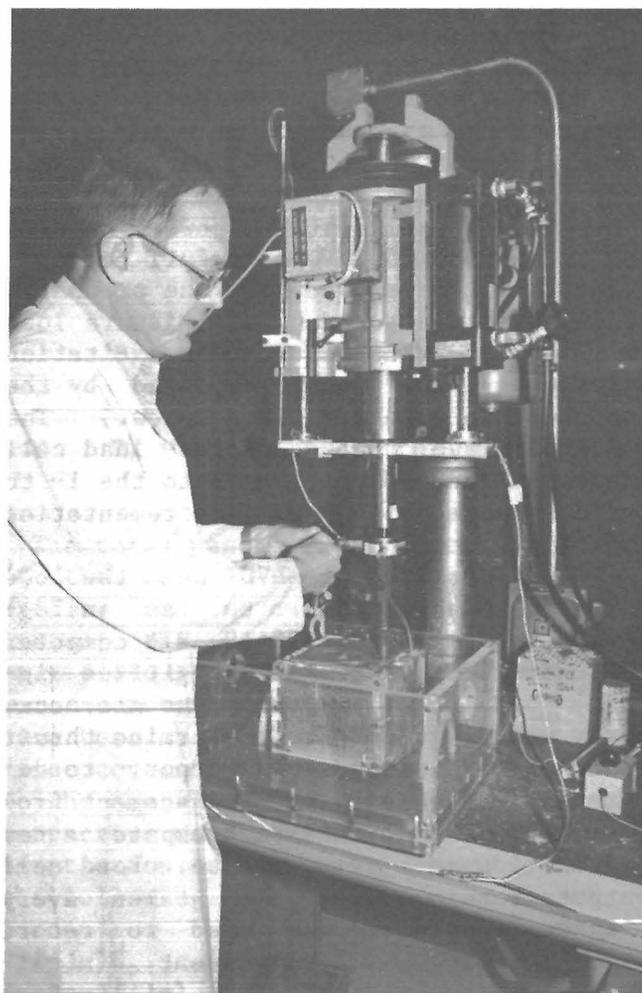


FIGURE 1.—Laboratory drilling apparatus.

and containment when the drilling fluid overflowed the sample-holding box. The baseplate was fitted with handle grips to facilitate removal of the rock cube and holding box from the larger box. A 3-mm-thick textured rubber mat was mounted on the drill press table to prevent slippage or rotation of the box assembly during drilling.

A peristaltic pump, fitted with two pump heads, was used to simultaneously pump fresh flushing fluid through the drill and pump spent flushing fluid and rock particulates out of the sample-holding box. Lengths of 7-mm-OD plastic tubing and 5-mm-ID, 12-mm-OD Tygon Masterflex pump-type tubing were used throughout the pumping system.

Electronic

The vertical displacement of the bit was measured with a dc-to-dc linear variable differential transformer (LVDT). Linear range spanned 150 mm with a linearity deviation of 0.10 pct of full range. LVDT excitation was 15.0 V dc from a regulated solid-state power supply; output spanned ± 5.0 V dc at full scale.

The thrust developed from the pneumatic cylinder was measured by a miniature load cell of 227-kg capacity. An excitation voltage of 5.0 V dc was supplied by the computer interface. (See below.) The millivolt-level output of the load cell was amplified 40 dB (100 X) to the 1- to 2-V-dc range with an instrumentation amplifier.

The outputs from the LVDT and the load cell were connected to an analog-to-digital converter (ISAAC 91A computer interface), which sent the digitized signals to a microcomputer. The microcomputer was programmed to determine thrust values from the load cell output, to determine the change in displacement from the LVDT output, and to compute a new penetration rate every minute. Load cell output readings were also taken every minute. A printer was used to record time (minutes), displacement (millimeters), penetration rate (millimeters per minute), and load (kilogram).

DRILLING PROCEDURE

The cubes of Sioux Quartzite and Westerly Granite were marked off for 49 equally spaced holes to be drilled in a random manner as dictated by a computer-generated random number sequence. Sioux Quartzite cubes were aligned so that drilling occurred perpendicular to relict bedding planes. Drilling perpendicular to the bedding planes ensured that the material encountered in each drill hole would be as similar in nature as possible.

Before drilling of each hole was started, the rotating drill was briefly contacted, under load, with the rock surface to "seat" the drill bit. This procedure, referred to as "collaring," was done to circumvent any potentially damaging skewed or wobbly startup of the bit under test conditions. Next, the initial starting depth on contact with the collared drill hole was measured and keyed into the computer for subsequent displacement and penetration rate computations. Other basic information needed to identify the test drill hole, rock type, additive, and additive concentration was also keyed into the computer. With these steps completed, the drilling operation was begun by starting the drill rotation, the fluid flow, and the air pressure (providing full thrust) with subsequent startup of the computer data logging as the drill bit contacted the collared drill-hole surface. Drilling in the hole continued until a preset voltage level (indicating maximum allowable penetration of the drill) triggered an audible buzzer signal from the computer. At that point the operator stopped the drill rotation and the fluid flow and decreased the air pressure, thus retracting the bit. The test block was then repositioned so that the drill bit was directly over the next drill hole according to the randomized drilling schedule.

The combination of drill thrust and rotational speed can be varied until the diamond-impregnated bit will self-sharpen, i.e., the exposed diamonds will be worn and broken out of the matrix, the

matrix will be worn away, and fresh diamonds will be exposed. For drilling in Sioux Quartzite with a drill thrust of 150 kg, the rotational speed of the drill has to be about 1,000 r/min for the bit to self-sharpen. Because it was not possible to determine if an observed enhanced drilling effect under the conditions for bit self-sharpening was due to the chemical additive phenomenon or the exposure of one or more fresh, sharp diamonds, all drilling tests were run with a drill thrust and rotational speed that did not result in self-sharpening (150-kg drill thrust and 100-r/min rotational speed). The dull bit therefore had to be sharpened after every test.

Depending upon rock type, sharpness of the drill bit, and/or performance of the additive solution, an individual drilling test encompassed from 3 to over 20 drill holes. Holes were drilled approximately 100 to 105 mm in depth. Before each water or additive test, the drill bit was resharpened by brief drilling (1 to 2 min) into a high-alumina-content refractory brick to a sharpness level corresponding to an initial penetration rate of about 5 to 6 mm/min. Drilling was begun at this sharpness level, and data were acquired throughout the test. Parameters recorded include elapsed time, load, displacement, and penetration rate data. However, it was not until the average penetration rate of the drill declined to 4.5 mm/min that the data were used for comparison of drilling performance between tests. Drilling continued with either water or a given additive concentration over a span of several holes, until the average penetration rate for a given hole had fallen to 2.0 mm/min. At this point the test was terminated and the bit was resharpened in preparation for another test.

This procedure was followed for both rocks and all additive solution concentrations tested. When one rock cube was used for drilling tests with water and several different additive solution concentrations, the water test, or test with the lowest additive solution concentration, was completed first. Subsequent drilling tests on the same cube were conducted with the lowest additive solution

concentration first, moving sequentially to the highest additive solution concentration.

Twelve replicate drilling tests in Sioux Quartzite and three replicate drilling tests in Westerly Granite were conducted using distilled, deionized water (DDIW) as the drilling fluid. Five replicate drilling tests on Sioux Quartzite were conducted with the ZPC concentration solution of each of the chloride salt additives, while only two replicate tests were conducted with the ZPC concentration of $\text{Al}(\text{NO}_3)_3$. Three replicate drilling tests were conducted on Westerly Granite with the ZPC concentration solutions corresponding to the ranges of both quartz and K-Na feldspars.

PROCEDURE FOR CALCULATING DRILLING RESULTS

After each individual hole was drilled, the penetration rate for that hole was calculated by the equation

$$P_r = P_h / T_h, \quad (1)$$

where P_r = penetration rate for that hole, mm/min,

P_h = total penetration for that hole, mm,

and T_h = total time for that hole, min.

The total penetration, which is the sum of the depths reached in all holes drilled, and the cumulative time from the instant the penetration rate was 4.5 mm/min to the instant it was 2.0 mm/min were determined for each drilling additive test. Total penetration for additive concentration i , P_{ai} , was compared to the average total penetration for the respective water-only tests, P_w , and the penetration effect was determined using the following equation:

$$E_{pi} = [(P_{ai} - P_w)/P_w] * 100, \quad (2)$$

where E_{pi} = the penetration effect for additive concentration i , pct,

P_{ai} = the total penetration for drilling with additive concentration i , mm,

and P_w = the average total penetration for drilling with DDIW alone, mm.

Total elapsed time for additive concentration i , T_{ai} , was compared to the average total elapsed time for the respective water-only tests, T_w , and a bit life effect was determined by the equation

$$E_{bi} = [(T_{ai} - T_w)/T_w] * 100, \quad (3)$$

where E_{bi} = the bit life effect for additive concentration i , pct,

T_{ai} = the cumulative time for drilling with additive concentration i , min,

and T_w = the average cumulative time for drilling with DDIW alone, min.

ZETA POTENTIAL CONSIDERATIONS

The Stern model of the electrical double layer, shown in figure 2 (10),

presents a fairly simple and useful picture of the electrical potential around a

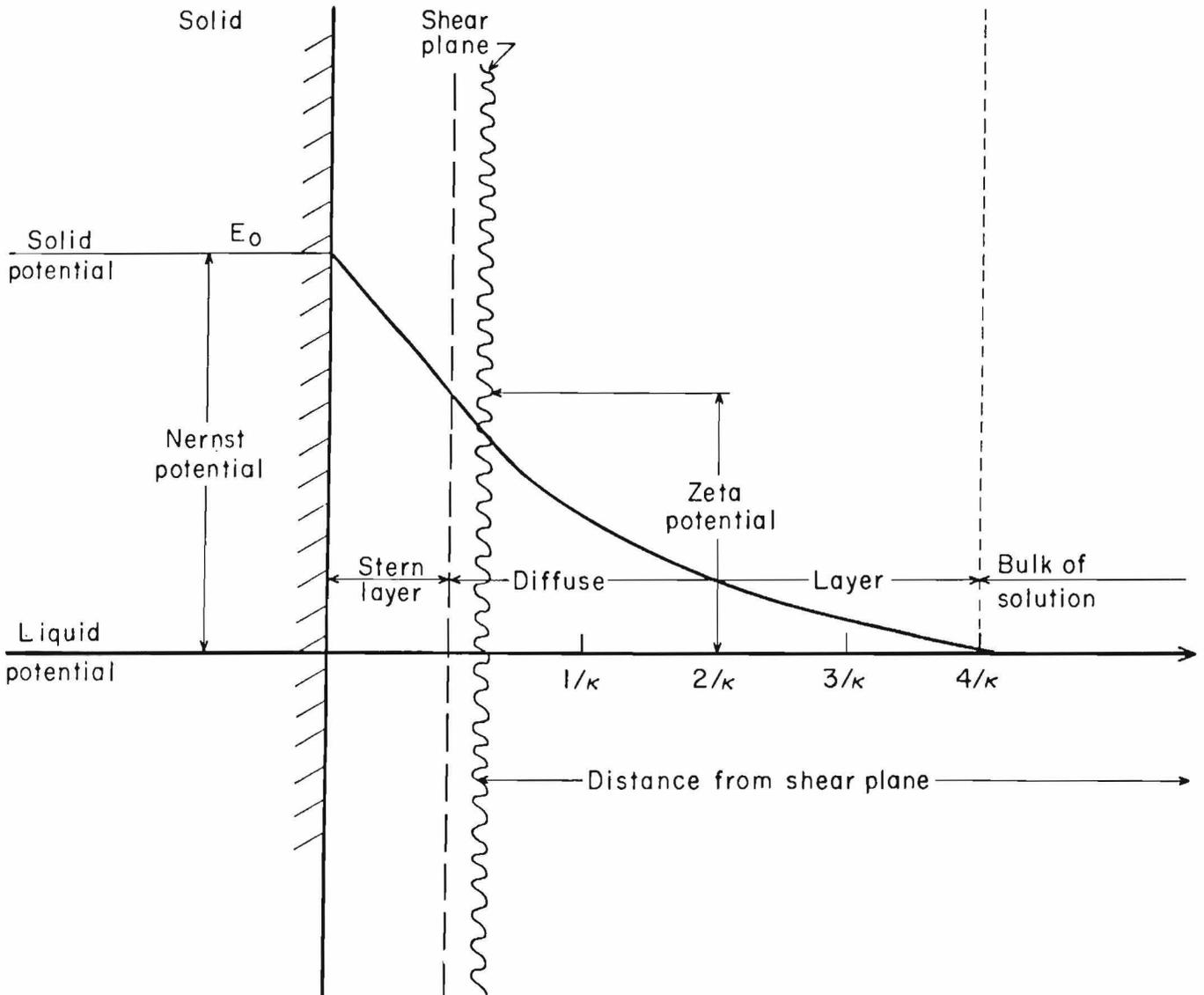


FIGURE 2.—Stern model of electrical double layer.

solid in a liquid. It predicts electrical potential based on the ionic diffuse double-layer theory. The double layer is set up between the solid surface and the bulk solution and is comprised of the Stern layer and a diffuse layer. In the Stern model, the solid has a rigidly fixed charge, and the Stern layer is a practically immobile layer of oppositely charged ions of the liquid adsorbed on the solid. Farther away from the solid is a second layer (hence double layer), which is a diffuse region of charge comprised of mobile positively and negatively charged ions. This layer may have a net charge of the same or opposite sign from that of the tightly held adsorbed first layer. The total electrical potential difference, E_o , that develops between the solid surface and the bulk solution (across both the Stern and diffuse layers) is called the Nernst potential. This potential is the balance between electrostatic attraction of the solution counter ions to the solid surface and their tendency to diffuse away from the surface. The zeta potential is the potential drop across the diffuse layer and is readily varied through changes in bulk solution concentration.

The distance over which there exists a concentration gradient is very small. The double-layer thickness, $1/\kappa$, is function of ionic strength and temperature. At room temperature, for example, in a 10^{-5} mol/L NaCl solution, $1/\kappa$ is

about $0.1 \mu\text{m}$, or $1,000 \text{ \AA}$. As the zeta potential goes to zero, the diffuse layer thickness is compressed until the Nernst potential drop occurs totally within the Stern layer.

The zeta potential of most solids is negative in water of near neutral pH (6 to 7). Addition of cations such as Al^{3+} , Ca^{2+} , and Na^+ will reduce the magnitude of this negative potential until ultimately the sign of the diffuse layer charge is changed.

Zeta potential values are scarce in the literature, and although accurate for the conditions encountered when determined, they cannot be used blindly for other applications since they are quite sensitive to differences in water composition, differences in structure of the solid, and minor differences in the phases present in the solid. Zeta potentials for discrete mineral phases from different sources should be in agreement; however, zeta potentials for rocks of the same general mineral composition but from different geologic formations can vary widely because of variances in the way the mineral phases in the rock are distributed. Thus, it is wise and prudent to determine zeta potentials for each particular rock being drilled, in the same fluid used in drilling the rock, and not rely on literature zeta potential values as generic zeta potential values for any particular rock.

ZETAPOTENTIAL DETERMINATIONS

All of the zeta potential measurements were run on a Komline Sanderson model ZR-11 zeta reader (fig. 3). Before each rock-chemical additive test, DDIW was flushed through the zeta reader to clean out any particles remaining from previous tests. This flushing continued until the specific conductance (SC) registered $<5 \mu\text{mho/cm}$, and no particles were detected on the viewing screen. With a thoroughly cleaned system, each rock-chemical additive test was started with 1,000 mL of DDIW to which approximately 0.2 g of either finely ground Sioux Quartzite or Westerly Granite was added. Zeta potential readings were determined for the

rock particles in DDIW by matching the grid line speed on the viewing screen to the speed of a rock particle moving in an electric field of 5 or 10 V/cm, using an adjustable potentiometer. When the grid and particle speeds were matched, the zeta potential in millivolts was displayed on a digital readout. Thirty particle velocity readings were taken to get a statistically valid average, with temperature and specific conductance also being noted. After the rock-DDIW readings were completed, a precise amount of additive concentrate was added to the system. Again, 30 readings were recorded, along with the temperature and

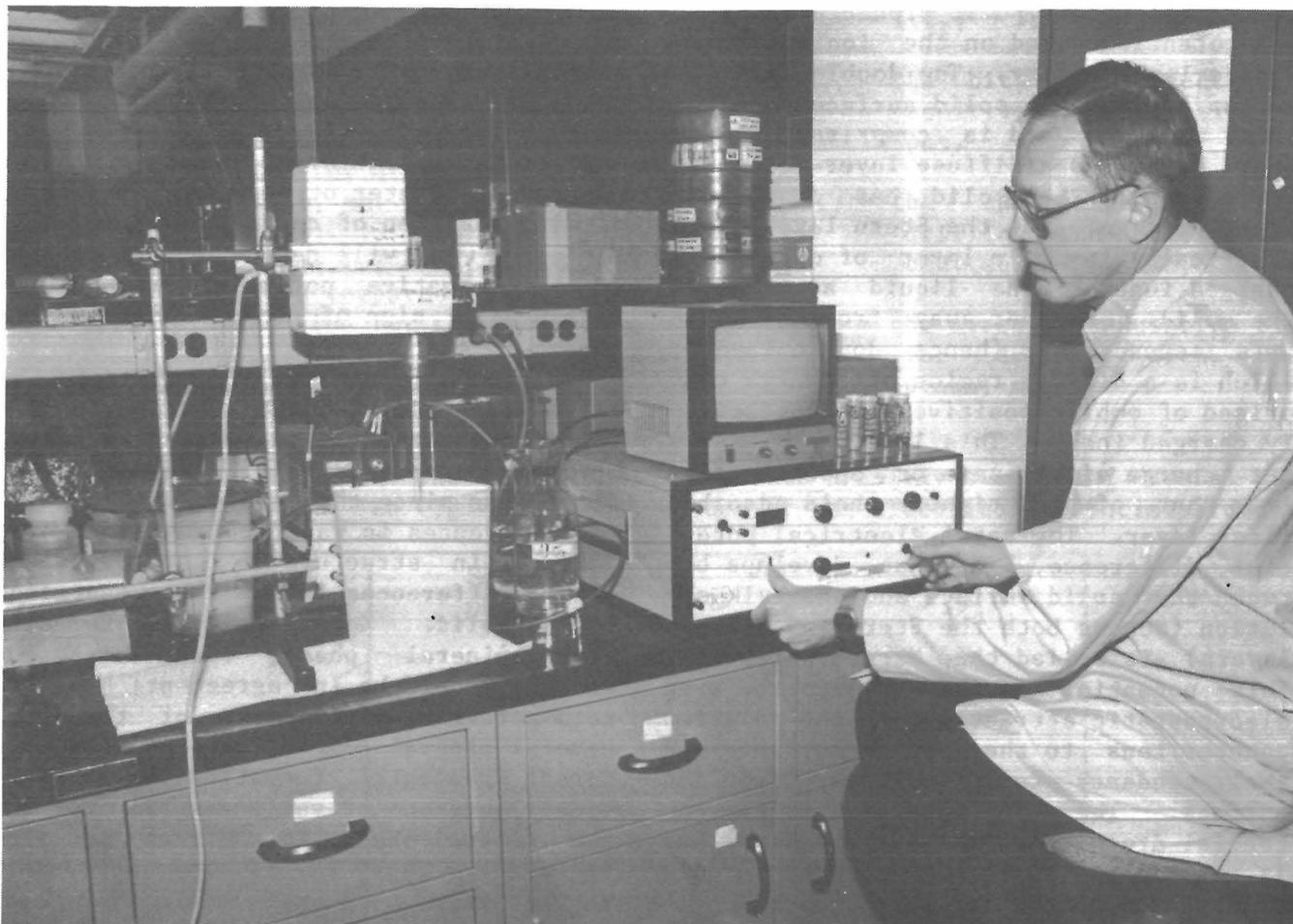


FIGURE 3.—Zeta reader.

specific conductance. Precise volumes of concentrate were added sequentially, and average zeta potential values were determined until several positive zeta potential values were obtained. The zeta potentials for both rocks tested were negative in DDIW and remained negative until a specific concentration of chemical additive was reached, wherein the particles were motionless, or nearly motionless. This represented the zero-point-of-charge (ZPC) concentration. To determine the ZPC concentration, zeta potential values were plotted versus additive concentration for three complete sets of tests, ranging from the high negative zeta potentials determined in DDIW through the ZPC point, and continuing on into the positive zeta potential region. The additive concentration values where the curve crossed the zero zeta potential line were determined and averaged to give

the ZPC concentration. Zeta potentials were determined for Sioux Quartzite in AlCl_3 , $\text{Al}(\text{NO}_3)_3$, CaCl_2 , NaCl , and ZrCl_4 solutions. Westerly Granite was tested in AlCl_3 only. These were the same rock-chemical combinations tested in the drilling research.

The results of the zeta potentials determined for Sioux Quartzite are given in table 3. It should be noted that for Sioux Quartzite the ZPC concentrations of the chloride additive series decrease with increasing valence. For +1 valence (sodium) the ZPC concentration is 2.2×10^{-1} mol/L; for +2 valence (calcium) it is 1.6×10^{-2} mol/L; and for +3 valence (aluminum) it is 6.8×10^{-7} mol/L. The +4 valence zirconium ion behaves more like a +3 valence ion as its ZPC concentration is close to that of the trivalence aluminum ion. Recent evidence (17) indicates that in aqueous solutions,

zirconium does not exist in the +4 state; nor is there any positive indication of the existence of discrete zirconyl ions, ZrO^{2+} . From these observations it would appear that Zr salts probably hydrolyze in water to give predominantly a tri-valent complex ion, such as $Zr(OH)^{2+}$.

The results of zeta potential determinations for granite mineral components are given in table 4. For Westerly Granite, the three main component minerals and their relative abundance are alkali feldspars, 65 pct; quartz, 25 pct; and biotite, 7 pct. The $AlCl_3$ ZPC concentrations for these three mineral components are 1.1 to 1.5×10^{-6} mol/L, 7.3×10^{-7} mol/L, and 3×10^{-6} mol/L, respectively. Table 5 gives chemical analysis data for six feldspar mineral separates, spanning the entire range of potassium, sodium, and calcium feldspars. Zeta potentials in $AlCl_3$ -DDIW solutions for these same feldspars are presented in table 4. Figure 4 is a composite of the feldspar zero-zeta-potential (or ZPC) data of table 4 and the feldspar chemical analysis data of table 5. These data in figure 4 demonstrate that more $AlCl_3$ must be added to feldspar powders in solution to achieve a ZPC as the silica and alkali (Na,K) content of the feldspar increases, or as the alumina, calcium, and magnesium content decreases.

TABLE 3. - Zeta potential results for Sioux Quartzite

Inorganic salt tested	Field, V/cm	Zeta potential in DDIW, mV	ZPC concentration, mol/L
$AlCl_3$	10	-25.60	6.8×10^{-7}
$CaCl_2$	5	-22.20	1.6×10^{-2}
$NaCl$	5	-21.90	2.2×10^{-1}
$ZrCl_4$	10	-21.80	1.4×10^{-6}
$Al(NO_3)_3$...	10	-21.40	4.3×10^{-7}

TABLE 4. - Zeta potential results for Westerly Granite mineral components in $AlCl_3$

Mineral component tested	Field, V/cm	Zeta potential in DDIW, mV	ZPC concentration, mol/L
Quartz.....	10	-18.20	7.3×10^{-7}
Biotite.....	10	-18.61	3.0×10^{-6}
Feldspar series:			
Microcline	10	-20.66	1.5×10^{-6}
Albite....	10	-16.95	1.3×10^{-6}
Oligoclase	10	-21.40	1.13×10^{-6}
Andesine..	10	-18.20	7.4×10^{-7}
Bytownite.	10	-17.30	3.7×10^{-7}
Anorthite.	10	-13.14	2.4×10^{-7}

TABLE 5. - Whole-rock major oxides analysis of feldspar mineral separates, percent

Oxide	Micro-cline	Albite	Oligo-clase	Ande-sine	Bytown-ite	Anor-thite
SiO_2	65.46	64.18	62.04	53.06	48.78	43.86
Al_2O_3 ...	18.33	20.03	21.35	25.51	28.72	34.77
Fe_2O_357	Trace	Trace	.51	.33	.88
FeO	Trace	Trace	Trace	Trace	Trace	Trace
MgO	Trace	Trace	Trace	Trace	.27	.17
CaO66	2.80	4.48	10.91	18.05	21.13
Na_2O	4.85	9.71	8.49	4.85	2.56	.50
K_2O	6.99	.54	.44	.57	Trace	Trace
H_2O^+	Trace	Trace	Trace	Trace	Trace	Trace
TiO_2	Trace	Trace	Trace	.30	Trace	Trace
P_2O_513	Trace	Trace	.10	ND	ND
MnO	Trace	ND	ND	ND	ND	ND
BaO	ND	ND	ND	ND	ND	ND
Total.	96.99	97.26	96.80	95.81	98.83	101.23

ND Not detected.

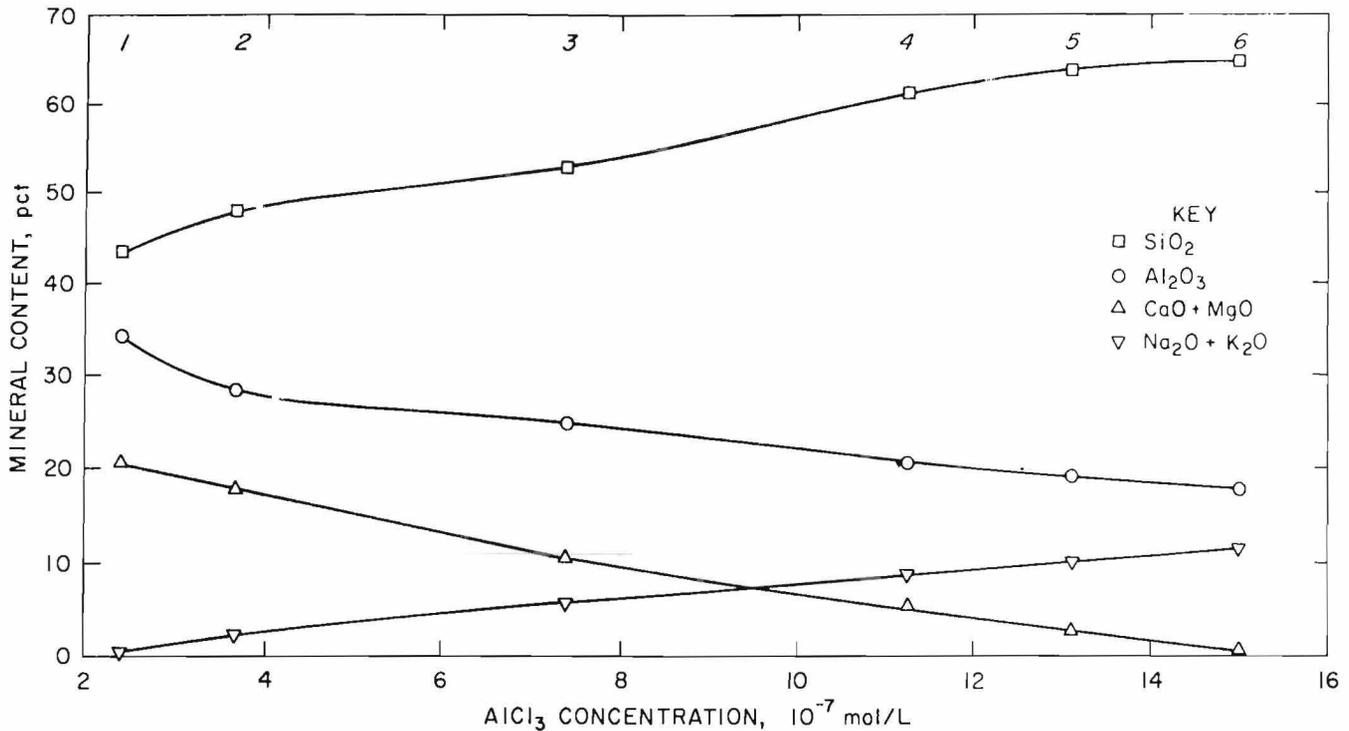


FIGURE 4.—Plot of feldspar chemical analysis as a function of zero point of charge concentrations. 1, Anorthite; 2, bytownite; 3, andesine; 4, oligoclase; 5, albite; 6, Microcline.

RESULTS AND DISCUSSION

SIOUX QUARTZITE

Penetration and bit life effects are listed in table 6, for the drilling of Sioux Quartzite with various concentrations of five inorganic salts: AlCl_3 , CaCl_2 , NaCl , ZrCl_4 , and $\text{Al}(\text{NO}_3)_3$. Graphical displays of the data are given in figures 5 and 6 for the penetration and bit life effects, respectively.

For drilling Sioux Quartzite with AlCl_3 solutions (table 6 and Figure 5A), a maximum penetration effect of 104 pct was obtained with a 6×10^{-7} mol/L AlCl_3 solution as the drilling fluid, although the penetration effect of 99 pct for a 5×10^{-7} mol/L AlCl_3 solution is close to this maximum. From table 6 and figure 6A, it can be seen that the maximum extension of bit life of about 99 pct was obtained with the 5×10^{-7} mol/L AlCl_3 solution; however, the bit life extension with the 6×10^{-7} mol/L AlCl_3 solution is still 85 pct. The concentrations of both

the 5×10^{-7} mol/L and the 6×10^{-7} mol/L AlCl_3 solutions are close to the ZPC concentration of 6.8×10^{-7} mol/L AlCl_3 determined with the zeta potential data obtained on the zeta reader.

In preparing the low-concentration solutions used in these tests, larger differences between the measured concentrations of solutions and actual concentrations of solutions are more probable for the zeta reader solutions than for the drilling test solutions since any errors in measurement of the small quantities of additive additions will be magnified more for zeta reader solutions because of the much smaller volume of DDIW to which these AlCl_3 additions are made.

A secondary performance peak of lower magnitude was obtained in drilling with a 1×10^{-5} mol/L AlCl_3 solution, where the penetration increased by 80 pct and bit life was extended over 73 pct. This second peak is not clearly understood at

TABLE 6. - Sioux Quartzite drilling results

Conc, mol/L	Average penetration effect, pct	Average bit life effect, pct	Repliques	Conc, mol/L	Average penetration effect, pct	Average bit life effect, pct	Repliques
AlCl ₃ SOLUTIONS				NaCl SOLUTIONS			
1 × 10 ⁻⁸ ...	-33.53	-33.76	1	9 × 10 ⁻² ...	16.52	5.30	1
1 × 10 ⁻⁷ ...	40.12	44.69	2	1 × 10 ⁻¹ ...	14.86	5.30	1
5 × 10 ⁻⁷ ...	98.50	98.71	1	2 × 10 ⁻¹ ...	115.03	76.35	5
6 × 10 ⁻⁷ ...	103.83	85.12	5	3 × 10 ⁻¹ ...	-3.50	-6.59	1
7 × 10 ⁻⁷ ...	62.87	35.02	2	5 × 10 ⁻¹ ...	2.22	15.49	1
8 × 10 ⁻⁷ ...	61.99	40.96	1	ZrCl ₄ SOLUTIONS			
1 × 10 ⁻⁶ ...	28.60	23.13	2	1 × 10 ⁻⁷ ...	33.32	40.12	2
3 × 10 ⁻⁶ ...	17.21	22.28	1	5 × 10 ⁻⁷ ...	-9.57	-1.49	1
5 × 10 ⁻⁶ ...	52.47	50.31	2	9 × 10 ⁻⁷ ...	39.54	35.87	1
7 × 10 ⁻⁶ ...	35.81	34.17	1	1.4 × 10 ⁻⁶ ...	96.29	67.71	5
1 × 10 ⁻⁵ ...	79.64	73.23	2	5 × 10 ⁻⁶ ...	4.48	-8.29	2
5 × 10 ⁻⁵ ...	60.32	44.36	1	1 × 10 ⁻⁵ ...	43.37	30.77	1
1 × 10 ⁻⁴ ...	50.40	54.55	1	1 × 10 ⁻⁴ ...	-46.33	-36.31	1
CaCl ₂ SOLUTIONS				Al(NO ₃) ₃ SOLUTIONS			
1 × 10 ⁻⁵ ...	0.87	13.81	1	1 × 10 ⁻⁷ ...	-14.34	-5.01	1
1 × 10 ⁻⁴ ...	53.23	36.01	1	3 × 10 ⁻⁷ ...	84.46	55.16	1
1 × 10 ⁻³ ...	28.32	24.83	2	4.33 × 10 ⁻⁷ ...	98.09	63.50	2
5 × 10 ⁻³ ...	87.32	73.23	1	5 × 10 ⁻⁷ ...	-24.32	-16.35	1
7 × 10 ⁻³ ...	32.60	5.30	1	1 × 10 ⁻⁶ ...	11.38	18.82	1
9 × 10 ⁻³ ...	68.12	52.85	2				
1.13 × 10 ⁻² ...	96.53	72.67	5				
2 × 10 ⁻² ...	-14.18	5.74	1				
3 × 10 ⁻² ...	-7.46	-1.49	2				
4 × 10 ⁻² ...	1.42	5.30	1				
5 × 10 ⁻² ...	-17.18	-6.59	1				
7 × 10 ⁻² ...	-3.70	10.39	2				
1 × 10 ⁻¹ ...	1.56	20.58	1				

this time. Early in the research it was thought to be an artifact or error due to data scatter from rock inhomogeneities. But replications of this experiment at the same concentration level showed these observed data to be repeatable. Further research is needed to determine causes for this second peak.

The drilling penetration effect data for Sioux Quartzite with divalent CaCl₂ solutions (table 6 and figure 5B) show a maximum penetration enhancement of 97 pct when drilling with 1.13 × 10⁻² mol/L CaCl₂ solutions, together with a bit life extension of about 73 pct (table 6 and figure 6B). This solution concentration is again close to the ZPC concentration of 1.6 × 10⁻² mol/L CaCl₂.

For monovalent NaCl, a maximum penetration effect of 115 pct (table 6 and figure 5C) and maximum bit life effect of

76 pct (table 6 and figure 6C) were both obtained when drilling with a 2 × 10⁻¹ mol/L NaCl solution. This is very close to the ZPC concentration of 2.2 × 10⁻¹ mol/L NaCl.

The fourth ionic salt, ZrCl₄, was tested as representative of a salt with a tetravalent (+4) cation. However, as was hypothesized in a previous section, Zr appears as a trivalent complex ion such as Zr(OH)³⁺ in solutions and thus has a ZPC concentration of 1.4 × 10⁻⁶ mol/L ZrCl₄, which is near that of the Al³⁺ ion. A maximum penetration effect of 96 pct (table 6 and figure 5D) and maximum bit life extension of 68 pct (table 6 and figure 6D) resulted when drilling with a 1.4 × 10⁻⁶ mol/L ZrCl₄ solution, which is the ZPC concentration. As in the case of drilling of Sioux Quartzite with AlCl₃ solutions, secondary maxima of lower

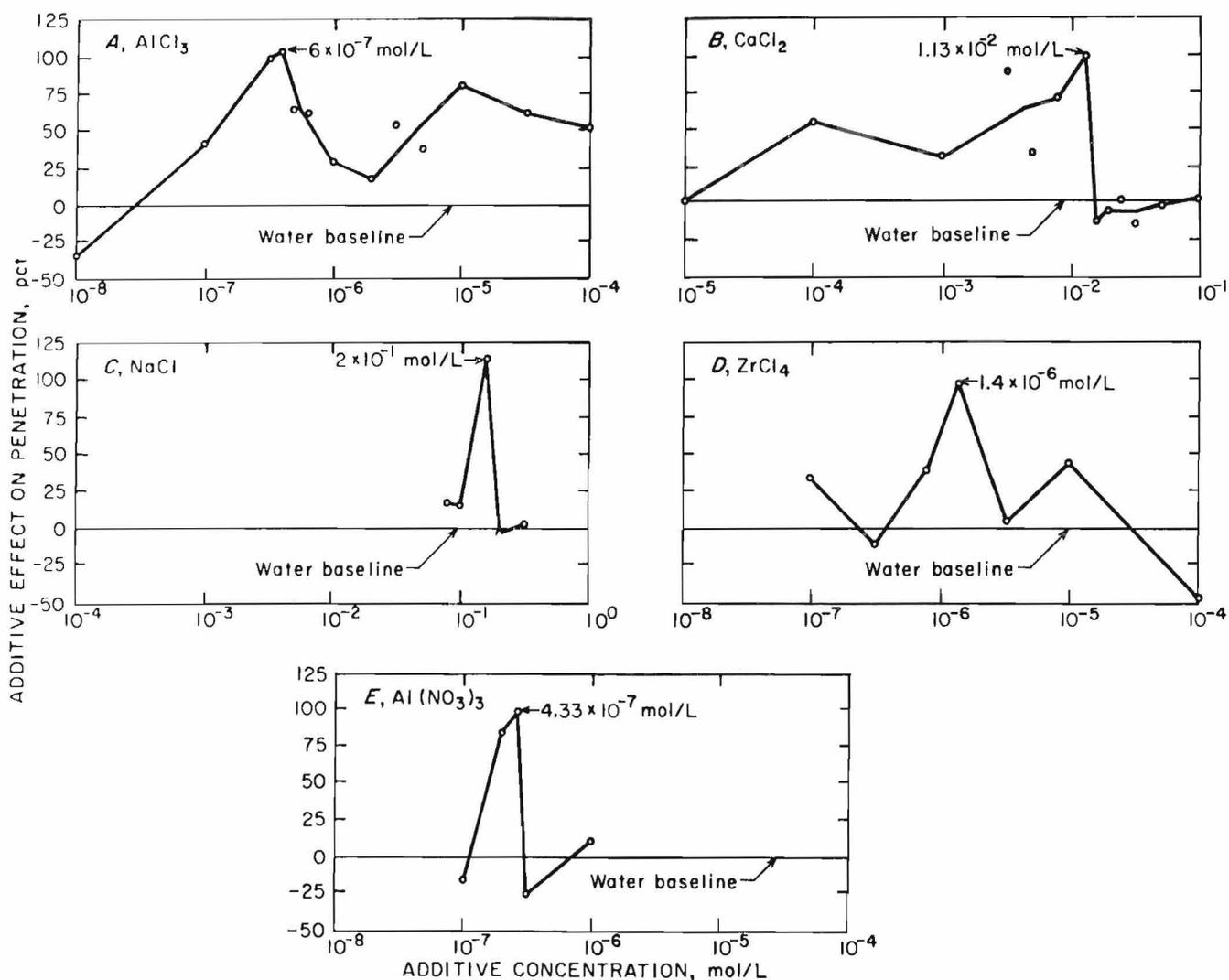


FIGURE 5.—Zeta potential control of drilling penetration of Sioux Quartzite.

magnitude, 43 pct and 31 pct, respectively, are observed in both penetration and bit life effect data for 1×10^{-5} mol/L concentration ZrCl₄ solutions.

From the work with the various chloride salts as drilling additives, it appeared that the cations provided the greatest share of zeta-potential control and thus drilling performance improvements. To investigate what effect the anion had on the zeta potential and the corresponding drilling performance, several tests were conducted with Al(NO₃)₃ solutions as the drilling fluid. The ZPC concentration for Sioux Quartzite in Al(NO₃)₃ solutions is 4.33×10^{-7} mol/L, which is slightly less than the ZPC concentration for Sioux Quartzite in AlCl₃ solutions (6.8×10^{-7}

mol/L). This reduction in ZPC concentration is attributed to the difference in anions. From the principles of polarography, it is known that NO₃⁻ ions are less active in an electrocapillary sense than Cl⁻ ions; i.e., the Cl⁻ ions are more readily adsorbed and thus change the surface tension (relating to surface energy) more than the NO₃⁻ ions. The NO₃⁻ ions, being less specifically adsorbed, need less aluminum cations to neutralize their adsorbed anion charge; thus the ZPC concentration is lower for Al(NO₃)₃. The maximum penetration effect of 98 pct (table 6 and figure 5E) and maximum bit life effect of 64 pct (table 6 and figure 6E) are obtained when drilling with the ZPC concentration of 4.33×10^{-7} mol/L

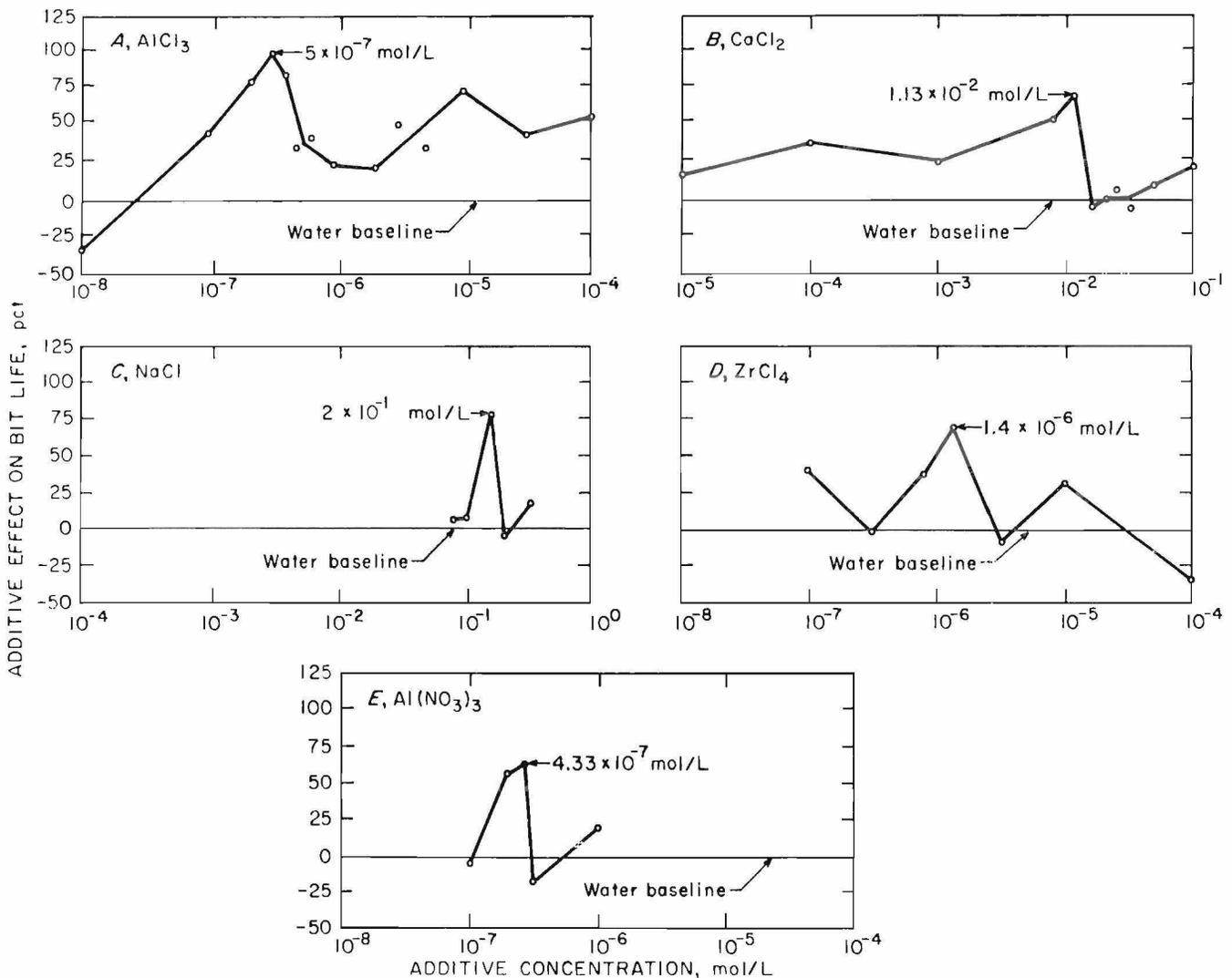


FIGURE 6.—Zeta potential control of drill bit life in drilling of Sioux Quartzite.

Al(NO₃)₃. The Al(NO₃)₃ penetration effect is of the same magnitude as that for AlCl₃ (98 pct versus 104 pct); however, the Al(NO₃)₃ bit life effect is much less (64 pct versus 99 pct). The reason for the difference in bit life effect is not known, but is associated with differences in anionic properties in solution.

WESTERLY GRANITE

The results of the drilling investigation of Sioux Quartzite with inorganic salt solutions of AlCl₃, CaCl₂, NaCl, ZrCl₄, and Al(NO₃)₃ as drilling fluids have shown that drilling efficiency and bit life extension were at their maximum when drilling at or near the ZPC concentrations of these salt solutions. To

determine how the drilling performance of a multimineralic rock would vary as a function of additive concentration, drilling tests were performed on Westerly Granite with AlCl₃ solutions as drilling fluids.

Penetration and bit life effects for Westerly Granite are listed in table 7 and graphically displayed in figure 7A and 7B, respectively. These data show enhancement of both penetration and bit life when drilling with the ZPC solution concentrations of AlCl₃ in Westerly Granite. A significant finding, however, is that "ZPC-controlled drilling" of Westerly Granite reflects its multimineralic composition. Each mineral component of Westerly Granite has a different ZPC concentration of AlCl₃ at which enhancement

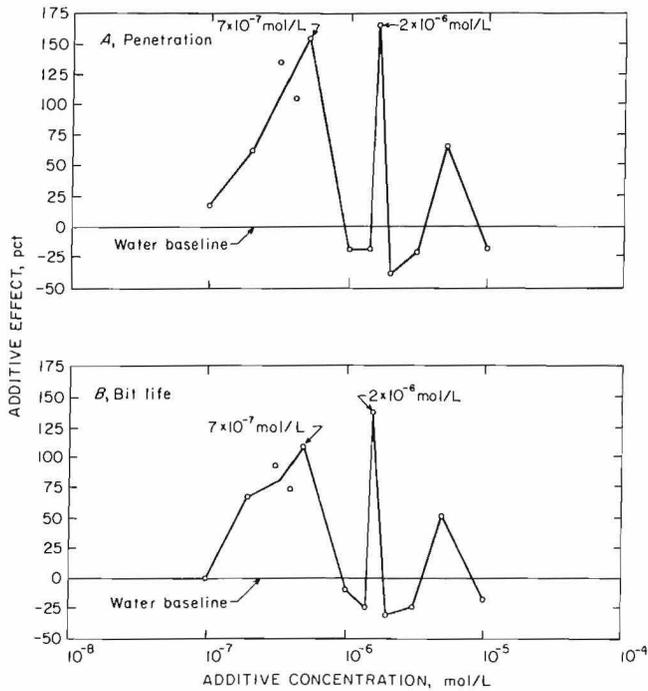


FIGURE 7.—Zeta potential control of drilling penetration and drill bit life for Westerly Granite.

of drilling penetration and bit life is obtained. Penetration in Westerly Granite improved 155 pct above the DDIW baseline values when drilling with an AlCl_3 solution concentration of 7×10^{-7} mol/L, which is very near the ZPC concentration for quartz in AlCl_3 solutions of 7.3×10^{-7} mol/L. A maximum penetration increase of 165 pct was obtained when drilling with an AlCl_3 solution of 2×10^{-6} mol/L concentration, which is very near the ZPC concentrations determined for the three sodic and potassic feldspars, microcline (1.5×10^{-6} mol/L

TABLE 7. - Westerly Granite drilling results for AlCl_3 solutions

Conc, mol/L	Average penetration effect, pct	Average bit life effect, pct	Number of replicates
1×10^{-7}	18.66	0.83	2
3×10^{-7}	62.05	67.28	2
5×10^{-7}	133.75	92.72	2
6×10^{-7}	104.50	73.92	1
7×10^{-7}	154.66	109.00	2
1×10^{-6}	-17.45	-8.46	3
1.5×10^{-6} ..	-16.81	-22.70	1
2×10^{-6}	164.92	136.23	3
3×10^{-6}	-36.42	-29.23	1
5×10^{-6}	-19.79	-22.07	2
7×10^{-6}	66.72	52.01	1
1×10^{-5}	-16.31	-16.92	3

AlCl_3), albite (1.3×10^{-6} mol/L AlCl_3), and oligoclase (1.1×10^{-6} mol/L AlCl_3). Bit life correspondingly improved 109 and 136 pct. Third relative maxima in penetration and bit life effects of 67 pct and 52 pct, respectively, are obtained when drilling with a 7×10^{-6} mol/L AlCl_3 solution. The origins of these maxima are not known. Maxima in drilling performance were not observed for biotite, although the maxima at 2.0×10^{-6} mol/L AlCl_3 concentration could have a component due to biotite. Observing a biotite ZPC effect would be unexpected since (1) there is only 7 pct biotite in Westerly Granite, compared to about 25 pct quartz and 65 pct feldspar, and (2) biotite is a relatively soft and easily drilled mineral, compared to quartz and feldspar.

SUMMARY AND CONCLUSIONS

Drilling tests on Sioux Quartzite with varied concentrations of solutions of the inorganic salts AlCl_3 , CaCl_2 , NaCl , ZrCl_4 , and $\text{Al}(\text{NO}_3)_3$, and on Westerly Granite with varied concentrations of AlCl_3 , demonstrated simultaneous maximum increases in penetration per time and maximum extension of bit life when drilling with the additive solution concentrations at or near the ZPC concentration for the major mineral components for each rock type: quartz for Sioux Quartzite,

quartz and feldspars for Westerly Granite.

Maximum penetration effects of 104, 97, 115, 96, and 98 pct were obtained when drilling on Sioux Quartzite with solution concentrations at or near the ZPC concentration for quartzite in solutions of AlCl_3 (6.8×10^{-7} mol/L), CaCl_2 (1.6×10^{-2} mol/L), NaCl (2.2×10^{-1} mol/L), ZrCl_4 (1.4×10^{-6} mol/L, and $\text{Al}(\text{NO}_3)_3$ (4.3×10^{-7} mol/L), respectively. Corresponding maximum bit life extensions

of 85, 73, 76, 68, and 64 pct were also obtained when drilling at or near the ZPC concentration for quartzite in solutions of these five inorganic salts.

Maximum penetration effects of 155 and 165 pct were obtained when drilling on Westerly Granite with AlCl_3 solution concentrations at or near the ZPC concentration for quartz with AlCl_3 solutions (7.3×10^{-7} mol/L) and alkali feldspars with AlCl_3 solutions (1.1 to 1.5×10^{-6} mol/L). Corresponding maximum extensions of bit life of 109 and 136 pct were also obtained when drilling at or near the ZPC concentration for the respective mineral components in AlCl_3 solutions.

On the basis of these data, it is concluded that drilling with inorganic salt solutions at or near the ZPC concentration for quartzite and granite mineral components should result in greatly improved drilling performance and prolonged bit life. For salts of higher valence cations, it was found that less concentration of the salt is required in solution to achieve the ZPC concentration. For salts of anionic species that have less electrocapillary activity, it was also found that less of the salt is required in solution to achieve the ZPC concentration.

A simultaneous increase in penetration and extension of bit life is new to the mining industry. Bit life and

penetration have been generally viewed as inversely proportional to each other; i.e., increased penetration often occurs at the expense of bit life, or conversely, increased bit life means penetration has to be sacrificed. Laboratory drilling with ZPC concentrations of additive solutions for contained minerals has resulted in the best of both worlds in that increased penetration was obtained simultaneously with increased bit life. If this laboratory-observed drilling phenomenon is also applicable on a large scale, simultaneous increases in penetration per time together with extended bit life will result in increased mining productivity and substantial reduction in expenditures for bits.

Of the five inorganic salts tested to date, AlCl_3 had the best overall performance as an additive for chemically enhanced drilling. It is less expensive and has a greater bit life extension than $\text{Al}(\text{NO}_3)_3$. Based on the quantity needed to produce the enhanced drilling effect, the required expenditure for AlCl_3 is less than that for the four other inorganic salts tested. In addition, the low concentrations of AlCl_3 solutions needed to achieve the ZPC condition are not corrosive to most iron or steel drill and drill string components and should not have any adverse effect on the environment.

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