MEASUREMENT OF STREAMING POTENTIALS

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The use of streaming potential technique in studying the electrokinetic properties of mineral-water systems is described in detail. An automated apparatus that houses a single piece streaming cell and that is capable of continuous operation over long periods of time as well as operation at higher-than-ambient temperatures, is described. The advantages of the new system peraaking precise measurements and the various precautions and specific procedures to be adopted to obtain accurate and reliable readings are stressed.

Adsorption of inorganic as well as organic species on particles is often governed by the electrical properties of their surfaces in solutions. The determination of the electrical characteristics of the particle/solution interface and its change due to the presence of various relevant chemicals is therefore of major use for establishing mechanisms by which they act. Of the various electrokinetic techniques that are available for determining parameters that are useful measures of the electrical properties of the particle-solution interface, the most suitable for studying sieve-size particles is the streaming potential technique. For the measurement of streaming potential, most investigators use a cell similar in principle to that described by Fuerstenau[1], with either bright platinum or silver-silver chloride electrodes. Such conventional cells cannot be safely employed to conduct studies as a function of temperature since they have many glass joints that are prone to leakage, particularly under pressure, in the course of an experiment. Effect of temperature is a variable coming into increasing usage in mineral processing operations[2]. In addition, previous studies on semi-soluble minerals such as calcite[3], apatite[4] and sparingly soluble minerals such as quartz[5,6] have given evidence for significant changes in their electrokinetic properties as a function of aging time. Such changes are relevant to mineral processing operations where the crushed ore particles might not have reached equilibruim with the water in contact. In order to study the streaming potential precisely as a function of concentration of reagents, aging time and temperature, a new automated streaming potential apparatus was designed and built. The description of the apparatus as well as the most satisfactory procedures for accurate measurements are provided in this paper.

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DESCRIPTION OF THE APPARATUS

The apparatus is described under the following three sections : a) streaming potential cell ; b) automated gas flow system and ; c) electrical circuit.

a) Streaming potential cell :

The cell consists of two parts : the cell assembly and the electrode assembly. A schematic diagram is given in Figure 1. The former consists of two 500 cc pyrex glass bulbs (A) joined to each end of a semi-circular sample tube (B) of 1.3 cm inner diameter and 9 cm length. The semicircular part of a second cell, made for use when only limited amounts of mineral is available, has an inside diameter of 0.8 cm and a length of 7 cm. The bulbs are provided with No. 25 "O" ring joints, one inlet for gas, and another for the introduction of pH electrodes or thermometers. The "O" ring joints provide a seat for the electrode assembly.

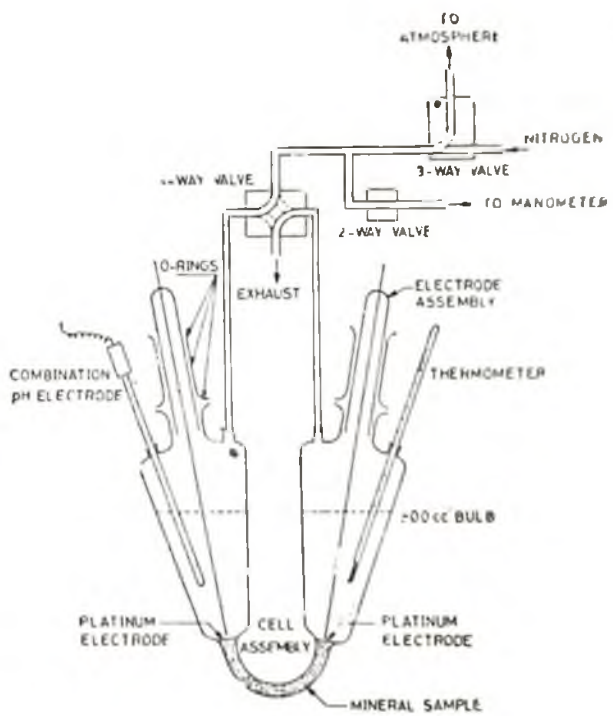


Fig 1 SCHEMATIC OF CELL AND ELECTRODE ASSEMBLY

The electrode assembly consists of two perforated platinum discs of about 2.0 cm diameter and 0.25 cm thickness. They are welded on one side to a platinum guaze (80 mesh) and on the other side axially to a 16 cm long thin platinum rod of 0.25 cm diameter. The electrode length is further increased to 33cm, by welding a thin tungsten rod of 0.3 cm diameter on to the platinum

rod. The electrode is fused to a 2.0 cm diameter and 13 cm long glass tube (F) with 2 circular grooves on it to hold two "O" – rings. This tube along with the electrode can be introduced into another glass tube (H) and be held inside this, with the help of the two "O" rings. The glass tube (H) is provided at one end with a suitable "O" ring joint for connecting it to the cell assembly described earlier. The above arrangement ensures free movement of electrodes inside the cell even after fixing the outer tube (H) in its position without any disturbance of the pressure inside the system and without introducing any torque at the electrode-glass seal while preparing the mineral plug.

b) **Gas Flow System :**

The various steps in measuring the streaming potential could be listed as under :

I) Pressurizing one of the bulbs of the cell – this is the starting point for streaming in one direction for, say, 15 seconds.

II) Connecting the other bulb to the atmosphere.

III) Connecting the pressurized bulb to the manometer.

IV) Locking the pressure in the manometer just one second before depressurizing the first bulb to record the streaming pressure.

V) Opening the first bulb also to the atmosphere.

VI) Repeating the above operations after, say, 15 seconds with streaming in the opposite direction.

Thus one cycle of streaming potential readings could be taken each minute. This is achieved by the use of three solenoid valves (one four-way valve, one three-way valve and one two-way valve all normally closed), these being controlled by a one-minute five-cam timer. A provision is also made to eliminate the 15 seconds interval between the two streamings. This enables instantaneous reversal of streaming, which would be useful during the conditioning of the mineral with the solution in question in that, now there is continuous streaming for several minutes, which gives not only better conditioning efficiency but also better utilization of time. Another main advantage is the elimination of various experimental errors, introduced by manual operation. In addition to the above, there is a set of two-minute one-cam timer and a ten-minute two-cam timer in the system. The first is to introduce a resistance in parallel to the mineral plug every alternate streaming cycle, so that the streaming potential under such conditions could also be obtained automatically. This reading is necessary to evaluate the plug resistance accurately at values of cell resistance that are too high for the use of an impedance bridge for resistance measurements. The second ten-minutes timer is for controlling the recorder chart drive. Table I gives the timing schedule of the operation of the solenoid valves for one complete cycle of streaming potential measurements. Table 2 gives an account of the various functions of the three solenoid valves. The above set-up is illustrated in Figures 1 and 2. The gas used for pressurizing the bulbs is water-pumped nitrogen passed through plugs of calcium chloride and ascarite, and wash bottles containing distilled water.

Table I. Time Schedule for the Timers

Time	1-Minute Timer		2-Minute Timer	10-Minute Timer Recorder		
sec	4-way valve	3-way valve	2-way valve	Decade register	1 and 2 mts timers	chart dr.
0	off	on	off	off	on	off
2	,,	,,	on	,,	,,	,,
14	,,	,,	off	,,	,,	,,
15	,,	off	,,	,,	,,	,,
25	on	,,	,,	,,	,,	,,
30	,,	on	,,	,,	,,	,,
32	,,	,,	on	,,	,,	,,
44	,,	,,	off	,,	,,	,,
45	off	,,	,,	,,	,,	,,
55	off	,,	,,	,,	,,	,,
60	1 min	cycle repeat	,,	on	,,	,,
120	,,	,,	,,	off	on	on
180	,,	,,	,,	on	on	,,
210	,,	,,	,,	off	,,	,,
300	,,	,,	,,	on	on	,,
300–600 system	off				off	off

Table II. Functions of the solenoid valves

Valve	When "on"	When "off"
4-Way	pressurizes RHS bulb of cell and opens the LHS bulb to atmosphere	pressurizes the LHS bulb and opens the RHS bulb to atmosphere
3-Way	pressurizes the system by opening the N_2 inlet valve	depressurizes and connects the system to atmosphere
2-Way	connects the mercury manometer to the pressure system	locks the manometric pressure

c) **Electrical System :**

The potential developed across the electrodes during streaming is fed to a high impedence electrometer (Keithley 616 electrometer) through a potential divider.

The output of the electrometer is fed into a recorder through another potential divider if necessary, which brings the electrometer output voltage (± 10 volts) into the working range of the recorder (± 100 mV).

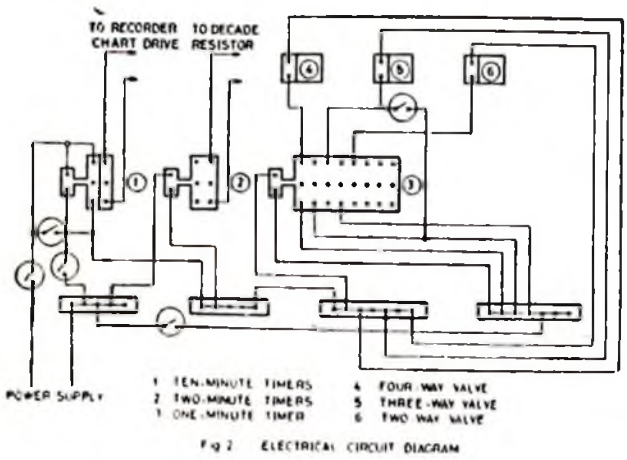


Fig 2 ELECTRICAL CIRCUIT DIAGRAM

For measurement of plug resistances which are less than 10^5 ohms, a General Radio Type 1650 B impedence bridge is used. When the resistance is greater than 10^5 ohms, it is determined by measuring the streaming potential with and without a known resistance in parallel to the mineral plug. The cell resistance is calculated using the formula :

$$R = \frac{(E/_p) - (E/_p)' R'}{(E/_p)'}$$

where R is the resistance of the test plug with solution, R' is the known resistance introduced in parallel to the plug, and $(E/_p)$ and $(E/_p)'$ are the streaming potential per unit pressure difference without and with the resistance in parallel respectively. It might be noted that proper grounding of the water bath is helpful for reducing stray currents while the cell is in the water bath.

MEASUREMENT OF STREAMING POTENTIAL

The accurate measurement of the zeta potential of a given particle/water system is rigorously governed by the actual procedure at each and every step. Such a procedure for measurement is given in detail below under various sections :

Electrode Cleaning :

The electrodes are cleaned before use by soaking them in aqua regia, followed by thorough washing with nitric acid solution, the concentration of which is continuously reduced from 2N to 10^{-2}N. Electrodes should then be stored in 10^{-2}N HNO_3 solution till further use. The "rest" potential difference between the two electrodes should be period cally checked while they are in the solution. If and when this exceeds a millivolt, the cleaning procedure should be repeated again. Any significant changes in the "rest" potential during experimentation should be checked.

Preparation of the Mineral Plug

Preparation of the mineral plug consists of transferring 300 cc of the desired solution into the cell that is immersed up to its neck in the constant temperature bath, placing one of the electrodes in its position in the cell, and transferring a previously determined amount of the mineral sample into the cell followed by intermittent pressurizing of the bulb a given number of times at a pressure of about 30 cm mercury head for satisfactory packing of the mineral against the fixed electrode. The secon l electrode is now placed in its position and satisfactory contact of this electrode with the mineral in the plug is verified. A much more reproducible plug resistance could be obtained with the new cell since packing is done under constant pressurizing conditions. A major advantage of this system is that gas bubbles produced inside the mineral plug when the temperature of the system is raised, could be easily dislodged by withdrawing one of the electrodes by a few millimeters and pressurizing each bulb alternatively a few times.

Streaming Potential Measurement

Streaming potential measurements are made after the solution is conditioned thoroughly by allowing it to flow back and forth several times and after the initial pH and temperatures are recorded. The streaming potential and the pressure can be read directly from the recorder chart.

Potential developed during streaming is often read as the streaming potential at known pressures. However, it is the change in potential at the instant the flow is stopped that must be read as streaming potential. This procedure minimizes the possible errors due to polarization of electrodes or motoelectric effects and permits measurements of streaming potentials as small as 0.1 mV even at high ionic strengths of the order of 10^{-1} mole/liter. With the polarization errors eliminated, values for the streaming potential at only a single value of pressure are necessary to evaluate the zeta potential. Ag/AgCl electrodes could also be used to reduce the polarization errors, but the ionic strength and pH range in which they perform satisfactorily is sometimes limited, depending on the system.

In the given setup, since each bulb is pressurized for the same length of time, the solution levels in each bulb

remains the same at the end of streaming in any given direction and hence the correction to the driving pressure due to the hydrostatic difference in the two bulbs remains constant. The above arrangement permits prolonged measurements and also helps ease the conditioning procedure.

After the streaming potential measurements are made for a given solution, the pH and temperature are recorded again. The solution in the cell is removed when desired by syphoning it under pressure from the bulbs. Several washings of the plug, by streaming water or a desired new solution through to one side and syphoning it, are essential before new readings are taken.

The zeta potential of the mineral is calculated from the formula :

$$\xi = 94.88 \times 10^7 \frac{\eta \, Ek}{D \, \Delta P}, \text{ mV}$$

where η, D and k are respectively the viscosity, the dielectric constant and the conductivity (mho/cm) of the solution at the measured temperature, ΔP is the driving pressure in cm Hg, and E is the streaming potential in millivolts.

Permeability of the plug can be determined in the present case using several techniques. One simple method is to measure the time required by the solution to flow between two given marks on the glass bulb. The flow rate of the exiting gas can also be easily measured.

RELEVANCE OF MEASUREMENTS

A recent paper[8] has a pertinent review of the streaming potential technique and it has been concluded that the slope of E (streaming potential) versus ΔP (driving pressure) plots must be used in calculating the zeta potential since the E versus ΔP plots, in the author's opinion do not generally pass through the origin. However, our recent experience shows that the plot does, indeed, pass through the origin if proper precautions in the electrode preparation and measurements are undertaken. Certain relevant features are discussed below :

a) Electrode Preparation and Pretreatment

Examples of various electrodes used in the past include platinum (bright, black and gray), gold, silver, silver/silver chloride and palladium. Use of these electrodes is generally on the assumption that they behave reversibly and do not take part in any reaction and thus act only for charge transfer in the system. Use of various pretreatments have been made to eliminate the surface impurities and to provide maximum surface area for charge transfer. However, work in the recent past has shown that none of these electrodes could be considered as completely reversible, nonpolarizable electrodes. For example, various oxides form at the platinum electrode surface under certain conditions and then dissolve particularly in the presence of chloride[9,10] ions. Presence of surfactants in the system can significantly alter the behavior of the electrodes and in cases where there is a redox couple generated, the "rest" potential could be altered[11].

Presence of sulfides in solution is also reported to affect the charge transfer at the electrodes due to the formation of a film at the electrode surface. During our experiments with sulfide minerals[12], experimental difficulties were experienced due to severe polarization problems. The major difficulty was due to unsteady potential difference across the two electrodes during the streaming when they were in contact with the sulfide particles. A satisfactory system was found to be the use of an additional pair of Ag/AgCl electrodes without having any physical contact with the mineral plug.

An effect of poorly prepared elelectrodes is shown in Fig. 3A and 3B where a set of electrodes properly

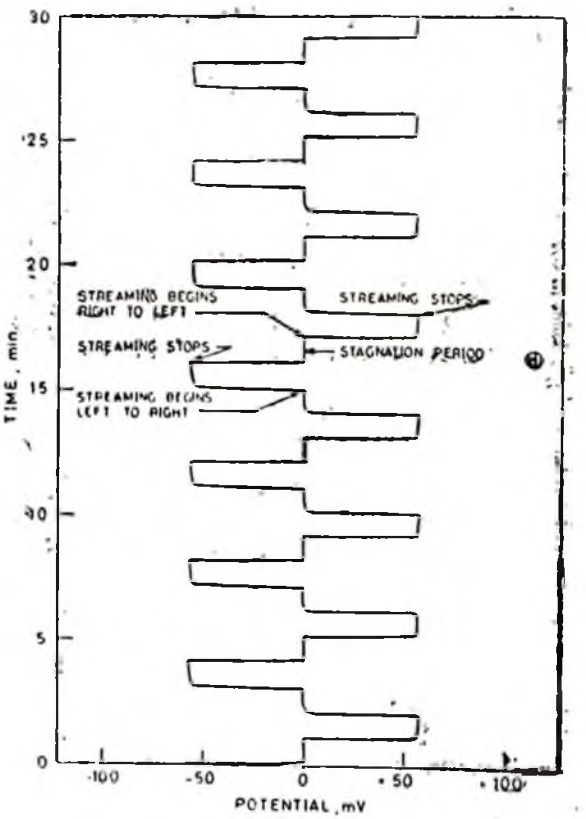


Fig 3a RECORDER OUTPUT WITH PROPERLY PREPARED ELECTRODES

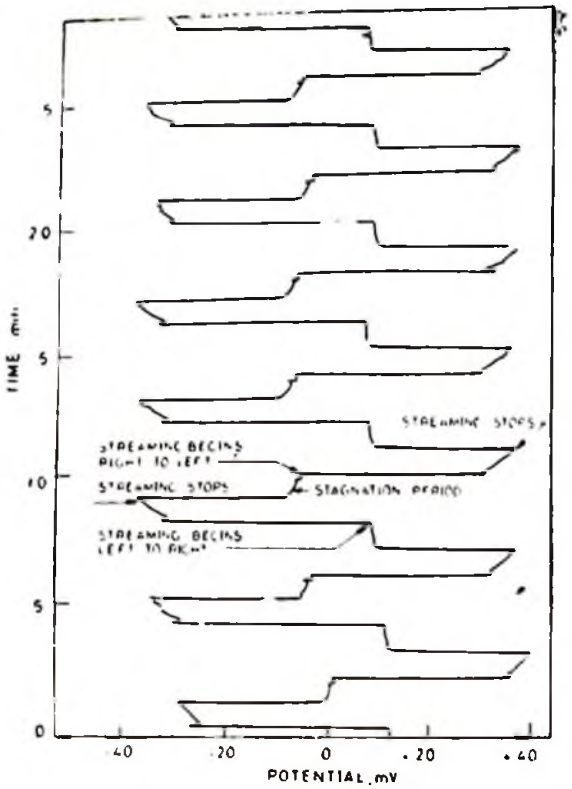
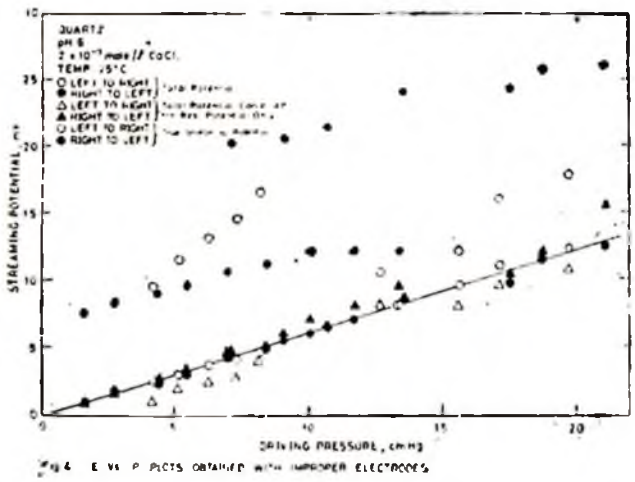


Fig 3b SIMILAR PROFILE WITH ELECTRODES HAVING APPRECIABLE REST POTENTIAL

prepared was compared against a set of electrodes having a "rest" potential in excess of 5mV. Such electrodes possess not only an unsteady "rest" potential but also significant polarization and asymmetry potentials. Use of such electrodes also results in significant scattering of the E versus $\triangle P$ plot with a nonzero intercept (see Figure 4).



MEASUREMENT OF "TRUE" STREAMING POTENTIAL

As mentioned earlier, potential developed during streaming is often read as the streaming potential at known pressures. It must be pointed out that if the electrodes suffer polarization problems, potentials measured in the above manner can be significantly different from the "true" streaming potential and when plotted can yield E versus $\triangle P$ plots with nonlinearity as well as nonzero intercepts. Change in potential at the instant the flow is stopped is what must be read as streaming potential. In Figure 5, this value corresponds

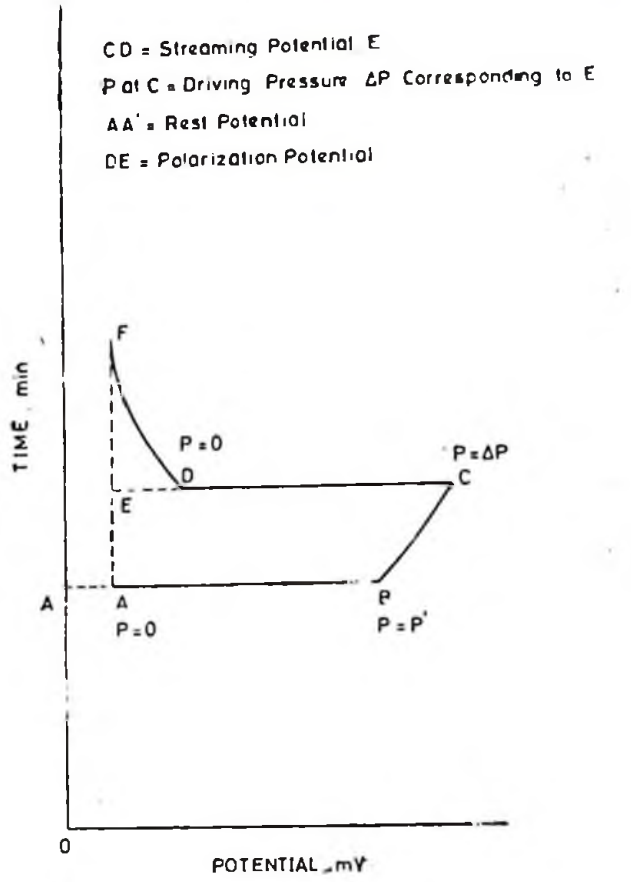


Fig 5. TYPICAL STREAMING POTENTIAL Vs TIME PROFILE

to CD. It might be noted that the total potential at the instant the flow is stopped, i.e., CE in this case, is greater than CD. This is because various other potentials develop during streaming in addition to streaming potential[13]. Figure 6 gives the E vs $\triangle P$ plot obtained using "true" streaming potential measured with electrodes prepared and monitored in the described manner for good performance. Care was also taken to eliminate errors arising from build-up of excessive asymmetry potential. It can be seen that the relationship is linear and that the intercept is negligibly small. Regression of the data gave the following equation for this case.

$$-E = 0.053 + 1.784\ \triangle P$$

where E is in millivolts and $\triangle P$ is in cm. Hg. The magnitude of artifacts introduced upon disregarding the polarization and rest potentials is illustrated in Figure 4.

Both the "true" streaming potential and the total potential during streaming are presented here for the purpose of comparison. It can be seen that the E vs ΔP plot obtained with the data for the total potential contains considerable scatter as well as nonlinearity in contrast to that obtained with the data for "true" streaming potential.

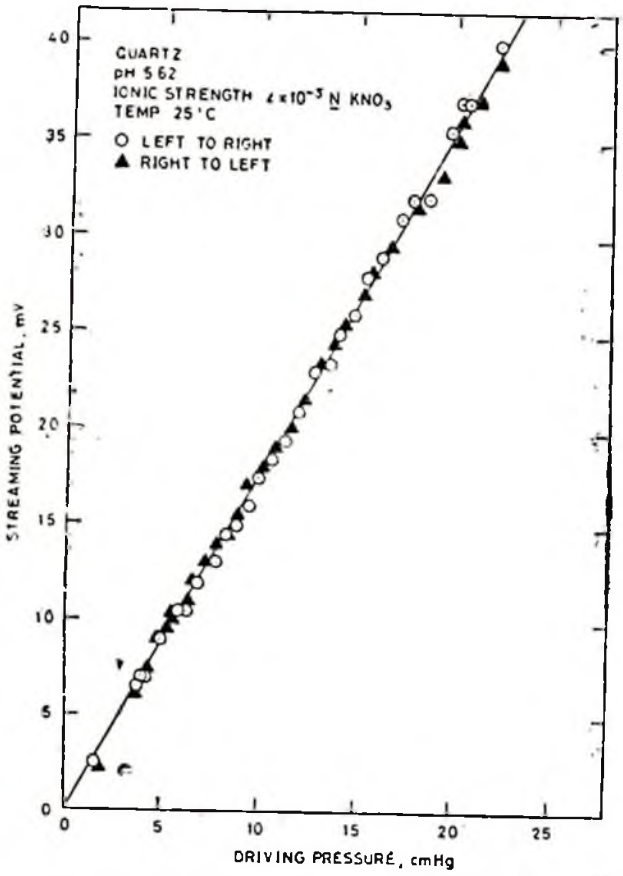


Fig 6. E Vs P PLOT BASED ON TRUE STREAMING POTENTIAL

Another point to note is the value that must be used for driving pressure for calculating "zeta" potential with CD (Figure 5) as streaming potential must be the one at C. In our set-up, in order to determine this pressure, the manometer is locked, manually in the work with Agar[3] and automatically in the recent work with Kulkarni[7], a fraction of a second before the flow stops and is read at leisure. Since this method always enable us to determine the driving pressure at C corresponding to the measured streaming potential CE, any change in pressure during streaming did not affect the test. It was therefore not necessary to maintain a constant driving pressure during an experiment and the method was hence indeed simpler as stated in our earlier work[3].

Elimination of Errors Due to Excessive Asymmetry Potentials

As the solution is streamed in a particular direction, along with the streaming potential, there are polarization potentials developed, often in different magnitudes at the two electrodes. The measured potential jump when the flow is stopped contains some asymmetry potential, but this should be only a very small fraction of the difference between the polarization potentials. The error introduced due to this can be reduced significantly by reversing the flow after each streaming. This is illustrated in Figures 7 A and 7B. In these figures, E vs. ΔP plots for a single system but using different measuring sequences are presented. Streaming potential plotted in Figure 7A was measured as a function of

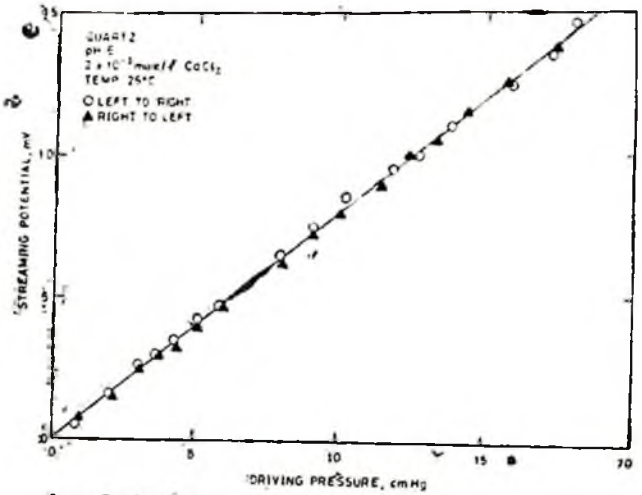


Fig 7a E Vs. P PLOT USING FLOW REVERSAL AFTER STREAMING IN EACH DIRECTION

driving pressure, starting with the maximum pressure and decreasing the pressure in stages, but with a reversal of direction of flow after each measurement. In other words, there was alternate back and forth streaming. It can be seen that a linear relationship exists between E and ΔP throughout the range of pressure tested and that the line passes through the origin. In contrast to this, the plotes in Figure 7B were made using readings

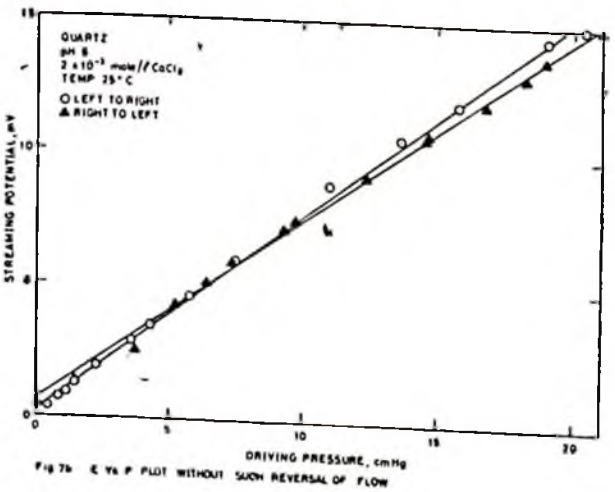


Fig 7b E Vs P PLOT WITHOUT SUCH REVERSAL OF FLOW

obtained without flow reversal after each streaming. Most of the solution was streamed to one bulb and readings were obtained starting at the highest pressure and decreasing the pressure slowly. For a complete span of zero to maximum pressure tested, the solution was streamed in only one direction with no reversal. The process was then repeated in the other direction of streaming. Unlike the one in Figure 7A, the plots in Figure 7B do show a definite curvature. E vs $\triangle P$ plots obtained individually for the left to right streaming do have finite intercepts. Reversal of flow after each measurement was found to be particularly useful when the electrode characteristics are unsatisfactory.

Finally, the danger of the presence of air bubbles inside the mineral plug cannot be ignored, particularly if there are significant temperature variations during an experiment. The air bubbles will indeed affect the results due to a number of reasons. In addition to the fact that the plug resistance will be permanently affected, there will be additional effects due to changes in their shape during streaming. Electrical properties of the bubble surface will also exert their influence. Result obtained for E as a function of $\triangle P$ with a plug that contained a few gas bubbles are given in Figure 8. Scattering of data, particularly at large $\triangle P$ values, as well as a measurable intercept for the plot is evident in this figure. Clearly special care is needed to avoid the air bubbles particularly while operating at elevated temperatures. The design of electrode assembly used in the present apparatus[1] facilitates easy removal of air bubbles before each streaming potential measurement.

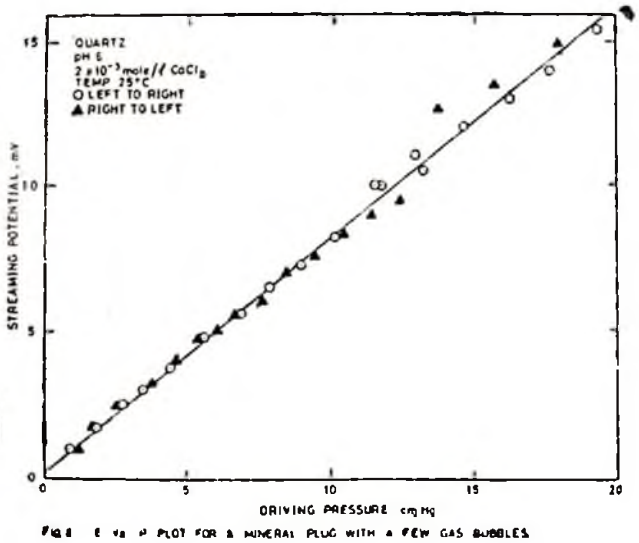


FIG. 8 E vs P PLOT FOR A MINERAL PLUG WITH A FEW GAS BUBBLES

CONCLUSIONS

Measurement of zeta-potentials is a most useful tool in studying the electrokinetic and surface characteristics of mineral-water systems. Even though such phenomena have been studied by colloid chemists over a long period of time, increasing use in mineral processing, however, is relatively recent. Its applications in such areas as flotation, flocculation, selective agglomeration, coagulation, filtration, sedimentation and the like cannot be provided in detail in this paper, since such an effort is in itself would be an extensive review. It has however been shown that using the streaming potential technique ad exercising proper care in preparation for the test and the actual measurement, one can get meaningful results to study the interaction of mineral particles and various ionic species in aqueous systems.

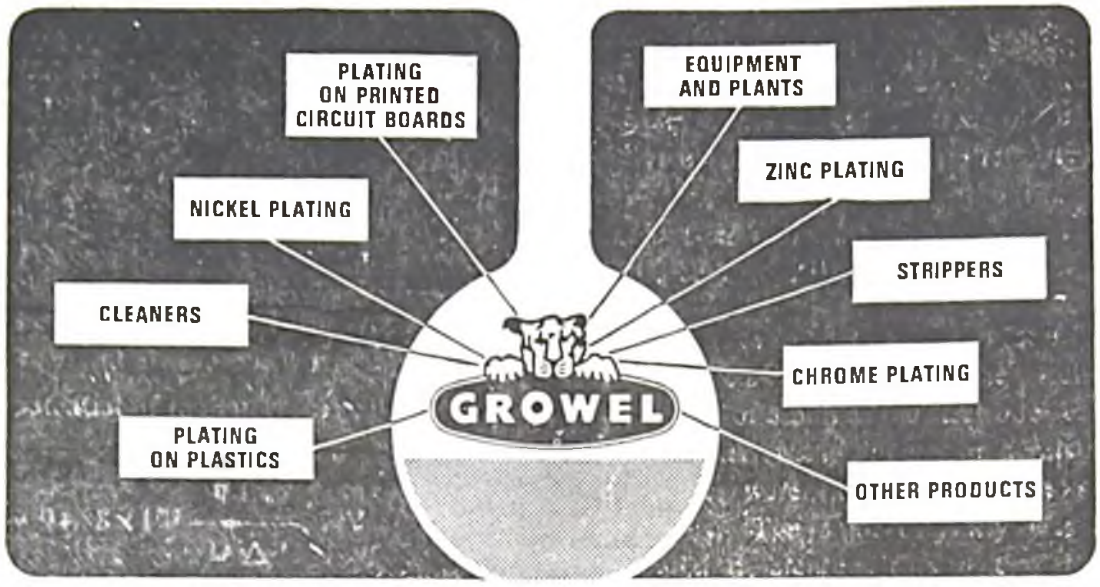
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