

Mines Branch Technical Bulletin TB 27

CONDUCTIMETRIC CONTROL OF
ALKALINE LEACH LIQUORS

by

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SYNOPSIS

A conductimetric method has been developed which is proving valuable for the determination of reagent concentrations in acid and alkaline leach liquors and pulps. The design and construction of a prototype equipment for this purpose are described in detail, with circuit diagrams and some discussion on practical operating problems.

Results of some test work on the detection and control of caustic soda in carbonate leach liquors and of lime in cyanide solutions are summarized and show the possible use of conductimetric controls in such alkaline leach solutions.

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CONTRÔLE CONDUCTIMÉTRIQUE DE LIQUEURS
DE LESSIVAGE ALCALINES

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RÉSUMÉ

On a mis au point un procédé conductimétrique qui s'est avéré utile à la détermination des concentrations en réactifs au sein des pâtes et des liqueurs de lessivage tant acides qu'alcalines. Les auteurs décrivent en détail le dessin et la construction d'un prototype servant à cette fin, avec schémas du dispositif ainsi que certaines considérations sur les problèmes pratiques de fonctionnement.

Les résultats de certains travaux expérimentaux sur la détection et le contrôle de la soude caustique au sein des liqueurs de lessivage carbonatées et sur la chaux au sein de solutions cyanurées s'y trouvent indiqués de façon sommaire, et on en déduit qu'il est possible de recourir aux contrôles conductimétriques pour de telles solutions de lessivage alcalines.

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INTRODUCTION

The measurement and control of the concentration of active reagents in leach liquors and other solutions constitute one of the basic operations in chemical extraction processes. In many cases this can be done by controlling the pH of the solution, whereas in other cases, due to low sensitivities of pH control at the extreme ranges, conductimetric methods are preferable. For very corrosive, erosive or dense liquors electrodeless methods for conductivity control are advantageous (1). In these methods a portion of the liquid forms part of an electrical circuit on which A.C. signals are impressed whose magnitude after detection is proportional to the conductivity of the liquid. Although capacitative methods have been used (2), most published methods depend on variations of an inductive circuit in which the current induced in the liquid links two separate inductances which are electrostatically shielded from each other (1, 3-6). Such units have been used among others to control acid leach solutions (1) and core and mud samples (4), but relatively few details of design have been published so far.

In a previous paper (1) the principles of the method have been discussed. Essentially, a sinusoidal voltage in the frequency range of a few kilocycles is applied to a toroidal coil which is fully immersed in the liquid under test. A second toroidal coil surrounding the same cylindrical portion of the liquid conductor as the first coil

will then have a sinusoidal voltage induced in it, whose magnitude depends on the conductivity of the liquid. In addition, the output voltage is proportional to the turns ratio of the two coils.

The sensitivity of such equipment to variations in concentration of the reagent in the liquid depends essentially on the percentage variation in conductivity for a given change in concentration of the reagent ions. This in turn depends on the specific ionization potential, the ionic mobility and charge, and the temperature of the solution. At a given temperature the "effectiveness" of a particular ion on the conductivity varies greatly for different substances (1). Useful control by this method is possible only if the reagent ion to be controlled is the only one varying in concentration or the most effective one present in the solution. If the conductivity may be changed significantly by simultaneous concentration variations in more than one component, then effective control can be achieved only if a second, independent parameter, such as pH or density, can be utilized simultaneously for the control of any second solution reagent (6). For example, in cyanide solutions containing lime, the hydroxyl ion of the lime has by far the dominant effect on the total conductivity (1). Hence, it is possible to control usefully the addition of lime to a cyanide solution, even with minor variations in cyanide concentration, but it would be useless to attempt to control the cyanide ion concentration of solutions containing

even small, but uncontrolled concentrations of lime. This problem will be discussed later in more detail.

The other major variable involved in conductimetric control is temperature. Most leach solutions show considerable variations in conductivity with temperature (1), and unless the temperature of the solution is already closely controlled, as it is in some leach circuits, it is imperative to provide electronic temperature compensation in the control circuit for use in any practical control system. Various methods for doing this have been proposed (7); the system described here utilizes thermistors for this purpose.

DESCRIPTION OF THE EQUIPMENT

In its simplest form the system requires merely a source of audio frequency oscillations, an inductive probe suitable for immersion in the liquid, and an A.C. voltmeter as the detector. For more practical applications, the latter may be replaced by a commercial recorder-controller unit using either a strip chart or a circular chart unit; a suitable balancing network to provide a differential output and a means of temperature compensation must also be included. Figure 1 shows a block diagram of such a system that is seen to be quite simple in essentials. For convenience of installation the oscillator circuit and the balancing circuits may be

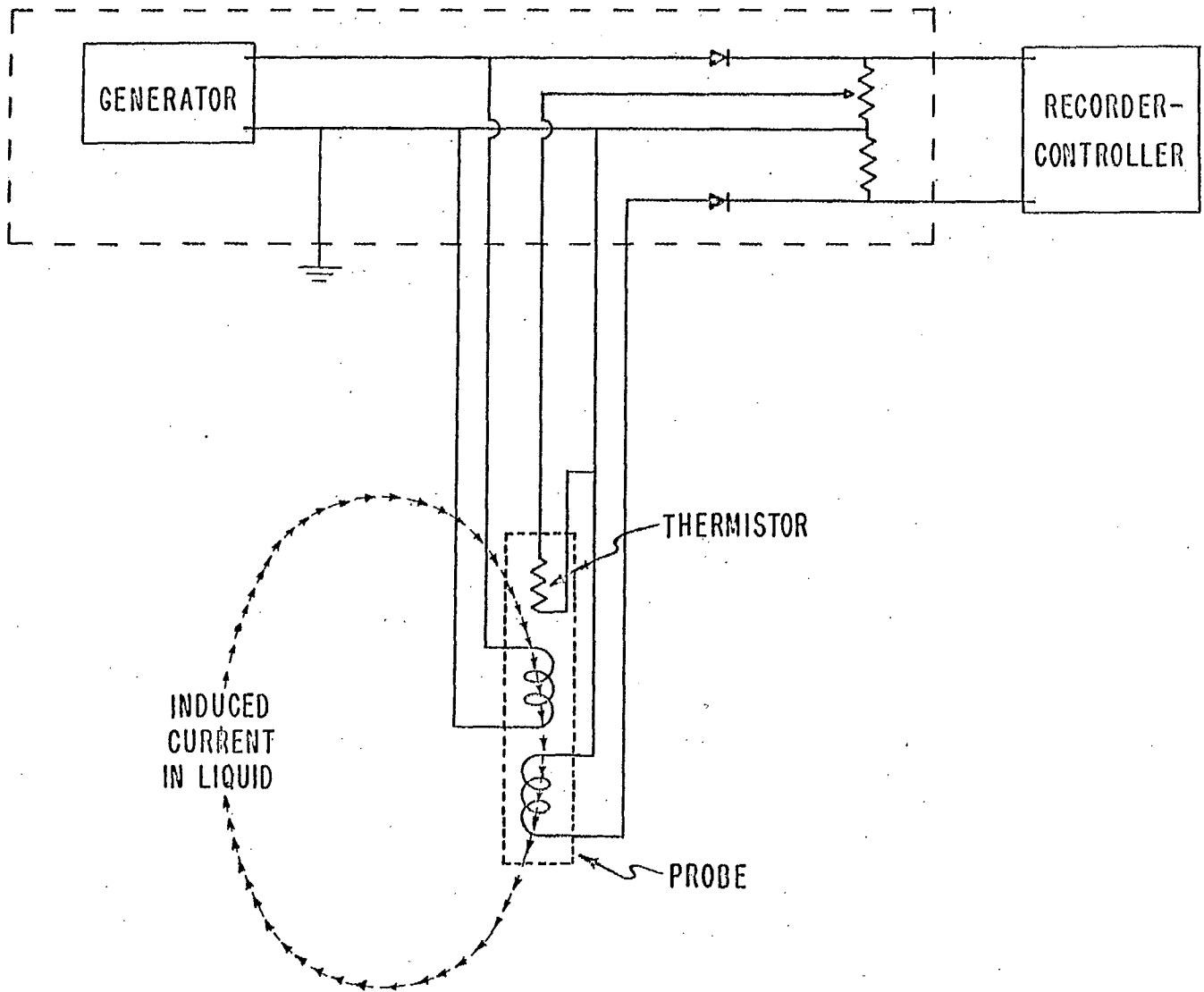


FIGURE I- BLOCK DIAGRAM OF SYSTEM

contained in the same unit. Figure 2 is a photograph of the prototype equipment used for test work so far; a description of the design and assembly of the more important parts follows.

a. The Conductivity Probe

The probe constitutes the central component of the system. It consists of two toroidal coils mounted on an insulating tube, through which the liquid under test can flow, and surrounded by an electrostatic shield which screens the coils from each other and from outside interference. The shield is shaped like an elongated doughnut and is supported by a long tube which acts both as a support and as a shield for the leads connecting the coils to the driving and indicating circuits. In addition, the probe houses a thermistor to provide automatic temperature compensation. Figure 3 shows a cross section of a typical probe. The supporting tube could be fixed at right angles to the axis of the coils (5, 6), but in the present design it was considered preferable to mount the coils in such a way, that the coil axis, and hence the direction of the liquid flow, is vertical to avoid silting up of the tube by slurries or precipitates.

Since the probe may be immersed in highly corrosive liquids, considerable care must be taken to cover it and the supporting tube with a sufficiently corrosion-proof compound. This requirement has in fact led to considerable difficulties and experimentation, since the covering compound must be resistant to corrosion and

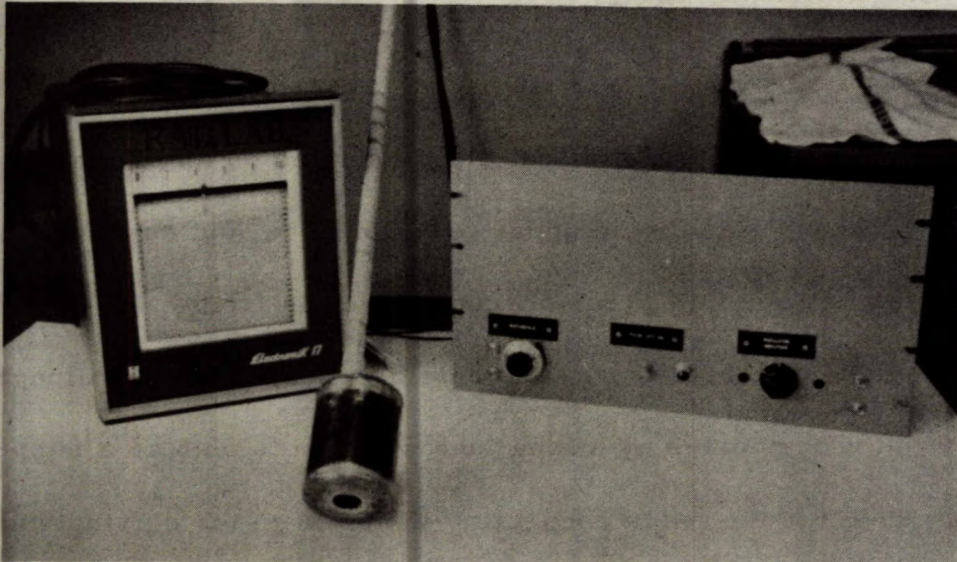


Figure 2 - Photo of complete system (probe uncoated)

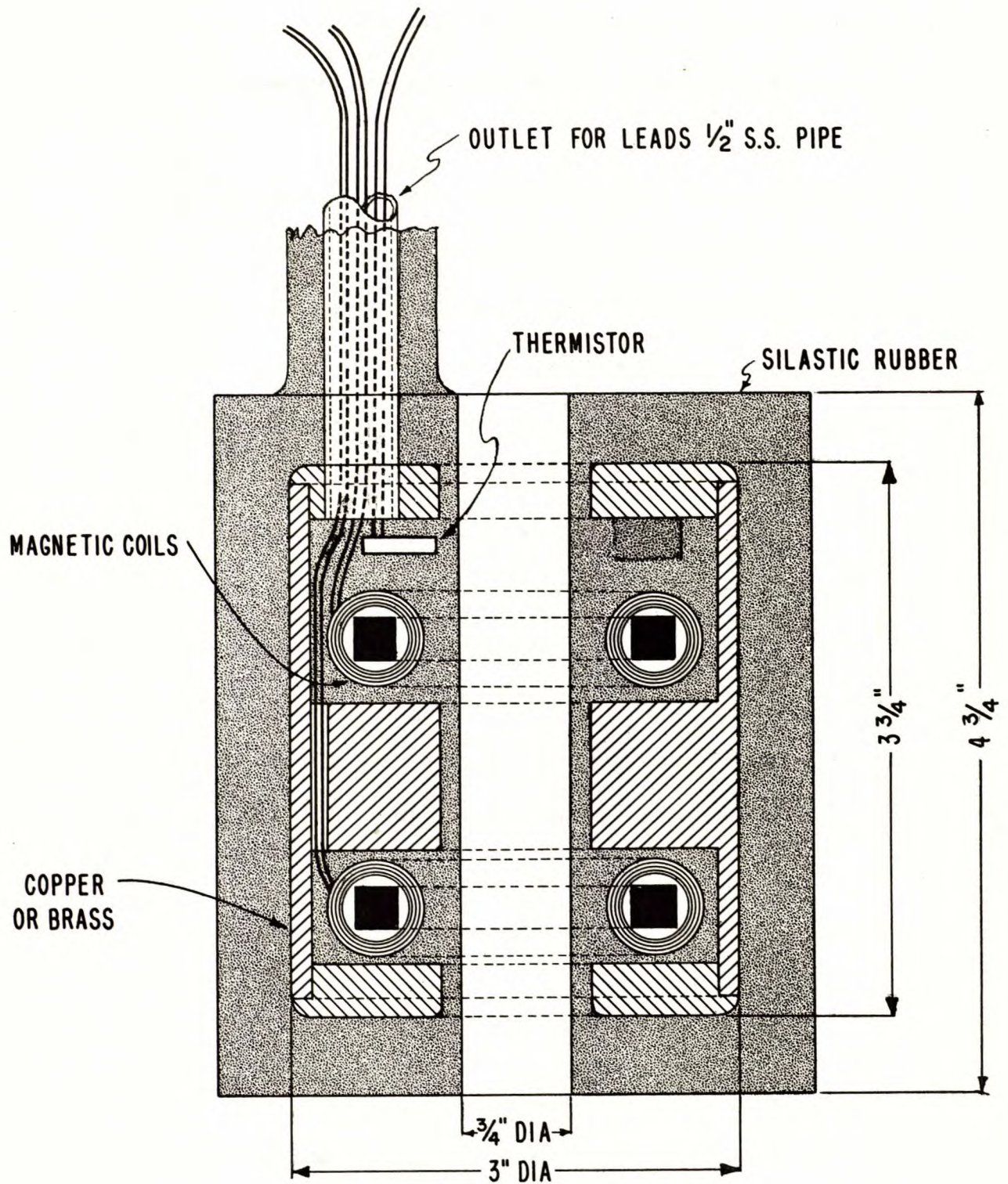


FIGURE 3—CROSS SECTION THROUGH PROBE

abrasion and yet be flexible enough to accommodate slight changes in dimensions of the metal shield with temperature without cracking. For use in acid surroundings, Dow-Corning Silastic compounds type 503 or 881 have been found satisfactory, provided that no sharp or abrupt corners exist on the underlying probe surface. In highly alkaline surroundings, Silastic compounds appear to deteriorate somewhat and epoxy resins have been used instead (e.g., Blachford type 305 with 660 hardener). These appear to be adequate, although probably a softer, more flexible compound may be preferable.

The toroidal coils determine the ultimate performance of the probe. However, in practice it has been found sufficient to use a cheaper type of core than is used for some oceanographic probes (8), and to omit specific compensation for variations in magnetic permeability with temperature. The cores used for the coils have been Mo-Permalloy tape-wound cores, $1\frac{1}{2}$ in. inside diameter with Nylon casing, Arnold Engineering Co. type 3 T 5320-P2. Similar cores made by other manufacturers would undoubtedly serve the same purpose.

A range of coils has been made up for test purposes.

For highest sensitivity the following coils have been used:

Primary coil: 50 turns, 20 SWG enamelled wire;

Secondary coil: 5000 turns, 36 SWG enamelled wire.

Each coil has been coated with Glyptal varnish and has been assembled inside the probe cavities which have been insulated with strips of varnished cambric.

b. The Generator and Detector Unit

Although for utility the generator and detector circuits have been housed in the same unit, their functions are clearly quite different (Figure 1) and they have to be shielded carefully from each other. This makes the design and layout quite critical; in addition, it was found that the final detector must have a differential sensitivity of 0.5 mV. This requires, of course, comparable stability in both the reference voltage and the output voltage from the probe and in turn demands high stability over both long- and short-term temperature variations from all components.

The generator circuit had to meet these stability requirements and in addition supply a heavy load current to the low impedance of the primary coil. For this reason it was considered expedient to use vacuum tube circuits for the time being, although transistor circuits can no doubt be designed to meet requirements.

An inductive circuit like that of the probe is highly frequency-sensitive and with the coils used some gain in sensitivity could be obtained by working at very low frequencies. However, to simplify filtering and shielding problems, it was decided to stay with a fixed oscillator operating at a frequency between 1 and 5 kilocycles. An RC oscillator with an amplitude stability of the order of 1 part in 10^4 was required. This need was met by the use of a modified Wien bridge circuit fed from a

well-regulated D.C. supply circuit. Figure 4 shows the complete circuit and it will be noted that part of the plate load of V_1 is common to both anodes. By this means the dynamic load of the system is shared by both halves of V_1 and any outside voltage variations are compensated for by corresponding bias changes. A pure sinusoidal output voltage is obtained by degenerative feedback which reduces the overall gain to just over 1.

To maintain stability and minimize load variation effects, the signal is taken from the cathode of the oscillator tube and amplified by a heavily fed-back amplifier with an overall gain of 10. Large capacitors and small resistors, highly derated, are employed in all critical RC circuits where temperature stability is essential. A step amplitude control has been provided and the signal is brought out to a five-pin socket for connection to the probe. For good stability it is important to avoid excessive changes in load as the resistance of the liquid loop varies, and this determines to some extent the design of the primary inductance and the probe dimensions. Dry performance testing of the whole probe system can be done easily by slipping a copper wire through the probe hole and connecting it to a calibrated or variable resistance of the order of 30-100 ohms.

Because of the danger of leakage and feedback, extreme care must be taken to provide proper grounding without ground loops. Similarly, the recorder used with the system must be grounded through the socket ground connection if serious instability is to be avoided.

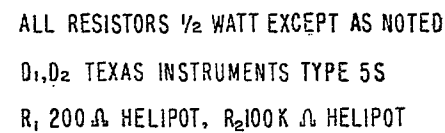


FIGURE 4- GENERATOR AND DETECTOR UNIT
FOR CONDUCTIVITY PROBE

c. The Detector Circuit and the Recorder/Controller

Figure 4 shows the bridge circuit used to compare the output voltage from the probe, rectified by diode D_1 , with a fraction of the oscillator output, rectified by diode D_2 . By varying the "Reference" control, either zero or mid-scale output, depending on the controller used, can be obtained for the particular solution conductivity which is considered "normal". Any deviation from this normal value will then appear as a differential voltage across the output terminals of the generator-detector unit and can be applied directly to the recorder input terminals.

Temperature compensation was originally obtained by means of a bucking winding on the primary coil, whose current was controlled by the variation in resistance with temperature of a thermistor resistor. However, it was found that this arrangement resulted in undesirable effects on the oscillator stability because of the transformer action and phase reversal between the two windings. For this reason the thermistor was transferred into the balancing network. The thermistor, now located in the top compartment of the probe, is connected across the signal half of the balancing network in such a manner as to counteract the temperature effect of the conductivity of the solution. To obtain the correct temperature compensation over the temperature range required, the probe must be immersed in turn in sample solutions maintained at the anticipated

extremes of temperature and the "Temperature Compensation" control R_1 , must be adjusted until the output is essentially independent of temperature. The thermistor in the probe described is General Electric thermistor rod, type R051, resistance 100,000 ohms at 25°C.

Several types of recorder have been used in conjunction with this system. For positive control a 10 mV full-scale potentiometer controller is preferred, as this provides wide enough variations in output indication to obtain the sensitivity required without hunting. Both strip chart and circular chart controllers have been used. Less sensitive potentiometer units (100 mV full-scale) have also been employed, but in this case it may be necessary to insert a stable amplifier to amplify the probe output voltage before rectification and balancing.

It should be stressed at this point that the treatment and indication of the probe output voltage can equally well be carried out by other means. It is possible to use a differential voltmeter on the output of the probe only or to use an independent null detector. Alternatively, it is possible to modulate the input signal to the probe and to use the modulation signal only after demodulation. Such variations can be explored readily whenever commercial production of such systems is contemplated; several variations of this kind have already been designed or are under review by the industry.

TYPICAL TEST RESULTS

After previous work had shown the usefulness of conductimetric control in acid leach circuits (1), its application to highly alkaline circuits was next investigated. Two such solutions appeared to be of immediate importance in the Canadian mining industry: the carbonate leach liquors used in the uranium extraction process at the Beaverlodge plant of Eldorado Mining and Refining Limited (9), and the cyanide solutions used by the majority of Canadian gold producers. In both cases the dominant ion, as regards conductivity of the solutions, is that of the hydroxyl reagent which is used to adjust the pH to the required optimum value. Test work was done, therefore, on representative solutions of both types to investigate the possible use of a conductimetric controller to control the addition of the active reagent. In both cases it was thought that the greater ruggedness and stability of the conductimetric probe compared with pH electrodes would result in more reliable, less troublesome and, ultimately, more economic control.

a. Carbonate Leach Liquors

Test work on Beaverlodge liquors was conducted in close liaison with staff of Eldorado Mining and Refining Limited, notably Mr. R.J. Tremblay and Mr. R.P. Bailey. The work was done in three stages: initial tests with synthetic solutions, pilot

plant tests with Beaverlodge leach liquor, and plant tests at the Beaverlodge mill. The reagent controlled was caustic soda, which previously had been added manually according to a set schedule.

The test solutions contained about 75 g/l Na_2CO_3 , 60 g/l Na_2SO_4 , 1 g/l $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$, and 5 g/l NaOH. Figure 5 shows the effect of adding varying amounts of caustic soda to these solutions. Each step is marked with the amount added and the change in caustic soda concentration it represents. The sensitivity to NaOH addition, better than 0.5 g/l, indicated by the recorder trace was considered more than adequate. This was confirmed subsequently at Beaverlodge and a permanent controller unit, designed by Electronic Associates Ltd., Willowdale, Ont., has been installed in the meantime.

b. Cyanide Leach Liquors

In the cyanide solutions used in the extraction of gold, the cyanide ion is relatively weak electrolytically and the conductimetric method does not lend itself to a determination or control of cyanide strength. However, at many mines lime is used to adjust the alkalinity of the solution, and tests have been conducted to investigate the possible usefulness of the conductimetric probe to control lime addition.

At the request of McIntyre Porcupine Mines Ltd., some tests were done on some typical cyanide liquors from their mill.

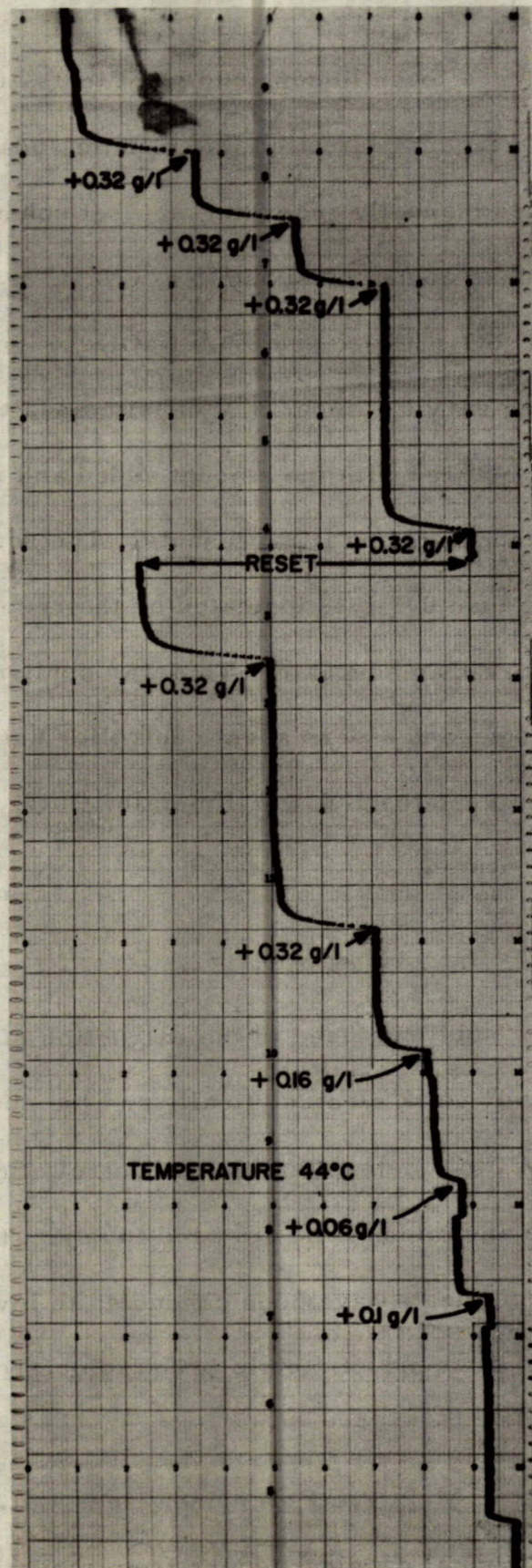


Figure 5 - Recorder trace - Addition of caustic soda to carbonate solution.

After increasing the detector amplifier gain somewhat, it was found that the probe could be used satisfactorily to detect and control the addition of batches of as little as 0.05 lb CaO per ton of solution.

Initial tests were conducted with a synthetic stock solution containing 0.76 lb/ton NaCN (0.38 g/l), 0.83 g/l NaCNS (equivalent to 0.58 g/l CNS^-), and 0.93 g/l Na_2SO_4 (0.63 g/l $\text{SO}_4^{=}$); pH was 10.3 initially, temperature 68°F. Lime was added in steps of 0.05 lb/ton up to a total of 1.35 lb/ton. Final titration indicated 0.72 lb CaO/ton solution as free lime, and a pH value of 12.0. The results of this test have been plotted in Figure 6. For control purposes a short, near-linear portion of this curve would be adequate. Good stability of operation was observed throughout the test.

The second test was done with the barren cyanide solution provided by McIntyre Porcupine Mines Ltd. This solution contained initially 1 lb/ton NaCN (0.5 g/l), 0.41 g/l CNS^- , and 0.16 lb/ton free lime. Lime was added again in successive steps, and the resultant recorder readings have been plotted in Figure 7. The effect of each successive addition of lime was readily visible on the recorder and underlined the feasibility of using the conductimetric probe to control the lime concentration in such solutions. At very high lime concentration there were subsequent changes in conductivity associated with secondary chemical reactions; these would not be of primary importance in controlling a leach circuit on stream.

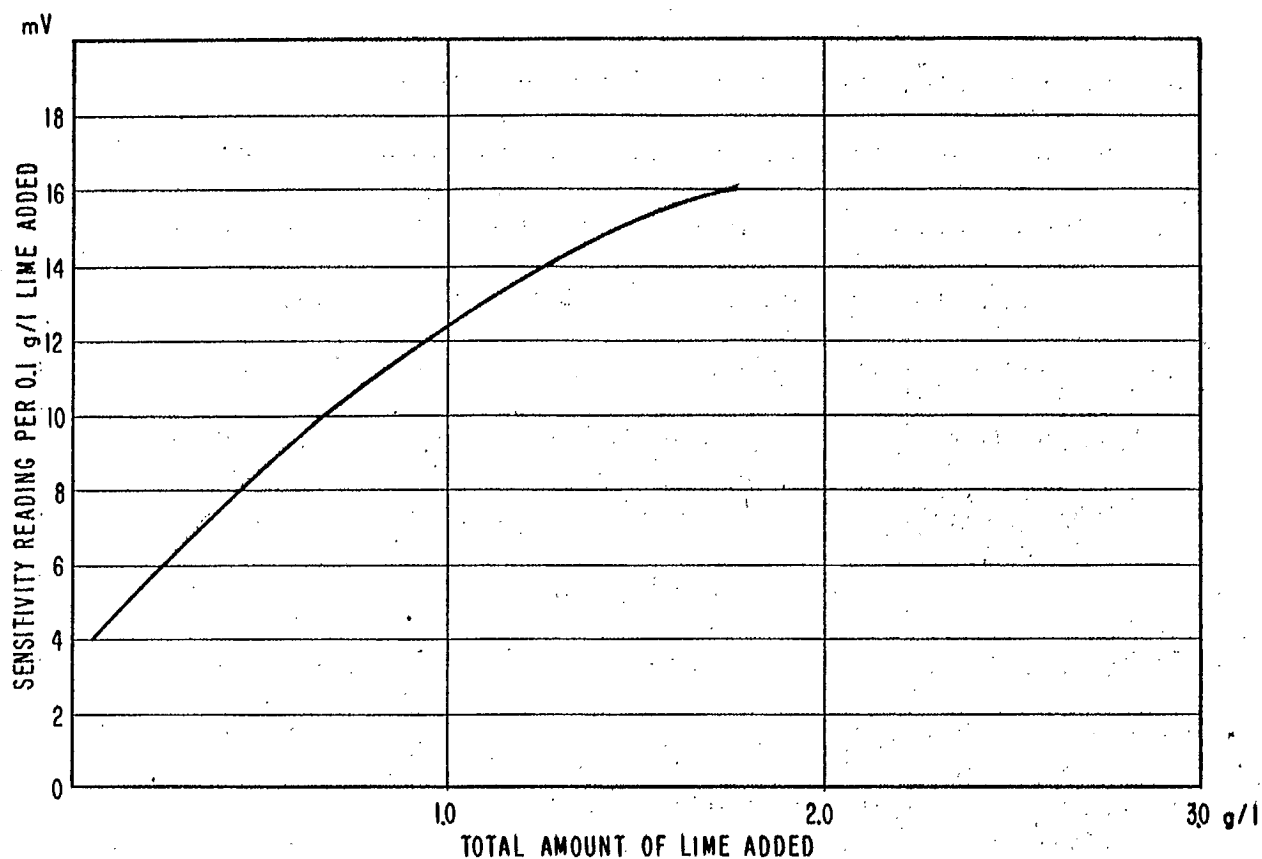


FIGURE 6 RESULTS FOR SYNTHETIC CYANIDE SOLUTION

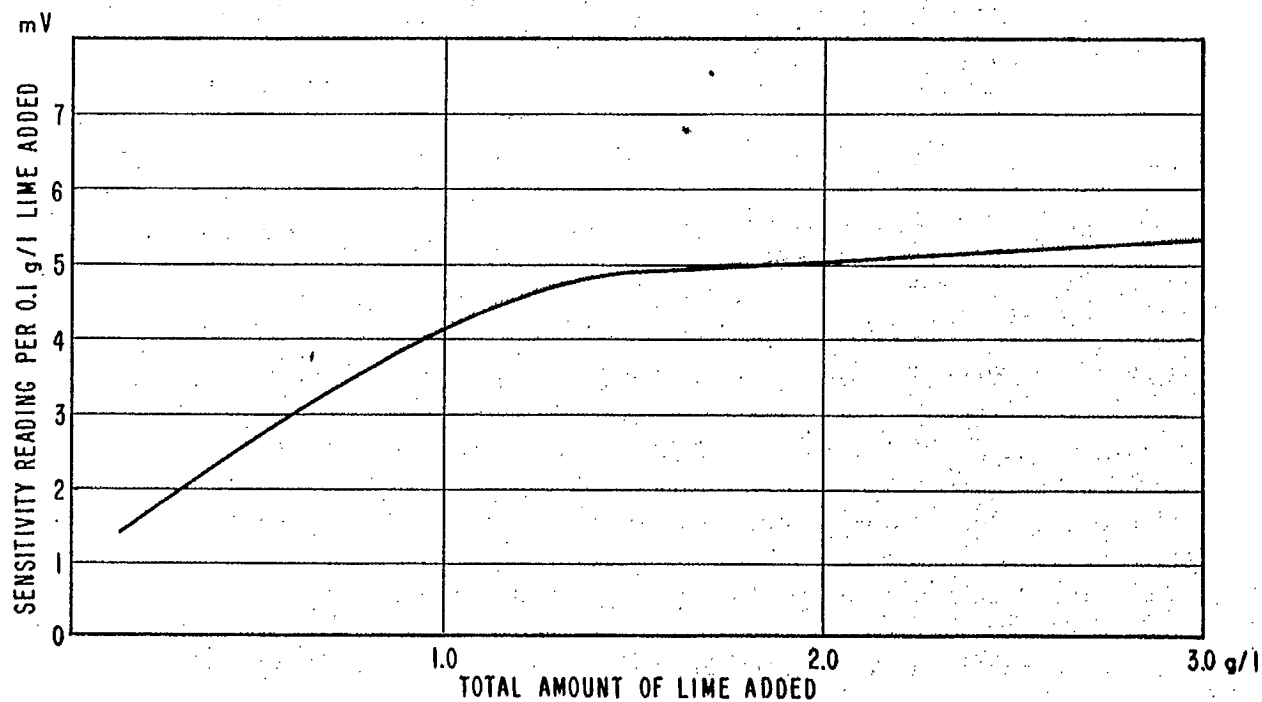


FIGURE 7 RESULTS FOR BARREN McINTYRE SOLUTION
NaCN 0.5 g/l, CNS 0.41 g/l, INITIAL FREE LIME 0.08 g/l

CONCLUSIONS

The tests done to date have shown that conductimetric methods of control can be applied equally well to alkaline and to acid leach liquors, provided that there is a dominant ion whose effect on conductivity with varying concentration is markedly greater than that of any other ions present. In the two cases investigated, the control of caustic soda and of lime in high-pH solutions appears to be quite practical and can be easily brought within the range of present industrial control practice and equipment. The two main difficulties encountered in practice are both solvable with a little care: the selection of a casing material for the probe to enable it to withstand the corrosive effects of the liquor can be met by the choice of a suitable paint or potting compound; problems of stability or drift require the design of a very stable oscillator to exacting requirements and considerable care in the layout of grounding lines and in the provision of a stable reference voltage. Both of these circuit requirements are commonly encountered in current industrial design and can be met by existing design procedures. The present report indicates the way in which these problems have been overcome in the Mines Branch unit.

The inherent simplicity and ruggedness of the conductimetric probe should ensure it an increasingly important place in the field of chemical control engineering, particularly in those chemical

extraction plants whose managements are becoming progressively more conscious of the importance of control and automation for more efficient and economic operation.

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