

ELECTROLYTIC MEASUREMENT OF LOW VELOCITIES IN WATER

by

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INTRODUCTION

There has long been a need for a device to measure low velocities in flowing water. Present instruments, including the Pitot tube, hot-wire anemometer, and blade or cup meters, are insensitive, erratic, or unstable in their response to low velocities, below approximately 0.5 foot per second. The writer began the study of electrolytic methods for the measurement of low velocities in 1946. In 1947 he presented a thesis [1] which included the results of a study of change in resistance of an electrolysis cell formed in water, caused by movement of the water. The principle of operation was not understood at that time and the investigation was continued.

By 1953 a somewhat clearer understanding had been acquired, at which time a paper was presented at the Third Midwestern Conference on Fluid Mechanics [2], describing the results of the investigation to that time. It had been discovered that the apparent resistance change of the cell occurred at the cathode and was related to the movement of dissolved oxygen molecules past it. This effect was observed as a voltage drop between the cathode and anode. That voltage drop was related to the velocity of the water by calibration in a towing tank, and an instrument was designed.

Further understanding was gained from the literature on polarography, which is the science of detecting the presence of various elements and compounds in an electrolyte by means of characteristic shapes of current-voltage curves for electrolysis cells containing these materials in solution. On the basis of the knowledge thus gained the factors involved in the design and operation of the instrument were recognized and it was then possible to separate and study the variables. The information thus obtained led to the development of an instrument for the electrolytic measurement of low velocities in water which shows promise.

PRINCIPLE OF OPERATION

In order to understand the operation of this device it is necessary to have some understanding of an electrolysis cell. When two electrodes are immersed in an electrolyte and a direct current from

an external source passed through the cell, there will be a drop in voltage between the electrodes, indicating resistance to the flow of current through the cell. This voltage drop occurs in three steps, a sharp drop at the anode, where the electrons leave the electrolyte, a lesser drop through the electrolyte, and a second sharp drop at the cathode, where the electrons enter the electrolyte. Since in this study the important voltage change is that at the cathode and for reasons of stability, which will be discussed later, the voltage drop at that electrode is measured against a standard calomel reference electrode. The latter will maintain a constant voltage drop between itself and the electrolyte for a wide variation in electrolyte composition. This reference electrode is formed in a glass container, the bottom of which is covered with a pool of mercury. Over the surface of the mercury is a layer of calomel, and the container is filled with saturated NaCl solution. Connection with the electrolyte in which it is immersed is made through a finely perforated glass disk in the side of the container. Electrical connection is made with the mercury pool through an immersed tungsten wire. The voltage drop between the mercury surface and the saturated NaCl solution remains constant and since there is no resistance to current flow between that solution and the electrolyte no further drop occurs. Thus is maintained a constant reference electrode.

Figure 1 shows schematically the voltage drops from anode to reference electrode and from the reference electrode to the cathode across an electrolysis cell formed in tap water, with the electrode materials used in this study. The current through the cell was 200 microamperes, the temperature 70 deg. F., the water contained

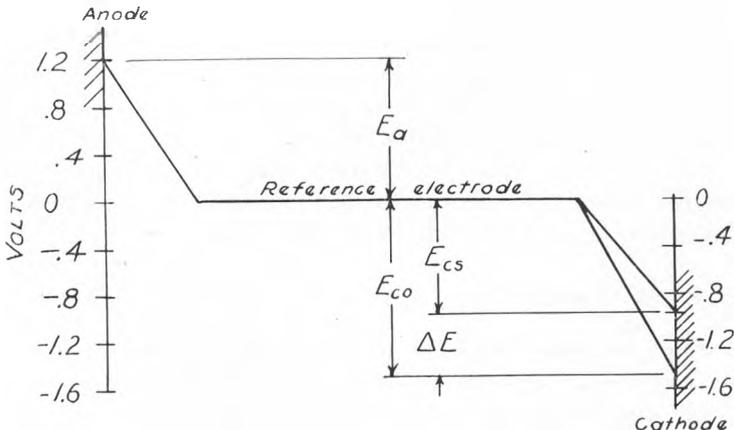


FIG. 1

approximately 300 parts per million of dissolved solids. For quiescent water the voltage difference E_a between the anode and reference electrode was 1.2 volts, the potential of the anode being positive with respect to the reference electrode. The drop E_{co} between the reference electrode and the cathode was 1.5 volts, the cathode being negative with respect to the reference electrode.

If the water is rapidly stirred, the voltage drop between anode and reference electrode remains the same, but that between the reference electrode and the cathode (E_{cs}) became 0.9 volt. This change ΔE is the result of the contact of dissolved oxygen molecules with the cathode. These molecules, while electrically neutral in solution, will, on contact with a negatively charged surface whose voltage is sufficiently below that of the water, take from that surface 4 electrons per molecule, thus facilitating the flow of electric current. If the total current through the cell remains constant, this easier flow will be observed as a smaller voltage drop between the cathode and reference electrode. This voltage drop can be related experimentally to the velocity of water past the cathode, thus permitting the use of the cell as a velocity-measuring device.

The change in voltage at the surface of the cathode with movement of the electrolyte past it is a phenomenon of considerable complexity. It has found practical usefulness in the determination of the presence of various ions in an electrolyte [3]. It will probably be best understood from a study of the relation between the current passing through the cell and the voltage difference between the cathode and the reference electrode. Curves of relation have been developed using a conducting film electrode, to be described in detail later, in tap water and in sea water, both quiescent and stirred. Stirring was accomplished with a magnetic stirring rod 2 inches in length, rotated at a speed of approximately 10 revolutions per second in a container 3 inches in diameter. The data are shown in Fig. 2.

At zero current flowing in the cell, the voltage difference between the cathode and the reference electrode is 0.35 volt. As current flow begins, the water remaining quiescent, the voltage increases with increase in current, following the section of the curve AB. All ions in the water and the oxygen molecules are participating in the current transfer, by the process of ionic migration. The current is sufficiently small, so that no concentration gradient is set up between the cathode surface and the liquid surrounding it for any ion. At a current of 20 microamperes per square centimeter, oxygen, which is the most easily reduced of any element at the cathode, begins to develop a concentration gradient. This is shown by the

section BC, which indicates that the voltage drop is increasing rapidly with small increase in current. Because of the formation of a concentration gradient, the oxygen molecules contact the cathode in progressively lesser numbers, until the rate of such contact is a constant and a function of the diffusion rate in the liquid.

Following the establishment of this diffusion gradient of oxygen, the other ions continue to carry the current and the voltage-current curve rises again at a rate essentially parallel to the section AB, until another ion establishes a diffusion gradient, resulting in a

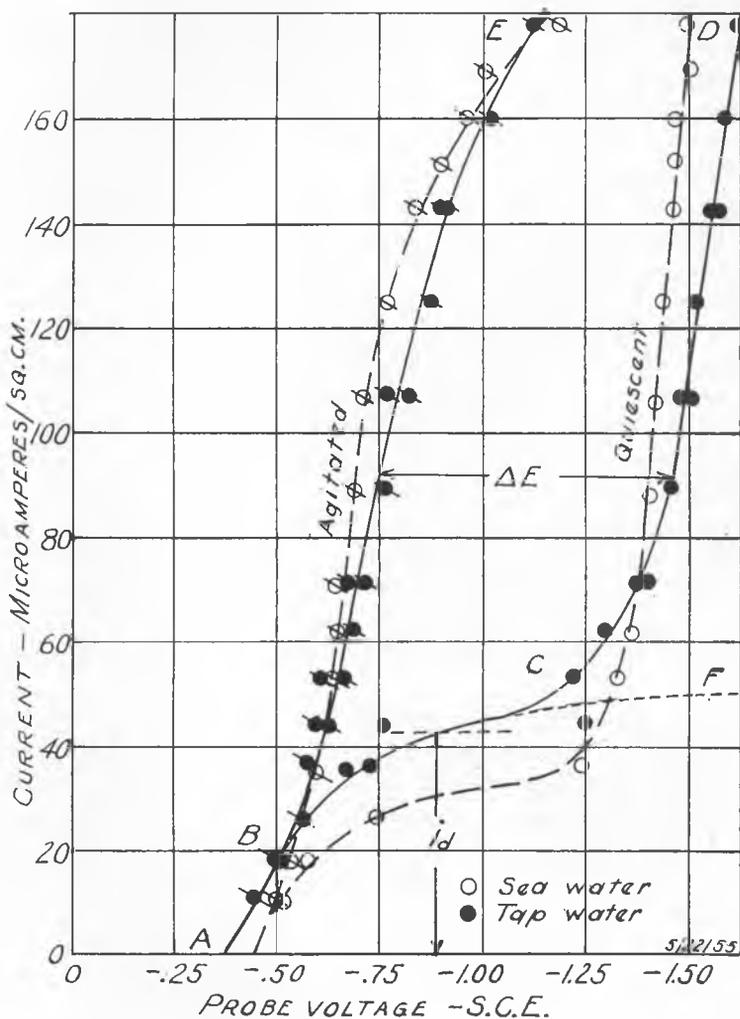


FIG. 2

second plateau. If the oxygen molecule were the only means of transferring electrons from the cathode, the curve would follow CF.

If the electrolyte is rapidly stirred, a different effect is noted. With stirring, the oxygen molecules are carried to the cathode more rapidly than they are reduced, hence no concentration gradient may form and the curve continues at practically the same slope as the section AB. With sufficiently high currents, even rapid stirring will not supply a surplus of oxygen molecules, and the curve begins to flatten, showing the formation of a concentration gradient, at E. This voltage difference between quiescence and rapid stirring is a function of the velocity of water movement past the cathode and can be calibrated experimentally. It is this principle upon which the operation of the device described in this paper is based.

INSTRUMENT DEVELOPMENT

Electrode Material

Once the principle of operation of the device was recognized and evaluated, the development centered about the determination of an electrode material which would be both responsive and stable. Many difficulties were encountered. In early experiments the voltage across the cell was used, but variations in anode potentials upset the readings. Platinum and gold wire were first tried for the cathode, while carbon, aluminum, zinc, iron, brass, the calomel reference electrode, and the metal of the flume were used as anode. Most of these combinations were responsive, but could not be made stable. Attention was then directed to aluminum, a material nearly at the opposite end of the electromotive series of elements from the noble metals, and having a small voltage difference at the liquid-solid interface. Somewhat better stability was obtained, but neither stability nor response were completely satisfactory [2].

The writer took the problem to Dr. Karl Kammermeyer, head of the Department of Chemical Engineering, State University of Iowa, who has been experimenting with conducting films on non-conducting base materials. These films are highly polished being only 3-5 angstroms thick, resistant to the action of all the common reagents, and have a relatively high voltage drop at the liquid-solid interface. These films are available commercially on $\frac{1}{4}$ -inch rods, which can readily be made into electrodes.

Two probes were used in the tests described in this paper. Earlier experiments were made with a probe formed from a single rod from which the coating was partly removed by grinding, so

that opposite quarter surfaces remained. This was used primarily to determine the effects of the different variables. It was mounted in a glass holder, in a rubber stopper, and placed in a 300-cc bottle, in which the water could be magnetically stirred. One surface was made the cathode, the other the anode. It was found that an anode of this material was stable, so that voltage changes were observed directly across the cell for the earlier work. Later, the reference electrode was adopted for these studies as well as for the recording of velocities in water.

The probe used for the velocity determinations consisted of a cathode formed by a semicylindrical conducting film surface, presented to the flow with the cylinder at right angles to it, so that the flow would pass over the film surface. The anode was a cylinder of the same material, with its axis parallel to the direction of flow so that the sweeping action over the surface would be minimized.

Electrical Circuitry

The external electrical circuit may be designed in either of two ways: with a low-voltage direct-current source, holding the voltage drop across the cell a constant; or with a high-voltage direct-current source and a high limiting resistor in series, producing a constant current through the cell. In the former, the changes produced by the movement of water past the probe are shown as changes in the current flow, while in the latter the changes are noted in the voltage across the cell or with respect to a reference electrode apart from the circuit. The method of constant current was adopted, as it was much easier to amplify the voltage changes so that they could be graphically recorded than to produce a voltage signal from the variable current, then to amplify and record.

It was discovered that much of the instability in the earlier instruments was caused by variations in the voltage drop from the anode to the water, apparently caused by anodic reactions with dissolved matter in the water. It was then decided to measure the voltage at the cathode against a standard reference electrode, consisting of a calomel cell, previously described. This system materially improved the stability of the instrument.

The circuitry selected is shown in Fig. 3. The current to the cell is supplied by a 45-volt battery, connected in series with a variable resistor covering a range from 0.1 to 2.5 megohms, which will give a current range from 450 down to 18 microamperes. The current can be held closely constant. A voltmeter and voltage change recorder are connected between the cathode and the standard reference electrode, thus completing the recording circuit.

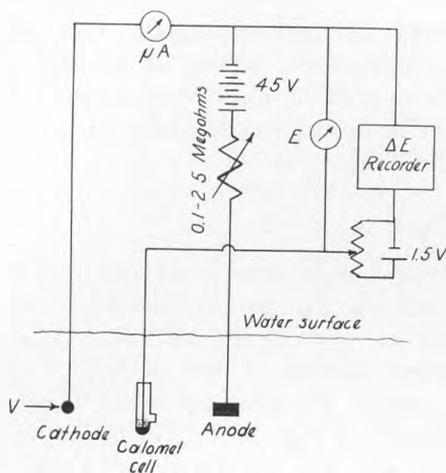


FIG. 3

EFFECTS OF VARIABLES OF THE WATER

There are many variables of the water, in addition to its dissolved oxygen content, on which this instrument's operation depends. They include the water temperature, hydrogen-ion concentration, the presence of dissolved solids, salt, principally, in sea water. Each was investigated in turn, holding the others as nearly constant as possible.

Dissolved Oxygen

Water practically free of oxygen was produced by boiling and cooling under a nitrogen atmosphere, which was maintained thereafter. For each test oxygen-free water was blended with varying ratios of oxygen-saturated water of the same chemical makeup. The water contained approximately 500 ppm of NaCl, to provide ionization. Dissolved-oxygen concentrations from approximately 1 to over 8 parts per million by weight, were produced. Voltages across the cell were observed when the water was quiescent and agitated. The difference is a function of the concentration, as shown in Fig. 4. Two anodes were used in these experiments, the coated rod and the calomel electrode, the solid curve shows the results of the first combination, the dashed curve the second. The dissolved oxygen was determined for each sample by chemical titration, following the Winkler method. The current density was 60 microamperes per square centimeter. It will be noted that above approximately 4 parts per million of dissolved oxygen the effect of oxygen

on the voltage change is relatively small. This would indicate that water at room temperature, which, if saturated, would contain about 8 parts per million of dissolved oxygen, could have a considerable variation in actual oxygen content without effect on the instrument's calibration.

Water Temperature

The effect of temperature was investigated under two conditions: First, the water was warmed to 116 degrees F., and allowed to cool while the readings of volt-change between quiescent and stirred water were recorded; second, it was cooled to 32 degrees F. and allowed to warm, while the readings were taken. The results of these tests are shown in Fig. 5. It will be noted that the change decreased by 6 percent over the range, at a rate of 0.075 percent per degree. It is not thought that such a change would be serious in the calibration of the instrument and could be allowed for. The results agree with those of Brdicka [4], who reported that the potential usually shifted toward a more positive value (easier reduction) with increase in temperature. Also, the diffusion rate, which measures the change in voltage along the curve BC in Fig. 3, will be greater, hence the voltage change will be less with increasing temperature.

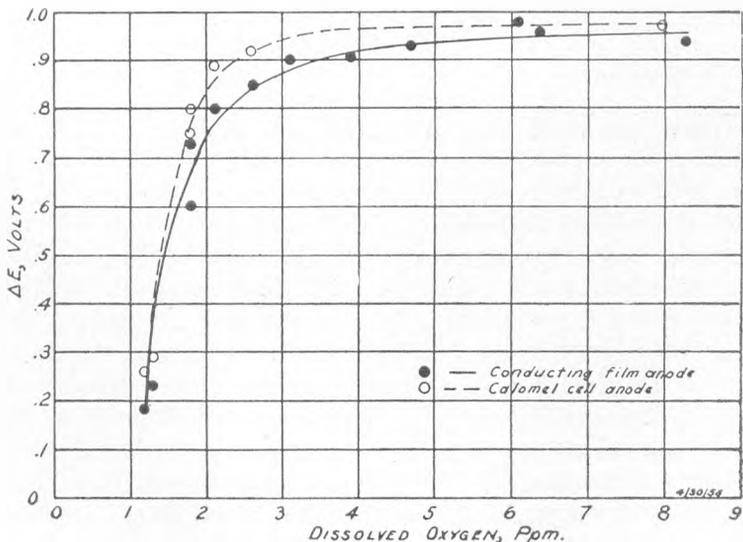


FIG. 4

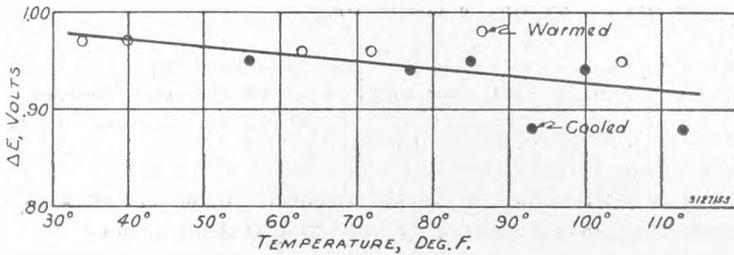


FIG. 5

Hydrogen-Ion Concentration

The effect of hydrogen-ion concentration was observed in water samples made progressively more basic or acid through addition of ammonium hydroxide and acetic acid. Determinations were made over a range of pH from 5 to 11.5. The results are shown in Fig. 6. While the voltage of the cathode relative to the reference electrode became larger with increasing pH, for both the quiescent and stirred water, the voltage change remained constant. Kolthoff and Lingane (Reference [3], p. 405) show polarographic waves of oxygen in current-voltage curves for pH concentrations between 3.0 and 12.0 pH, for quiescent water. These also indicate that the voltage referred to the reference electrode increased with increasing pH.

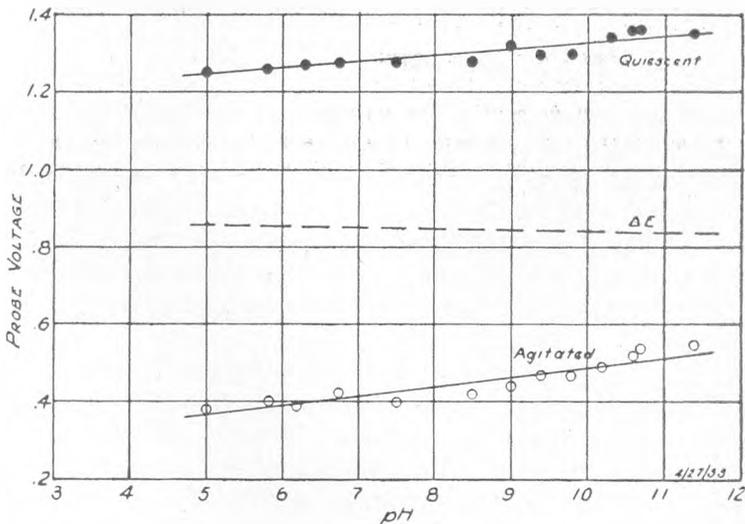


FIG. 6

Effects of Other Dissolved Substances

Other substances in the water besides dissolved oxygen are reduced at the cathode. The voltages at which these reductions begin are generally more negative than that for oxygen and little difficulty with the interference of those other substances in the oxygen reduction is anticipated, with the possible exception of hydrogen. The approximate voltages, referred to the standard calomel electrode, at which reduction of the more common elements begins is shown in Table I.

TABLE I

Approximate voltage, referred to the standard calomel electrode, at which reduction in water of common elements will begin, after Lingane and Kolthoff [3], Vol. 2.

Element	Voltage	Element	Voltage
Oxygen	-0.5	Aluminum	-1.8
Lead	.6	Calcium	2.2
Copper	.6	Magnesium	2.2
Hydrogen	1.0	Sodium	2.2
Manganese	1.5	Potassium	2.4
Iron	1.7		

Of considerably more importance is the fact that as the oxygen atoms are reduced they combine with water molecules to form hydroxyl ions in the diffusion layer, according to the equation



These ions will react with certain metals in the water and produce hydroxides, which, if insoluble, may be deposited on the cathode. Principal among these is $Ca(OH)_2$, which is very insoluble, being only 2 percent that of $Ca(Cl)_2$ at room temperature. Further, if glass is used as the nonconducting support for the electrodes, it will be attacked by the hydroxyl ions, with the removal of sodium and calcium from the surface. Further investigation of this aspect is indicated.

The effect of NaCl was studied. To samples of distilled water were added successively greater amounts of NaCl, producing a range in salinity from approximately 200 to 350,000 parts per million. The results of this are shown in Fig. 7, as voltage across the cell versus the salt concentration. As the salt content was increased, the voltage drop across the cell decreased for both the quiescent and stirred water, while the voltage change increased

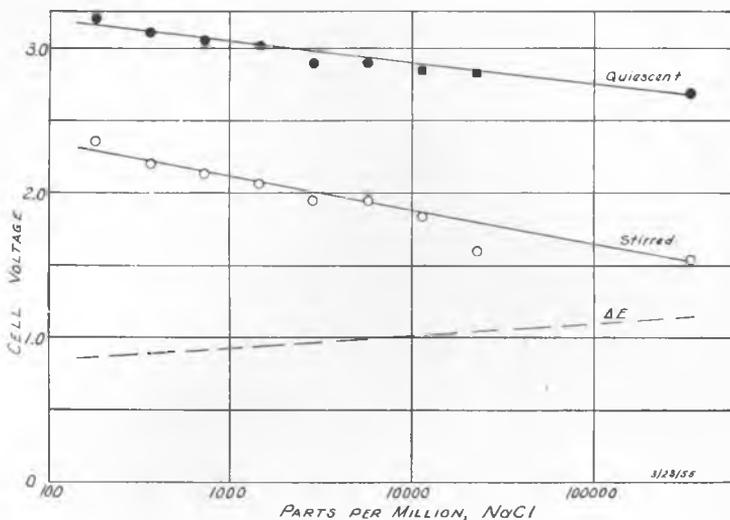


FIG. 7

slightly. However the effect was small and not thought to present a serious problem. If the device is to be used in sea water it should be calibrated in that medium.

INSTRUMENT DESIGN

The design of the sensing device for the instrument described in this paper was limited by the availability of the conducting material, which could be obtained only as a coating on a $\frac{1}{4}$ -inch rod. The cathode was made by mounting a short section of the rod at right angles to the direction of the water movement, so that the flow was across the surface of the conducting film in intimate contact with it. The anode was of the same material, mounted to the rear of the cathode. The reference electrode consisted of a standard calomel electrode, described earlier. This reference electrode was mounted between the cathode and anode, so that the ohmic drop in the water between the cathode and reference electrode would be small.

Following design of this sensing device it was discovered that a method of putting a highly polished platinum surface on glass was available, thus permitting the conducting platinum film to be placed on a probe of any desired shape. A glass probe was formed with leads to the front and rear ends, which were made hemispherical. One end was coated with the shiny platinum to an area of approxi-

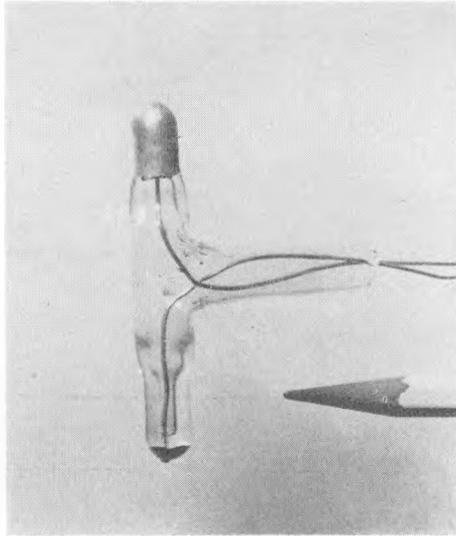


FIG. 8

mately one square centimeter, the other with a porous coating of several square centimeters, Fig. 8. While this probe was used for demonstration, it is not believed that the platinum will prove as stable as the conducting film previously experimented with. Such a film can also be put on a probe of this form.

The electric circuitry has been previously described. The voltmeter can be any standard high-impedance meter. A standard direct-current power amplifier and graphic recorder complete the circuit for recording. For field use a battery-operated amplifier and bridge circuit has been designed. It measures the voltage change between cathode and anode and can with little modification be adapted to measure that between the cathode and reference electrode instead.

CALIBRATION AND STABILITY

The conducting film probe described above was mounted on a towing-tank carriage at the Iowa Institute and moved through still water at speeds varying between 0.02 and 2 feet per second. Calibrations were carried out at three current densities, 133, 200, and 267 microamperes per square centimeter. The results are shown in Fig. 9. For velocities below 0.4 foot per second the calibration for each current density is a straight line on logarithmic plotting, the upper range increasing as the current is increased.

Stability was the problem of greatest concern in this study.

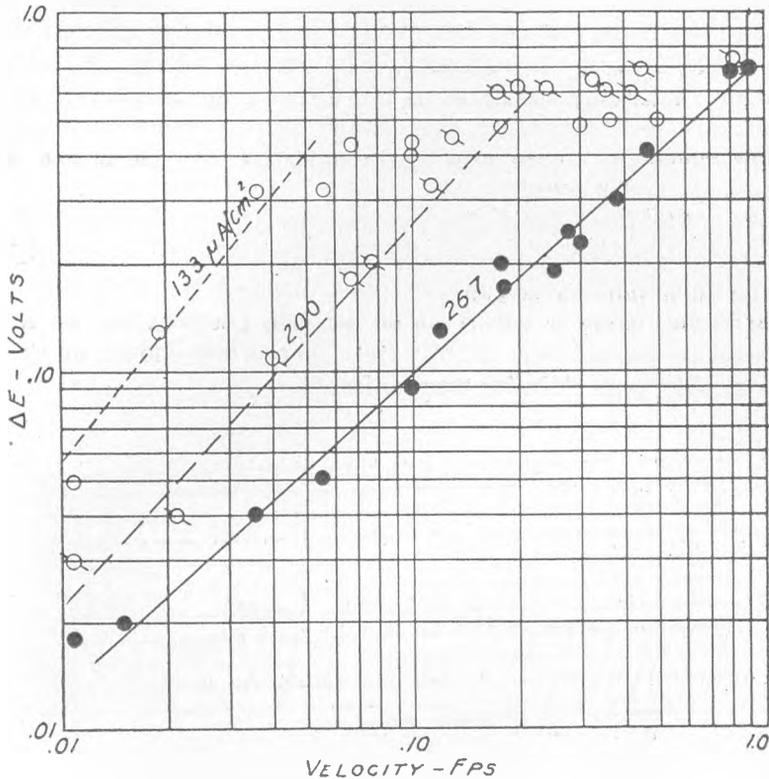


FIG. 9

Various combinations of cathode and anode were tried and their stability determined by making graphic recordings of the voltage behavior under conditions of constant and zero velocity. These tests were made at room temperature, using tap water and a probe current of 200 microamperes per square centimeter. The results are shown in Figs. 10a and 10b. Graph (a) is for the conducting film cathode and calomel anode, the voltage across the cell being recorded. It will be noted that the voltage drop for zero velocity drifted slowly, while that for constant velocity was nearly constant. The voltage after the water motion was stopped returned to a somewhat smaller value, indicating some instability. Graphs (b), (c), and (d) were for the conducting film (BK) cathode and brass anode, aluminum wire cathode and calomel anode, and gold cathode and calomel anode. Not only were these combinations unstable, their response was not as great as that for the BK-calomel electrode combination.

A test for stability of approximately 2 hours duration was then run with the BK cathode and anode. The results are shown in Fig. 11. Good stability is indicated. The voltage during agitation remained essentially constant, as did that during the period of zero velocity. More important, the voltage drop returned to its former value when the liquid was again agitated after a period of 90 minutes of zero velocity.

Stability tests were also run for the BK cathode and calomel reference electrode. Essentially the same results were achieved. Using this combination, graphs were made of the action of waves in a flume, using a period of 30 seconds between waves, and of turbulence downstream from a jet. These are shown in Fig. 12. Reasonably good stability was indicated.

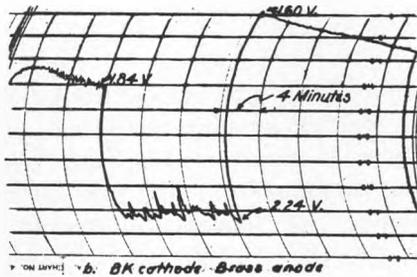
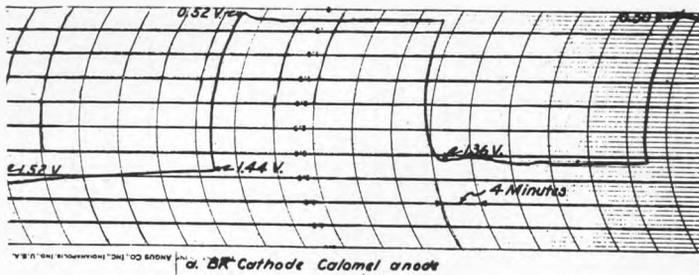


FIG. 10 A

CONCLUSIONS

It is believed that the instrument described will prove useful in the determination of low velocities in flowing water. So far as the writer knows, it is a new application of an old principle, and as such will require much further study and experimentation before it will have reached the stage of development of other velocity measuring instruments—the hot-wire anemometer, for example. Since the

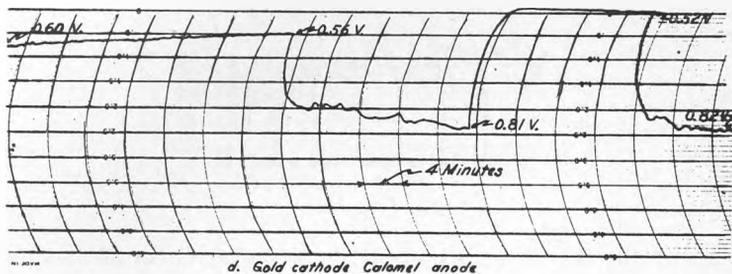
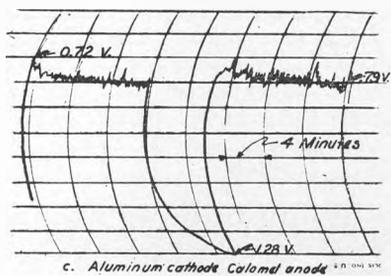


FIG. 10 B

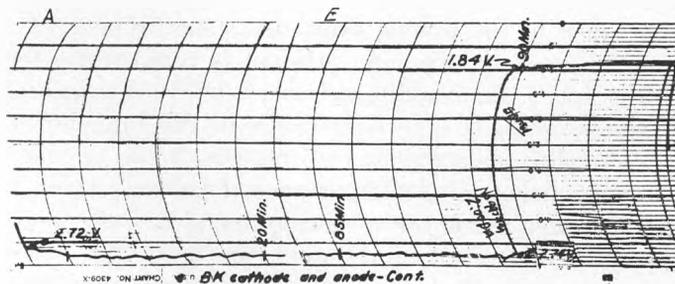
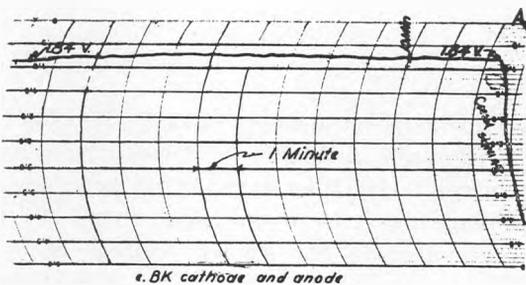


FIG. 11

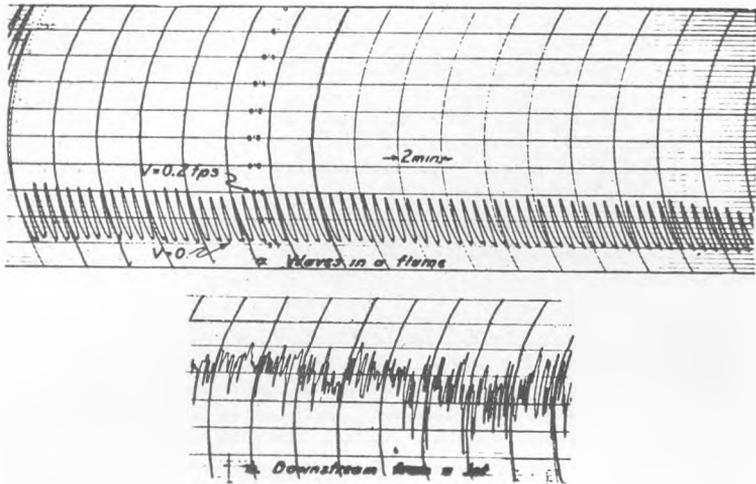


FIG. 12

makeup of the water in a closed circuit in a hydraulics laboratory can be closely controlled, calibration of the device and its use under such conditions should prove satisfactory. So far as its use in the field is concerned, only further experimentation and development will provide the answer.

DISCUSSION

Mr. Ripken emphasized the importance of Mr. Boyer's work because nothing is presently available for measuring velocities around 1 or 2 feet per second. He then asked what accuracy could be expected in measuring velocities in the range from 0.01 to 1 foot per second after compensating for known sources of error and instability. Mr. Boyer replied that he did not yet know the answer to this difficult question, but stated that in his measurements using tap water in the towing tank, occasional indications were off by 15 or 20 percent without any attempt to compensate for various things. He hopes that additional work he is now planning will improve the accuracy to 5 percent. Since no instrument is presently available, one with an accuracy of 5 percent would be a great help.

Mr. Craven discussed the importance of knowing the law governing the indication whenever a measurement is quite indirect. He felt that a more detailed study would be necessary to determine the extent to which dissolved oxygen and other phenomena affect the indications. Mr. Boyer agreed heartily, and emphasized the fact that he had looked into the mathematics of the subject and

found that differential equations had been developed for concentration gradients near cylinders and spheres. Also, some of the work done in Germany was confirmed by his own results.

Mr. Hubbard remarked that the frequency response of 20 cycles per second, though low, was probably adequate for the velocity range below 1 foot per second where the electrolytic method is applicable.

Mr. Gent wanted to know whether the electrodes had to be spaced about the instrument or whether they could be built in each side of a model so that there is no obstruction to the water. Mr. Boyer believed that a sweeping action very near the electrodes was very important so that any arrangement which placed them within a thick boundary layer would not be satisfactory.

It was then asked if any thought had been given to measuring the extreme variations in direction which usually accompanied low velocities in the field. Mr. Boyer recognized the need for this type of indication and felt that it was principally a hydraulic problem to make the flow past the sensing element depend upon the angularity of the flow.

Mr. Kolupaila asked whether the instrument could be modified to work at higher velocities by changing the electrode spacing. In reply, Mr. Boyer stated that the concentration gradient at the cathode was the primary factor in the instrument's indication, and that this gradient reached a limiting condition which did not depend on electrode spacing.

Mr. Hubbard commented on the great improvement which has resulted from the use of a reference electrode to eliminate the undependable anode effect.

Mr. Kalinske stated that this type of instrument is more or less a standard for measuring dissolved oxygen in quiescent liquids and is widely used by chemists and biologists for this purpose. However, it is also influenced by oxidizing and reducing substances which are present, such as chlorine, or any biological organisms that may be oxidizing or reducing organic matter, so that there are many secondary effects which will influence the readings besides the velocity of the fluid.

Mr. Boyer concluded by saying that he has had trouble with copper depositing on his cathode and that in polarographic research the oxygen is usually removed because it obscures the presence of many other substances. Similar problems exist at the anode, and chlorine did cause some trouble in the early experimental work.

REFERENCES

1. Boyer, M. C., "The Measurement of Velocity of Flowing Water by Electrical Methods," State University of Iowa M.S. Thesis, 1947.
2. Boyer, M. C., and Lonsdale, E. M., "The Measurement of Low Water Velocities by Electrolytic Means," Third Midwestern Conference on Fluid Mechanics, University of Minnesota, 1953.
3. Kolthoff, I. M., and Lingane, V. V., "Polarography," Interscience Publishers, New York, 1952.
4. Brdicka, R., "Collection of Czechoslovakian Chem. Comm." (see p. 234 of Ref. [3] above).