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CONDUCTIMETRIC MEASUREMENT AND CONTROL OF ACID CONCENTRATION IN LEACH PULPS

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MINERAL SCIENCES DIVISION

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Conductimetric Measurement and Control of Acid Concentration in Leach Pulps*

By G. G. EICHHOLZ** and A. H. BETTENS***

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SYNOPSIS

The development and application of a simple inductive method are described for the control of acid concentrations in leach pulps. This method avoids the difficulties arising in conventional conductivity cells because of corrosion of the cell electrodes and the need for filtering the leach liquor before introducing it into the cell. The design of such inductive units is discussed in detail, with particular emphasis on methods of compensating for temperature changes. The conductivities of a variety of leach pulps and slurries have been measured and it has been found that for a given acid concentration the nature and size of mineral particles is relatively unimportant. Possible applications of the system are described.

INTRODUCTION

IN the operation of leach plants for the extraction of metals from ore, careful control of reagent concentration and addition is important for proper and economic operation. In most cases such control is carried out by periodic sampling and chemical analysis; considerable savings may be obtained by a continuous and automatic system of measurement and control. One of the properties of leach pulps which is sensitive to variations in strong acid or base concentrations is the electrical conductivity. Various methods have been developed to utilize this property in controlling acid concentrations by a direct measurement of electric resistance between platinum contacts in a suitably designed cell (e.g. 1). Such methods suffer from corrosion and erosion effects on the

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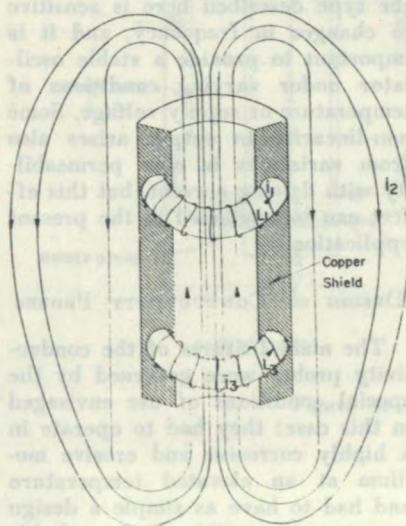


Figure 1.—Diagram of conductivity probe.

electrodes and are unsuitable in the case of dense slurries, where the measuring cell would be choked very rapidly and filtering of the pulp is rarely practical. These difficulties are avoided in contactless inductive methods. In their simplest form these depend on the change in inductance of a solenoid whose core is formed by the material whose conductivity is being measured, either in a direct circuit (2) or in bridge circuits of various degrees of sophistication (3, 4, 5). For optimum performance, such instruments must work at high frequencies, of the order of several megacycles.

A simpler operation at much lower frequencies is obtainable by the two-coil method, first described by Ruben (6) and since developed in various ways for pulp control (7) and salinity measurements (8). A slightly different form has been developed by the present authors specifically for use in leach tanks filled with strongly corrosive slurries, and some measurements have been carried out to correlate conductivity

with acid concentration, temperature, density, and operating frequency.

PRINCIPLES OF OPERATION

The sensing probe employed in this method consists of two toroidal coils, shielded electrostatically from each other and wound on ferromagnetic tape cores of high permeability. These two toroids are mounted some distance apart on a plastic tube through which the slurry may circulate. If the outside of the probe is fully immersed in the slurry, a conducting path is formed in which an induced current may circulate, which is fully linked with the flux in each of the toroidal cores. This situation is illustrated diagrammatically in Figure 1. If an external oscillator is connected to the upper coil L_1 , then the conductor formed by the slurry will have a current i_1 induced in it, whose magnitude depends essentially on the resistance it encounters. If the volume of slurry surrounding the probe is large, then its contribution to the electrical resistance of the current path becomes small compared with that of the column of slurry inside the tube. The magnitude of the current i_2 is, therefore, inversely proportional to the electrical resistance of the medium filling the tube, or, if the tube can always be considered filled uniformly, proportional to its electrical conductivity. The alternating current i_1 induces an alternating flux in the core of the second coil and hence an electromotive force proportional to it. By measuring the output voltage V_2 from the second coil L_2 , one thus obtains a measurement of the electrical conductivity of the slurry surrounding the probe.

Figure 2 shows the equivalent circuit for this system. The liquid path may be considered as a resistive circuit linked inductively with both coils. The total resistance of the liquid path R_2 can be expressed

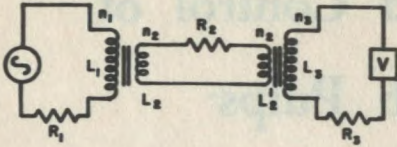


Figure 2.—Equivalent circuit.

in terms of the resistivity of the medium p as

$$R_2 = \rho (l/A)_{\text{eff}} = \frac{(l/A)_{\text{eff}}}{\sigma}$$

where σ is the electrical conductivity of the medium, and $(Al)_{\text{eff}}$ is the effective volume containing the current path l , made up of the cross section A times the path length of the slurry inside the tube, plus the contribution of the medium surrounding the probe. Considering the outside medium as consisting of many comparable resistance paths in parallel, its contribution to the total electrical resistance R_2 may usually be assumed to be negligible for a system of the type considered here. It follows that the precise location of the two coils along the tube is immaterial, as long as they are linked with the same current-carrying tube.

Using the usual symbols for the current components in Figure 2, one can set up the operating equations for this circuit.

The electromotive force set up in the liquid secondary

$$E_2 = \frac{n_2}{n_1} V_1,$$

assuming the resistance R_1 to be small, where n_1 and n_2 are the turns of the windings; n_2 , of course is equal to unity.

Hence

$$E_2 = \frac{V_1}{n_1}$$

and

$$i_2 = \frac{E_2}{R_2} = \frac{V_1}{n_1 R_2}, \dots \dots \dots (1)$$

neglecting the effective inductance L_2 of the liquid path.

The electromotive force E_3 in the second coil is proportional to i_2 :

$$E_3 = j n_3 \omega L_2 i_2 = \frac{j \omega L_2 n_3}{R_2 n_1} V_1 \dots \dots \dots (2)$$

where $\omega = 2\pi f$ is the angular frequency of the oscillator.

The output voltage

$$V_3 = \left[\frac{\omega k}{R_2} \cdot \frac{n_3}{n_1} \right] V_1 = K \sigma_2 V_1 \dots (3)$$

where k and K are calibration factors for a given system and frequency and σ_2 is the electrical conductivity of the slurry.

Both the conductivity of the slurries and the permeability of high-permeability core materials are greatly affected by changes in temperature, and for accurate work temperature compensation must be provided. This will be considered later. A highly inductive system of the type described here is sensitive to changes in frequency, and it is important to provide a stable oscillator under varying conditions of temperature or supply voltage. Some non-linearity in output arises also from variations in core permeability with driving current, but this effect can be neglected in the present application.

DESIGN OF CONDUCTIVITY PROBES

The main features of the conductivity probes were governed by the special conditions of use envisaged in this case: they had to operate in a highly corrosive and erosive medium at an elevated temperature and had to have as simple a design as was compatible with reliable plant operation. The central tube had to be large enough to avoid blocking by accumulating pulp, and provision had to be made for possible use as a control unit.

Three different probe units have

been made so far; they are illustrated in the picture, Figure 3. The first, and smallest, is the one used for most of the laboratory tests. It consists of two 4-79 Mo-Permalloy* cores, 1 in. inside diameter, which could be spaced a variable distance, from 1/2 in. to 2 in. apart. The core tapes are 4 mils thick in a Nylon casing. The coils are encased in a brass electrostatic shield which in turn is protected from the test solutions by a methyl methacrylate ("Lucite") case. The windings of the toroidal coils were determined experimentally. The primary, exciter coil consists of 25 turns, No. 34 gauge, and the secondary detector coil, of 1200 turns, No. 40 gauge. The fine gauge was used for reasons of space only.

The second probe used large cores with room for a 1 1/2 in. inner tube, surrounded by a copper shield, and was used for tests under actual plant conditions. These cores consisted of 2 mil 4-79 Mo-Permalloy tapes, again in a Nylon casing. The primary and secondary turn values were the same as before, with an extra winding of 200 turns on the primary core for the temperature compensation circuit. This probe was also protected by a Lucite case, and suspended by a stainless steel tube which contained the supply leads and the shielded detector cable. In a separate compartment in the probe a transistor oscillator was housed to serve as an independent, self-contained source of input power. Its circuit was based on that of

*Made by Arnold Engineering Co., Marengo, Ill.

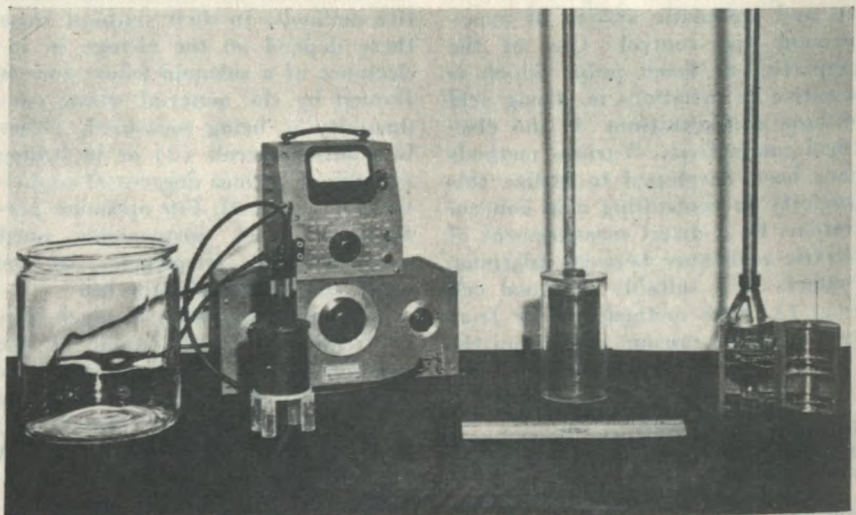


Figure 3.—View of conductivity probes.

(Complete detection system with Probe No. 1 on the left; Probes Nos. 2 and 3 in centre and at right).

Dulberger (9) with only minor modifications. As operation at one frequency only is required, the variable resistors in Dulberger's circuit have been replaced by appropriate fixed ones. For high-temperature operation, silicon transistors should be used in preference to germanium units.

The third probe was designed for easier assembly and better mechanical design. Its dimensions are indicated in Figure 4. A copper shield is again used with the same coils as those employed in the second probe. The probe is sealed by a layer of Tygon covered by a coating of silicone rubber. The temperature compensation is effected here by a rod-shaped thermistor housed in one of the legs of the stainless-steel spider supporting the probe. Provision is again made for alternative use of an internal or external oscillator.

TEST RESULTS

Although it is well known that the electrical conductivity of electrolytes varies with pH or acid concentration (10, 11), it was felt desirable to test the inductive conductivity probe in clear acid solutions first, both to confirm results obtained with other conductimetric devices and to establish the control potential of the device. For this purpose the probe was placed on a plastic tripod inside a large plastic bucket or glass jar, which was itself put inside a constant temperature bath. Care was taken to immerse the probe fully in the solution and to stir the solution. The acid concentrations were varied over a wide range; Figure 5 shows the results obtained for sulphuric acid and nitric acid solutions, as well as for sodium hydroxide. It is seen that the voltage output varies greatly with concentration in a near-linear fashion. No attempt was made to go to acid concentrations much outside the range of interest in leach work.

Although most practical measurements with the probe will be concerned only with variations in conductivity from a chosen value, it is often desirable to convert output readings into absolute conductivity values. For this reason a cylindrical glass cell, 60 cm long, with platinum electrodes, was set up horizontally and connected to a General Radio impedance bridge. It was calibrated with standard solutions of known conductivity (12) and the calibration curve is shown in Figure 6. By means of this cell the electrical conductivities of the sulphuric acid solutions were determined, and the

comparison graphs relating probe output voltage and conductivity are presented in Figure 7. The curves show the close relation between output voltage and conductivity of the liquid sample. Figure 8 illustrates the other two main variables, temperature and frequency. The system is quite frequency-sensitive as the coils have relatively high Q-values; however, in the absence of saturation of the cores, the slope of the conductivity plot at different acid concentrations remained the same at any given

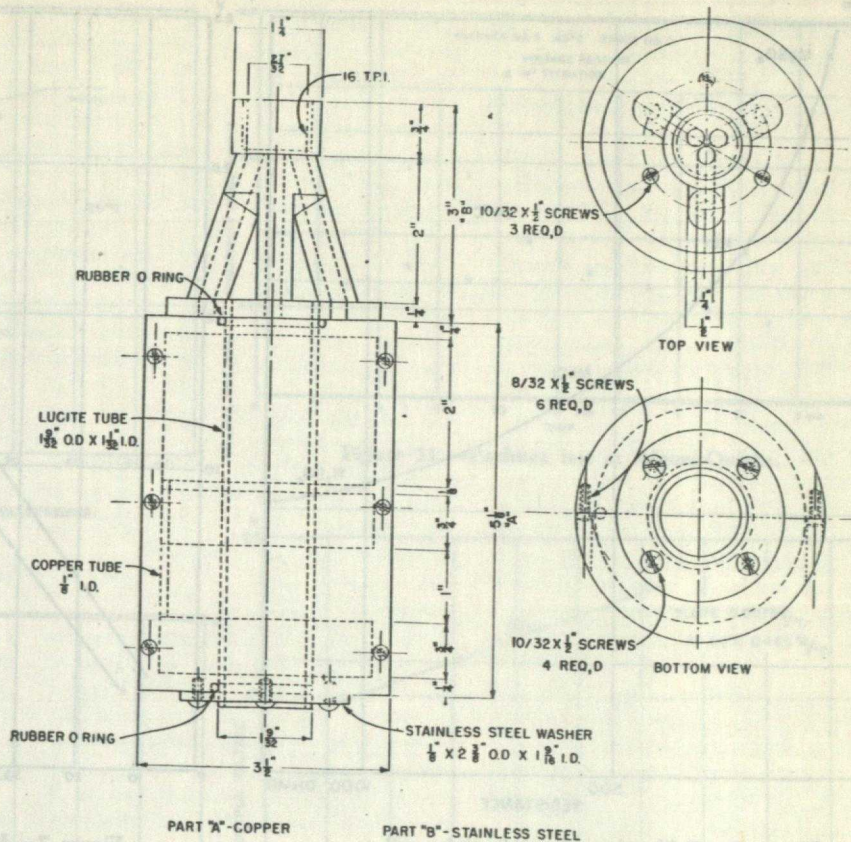


Figure 4.—Conductimetric probe.

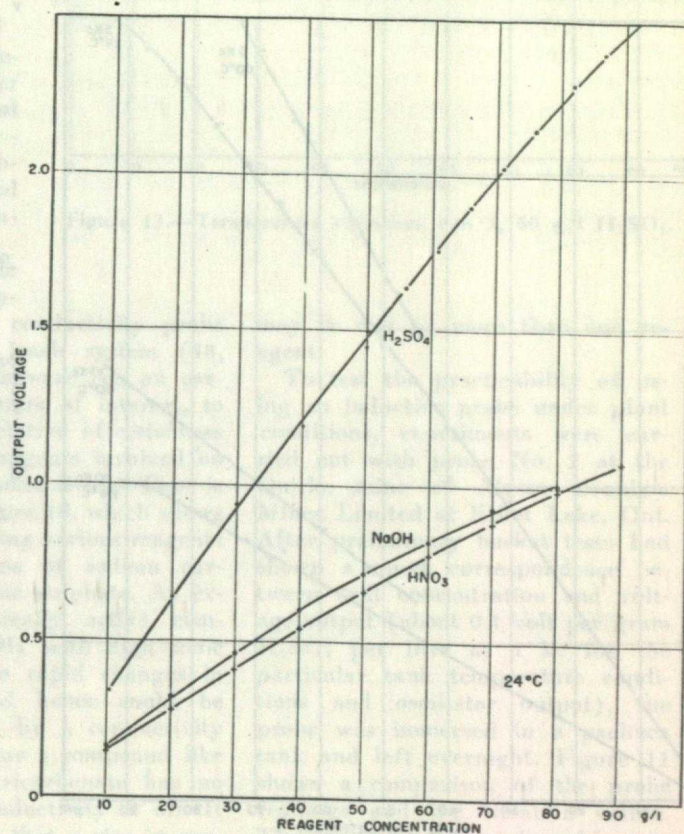


Figure 5.—Conductivity-concentration curves.

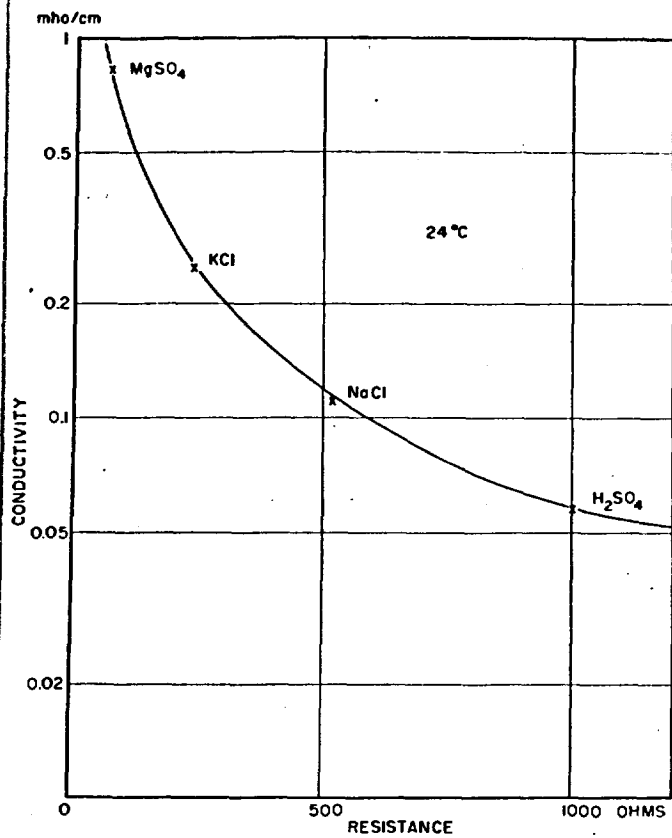


Figure 6.—Calibration of conductivity cell.

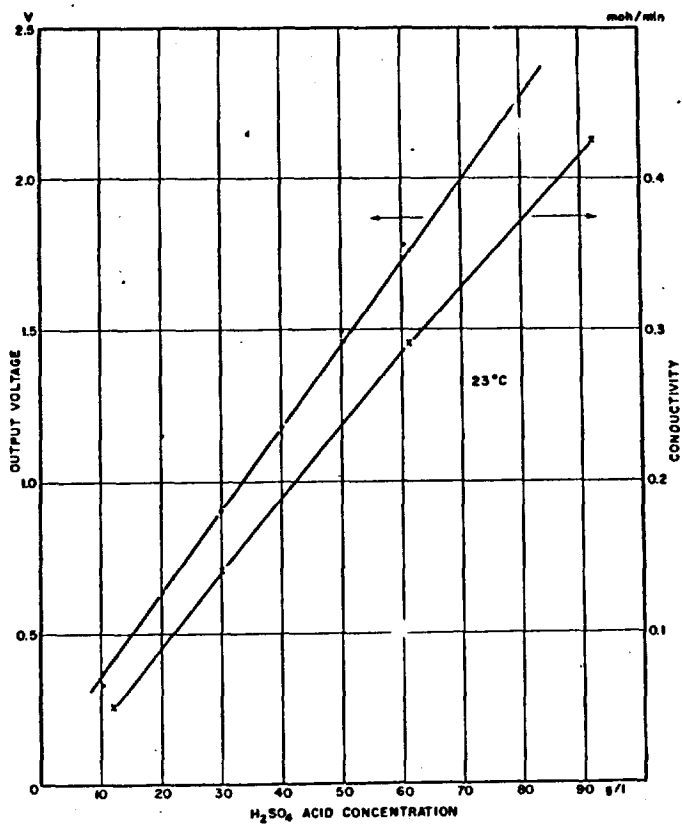


Figure 7.—H₂SO₄ conductivity measurements.

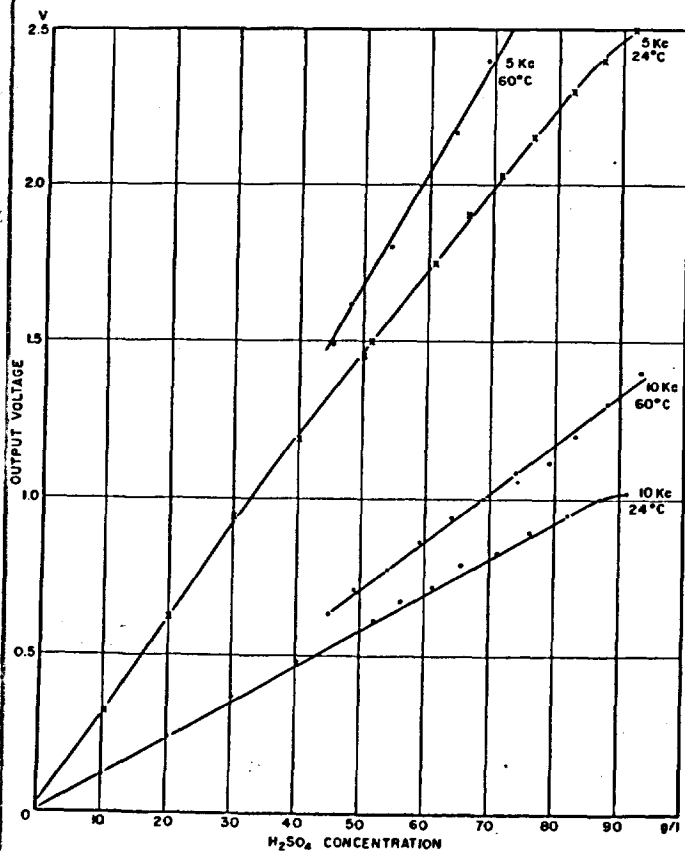


Figure 8.—H₂SO₄ conductivity measurements.

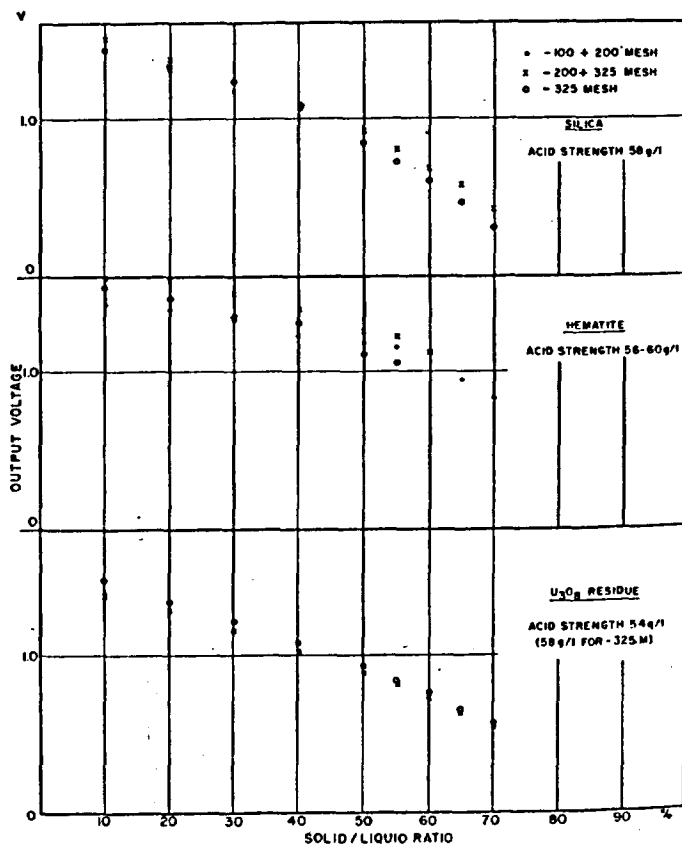


Figure 9.—Conductivity of H₂SO₄-pulp mixtures at 24°C.

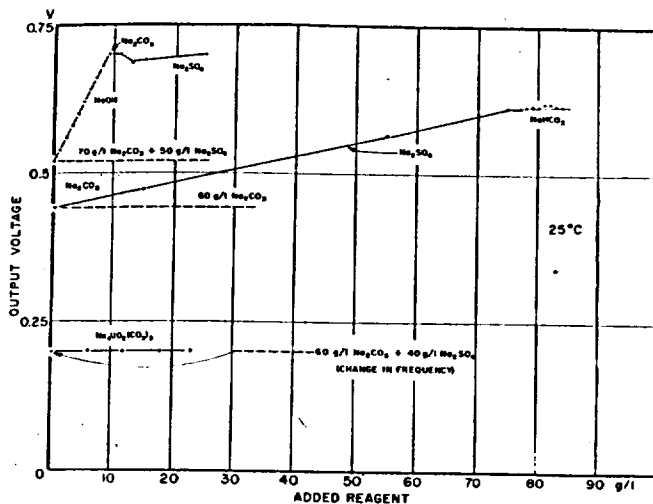


Figure 10.—Relative electrolytic effectiveness.

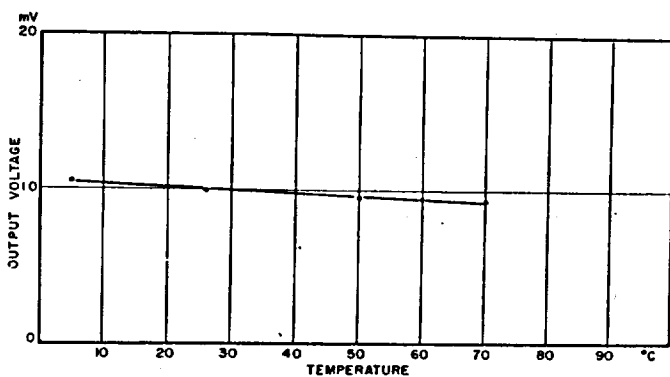


Figure 12.—Temperature effect of core permeability.

frequency in the 4-10 kilocycle range. This leaves temperature as the other factor to be controlled, except where leaching is done at a fixed temperature. In all other cases temperature compensation must be provided; this matter will be discussed later.

The main reason for adopting an electrodeless system is its superiority in pulps and slurries. To confirm the assumption that the electrical conductivity is essentially a function of acid concentration, tests were run with slurries of different composition and particle size. The results of these tests are shown in Figure 9 for slurries of silica, hematite, and uranium leach residue. It was found that for a given acid concentration the output voltage was unaffected by particle size or the nature of the mineral. In other words, the electric current is supported by the liquid conductor only, and the nature of the solids is immaterial for a given density value. Any scattering of points could be ascribed directly to variations in acid concentrations; this occurred particularly in the hematite tests, which were complicated by settling problems. Some of

the rise in conductivity for higher concentrations of hematite, however, can probably be ascribed to the iron content of the ore.

To investigate the possible application of the conductivity probe to a carbonate leach system (13, 14), several tests were run on carbonate leach liquors of interest, to determine the relative effectiveness of the various reagents involved on the electrical conductivity. This is illustrated in Figure 10, which shows the effect of adding various reagents to basic solutions of sodium carbonate and sodium sulphate. As expected, a chemically active compound like NaOH with high ionic mobility leads to rapid changes in conductivity, and hence could be easily controlled by a conductivity controller, whereas a compound like sodium uranyl tricarbonate has no effect on the conductivity at all. It can also be seen that a rise in conductivity in mixtures of this type

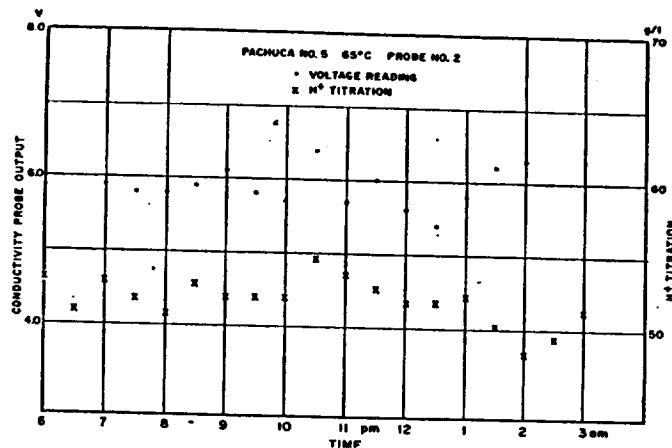


Figure 11.—Pachuca test at Algom-Quirke.

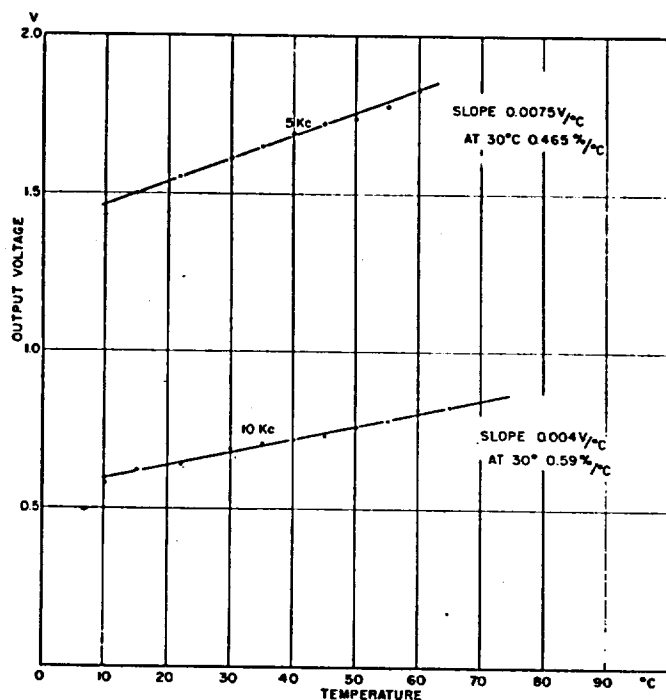


Figure 13.—Temperature variation, run 3, 60 g/l H₂SO₄.

may be due to more than one reagent.

To test the practicability of using an inductive probe under plant conditions, experiments were carried out with probe No. 2 at the Quirke mine of Algom Uranium Mines Limited at Elliot Lake, Ont. After preliminary bucket tests had shown a rough correspondence between acid concentration and voltage output (about 0.1 volt per gram H₂SO₄ per litre at 5 kc for the particular tank temperature conditions and oscillator output), the probe was immersed in a pachuca tank and left overnight. Figure 11 shows a comparison of the probe readings and the titration values. The latter are obviously subject to sampling variations, but a general

correspondence between the two sets of points is evident.

TEMPERATURE COMPENSATION

As mentioned previously, variations in temperature cause considerable changes in output. These are due partly to changes in core permeability with temperature, causing a variation of flux linked with the liquid path, and partly to intrinsic thermal effects on the conductivity (11). The effect of temperature on permeability was checked by replacing the liquid by a resistive wire loop and then placing the probe into an environment of varying temperature. The results are shown in Figure 12. The overall effect of temperature was determined in a series of tests, in which the leach solution, with the probe suspended in it, was placed into a variable temperature bath. Figure 13 shows the results obtained for a 60 g/l sulphuric acid solution, and Figure 14 those for a carbonate leach liquor. In both cases there is a strong positive temperature coefficient ranging from 0.46 to 1.96 per cent per degree centigrade at room temperature.

To overcome these temperature effects, some form of temperature compensation is required. Various forms have been suggested; Hinkelmann (8), for instance, proposes an elaborate feedback circuit. For the control of leach systems a simpler compensation system is considered to be adequate, consisting of a temperature-controlled bucking coil wound on the primary core, through which a small alternating current flows, whose magnitude varies as the temperature of the probe varies.

The temperature-sensitive element is a thermistor resistor, which had a room-temperature resistance of 100 ohms and a negative temperature coefficient. This resistance is large compared with that of the primary coil, so that the compensating circuit does not load down the oscillator. At the same time, to be effective the current through the compensating circuit must pass through more

turns than the primary coil; its characteristic can then be adjusted by means of a variable series resistance. Figure 15 shows various temperature characteristics obtainable for different coil windings and series resistances, as measured in a closed-loop secondary surrounding the primary. It is seen that the slope of the characteristic can be adjusted over a wide range by a suitable choice of components to match the slope of the temperature characteristic of the electrolyte. Figure 16 illustrates the degree of compensation obtained in an actual set of measurements. It should be noted that no distinction is made be-

tween the two sources of temperature variation in setting up the compensator resistance.

DISCUSSION OF RESULTS

The test work done so far has shown that the use of an inductive, electrodeless conductivity probe is practical and advantageous for high-density leach slurries. The precise configuration used would depend

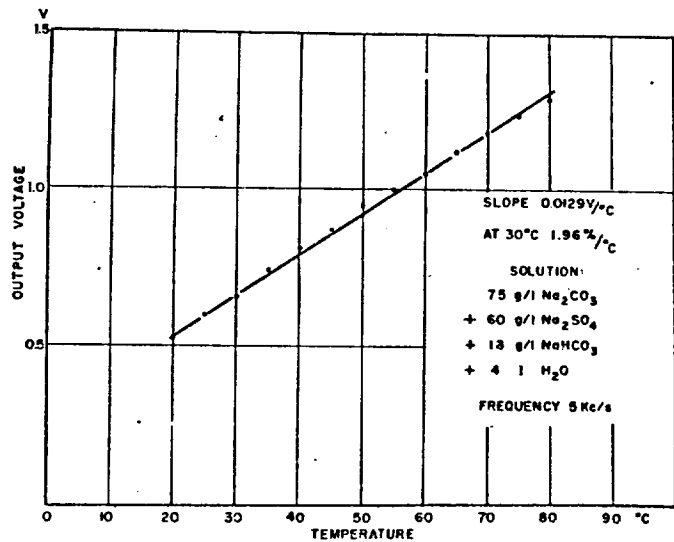


Figure 14.—Temperature variation, carbonate liquor.

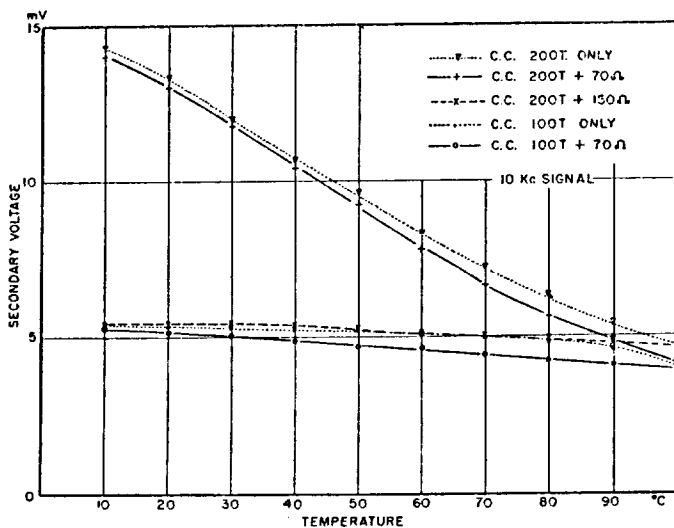


Figure 15.—Temperature compensation curves. Primary coil (25 turns) and compensating coil (c.c.) with thermistor.

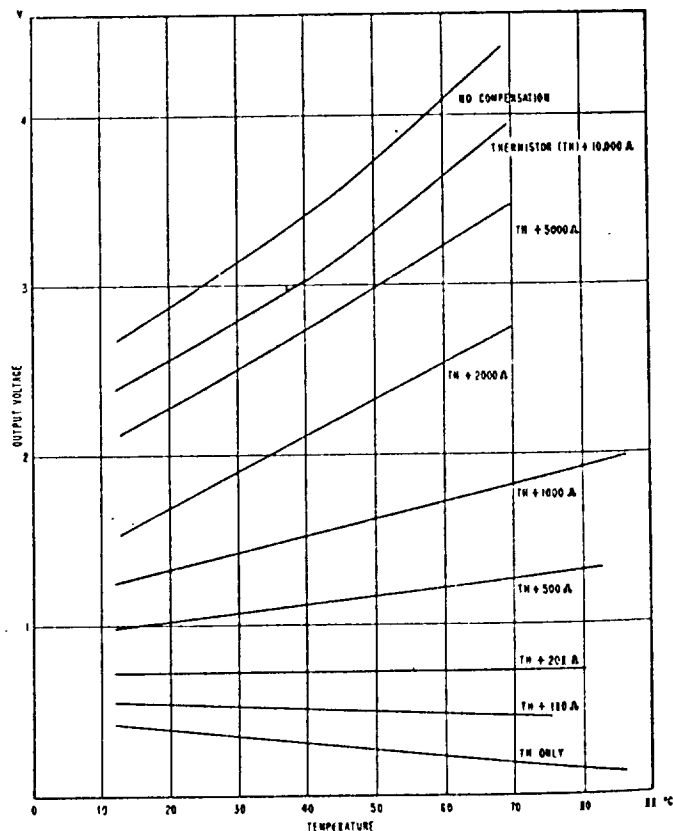


Figure 16.—Temperature compensation curves. Probe No. 3: Sulphuric acid solution (30 g/l).

rather on the purpose aimed for, i.e. whether measurement or control is the primary concern. For purposes of measurement the incorporation of a transistorized oscillator is a distinct advantage. Only D.C. supply lines to the oscillator and the shielded output leads need then be brought up to the outside of the tank, where a detector and a recorder could be mounted.

If the conductivity indication is intended for control of reagent addition, a slightly different system could be adopted which is outlined diagrammatically in Figure 17. The output from the detector coil is rectified and balanced against a rectified voltage derived from the oscillator. The difference voltage is then amplified and used to drive a pH-type controller-recorder.

The main merits of this system are its inherent simplicity and relatively low cost. The tests have shown that it should be adaptable to the measurement and control of almost any mineral slurry, as the electrical conductivity of the solution is the only material factor determining the output voltage for any given density. Apart from the design of the probe, which is not very complicated, standard units for generating and detecting audiofrequencies can be readily adapted for this purpose. Extension of this work to other slurries and solutions should present no difficulties.

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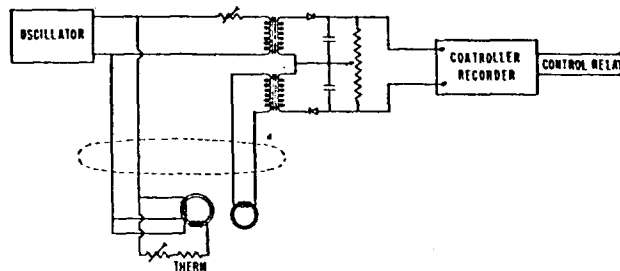


Figure 17.—Conductivity controller.

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