Evaluation of Chloride-Ion-Specific Electrodes as In Situ Chemical Sensors for Monitoring Total Chloride Concentration in Aqueous Solutions Generated during the Recovery of Plutonium from Molten Salts Used in Plutonium Electrorefining Operations

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ABSTRACT

Two commercially available chloride-ion-specific electrodes (CLISEs), a solid-state type and a membrane type, were evaluated as potential in situ chemical sensors for determining total chloride ion concentration in mixed sodium chloride/potassium chloride/hydrochloric acid solutions generated during the recovery of plutonium from molten salts used in plutonium electrorefining operations. Because the response of the solid-state CLISE was closer than was the response of the membrane-type CLISE to the theoretical response predicted by the Nernst equation, the solid-state CLISE was selected for further evaluation. A detailed investigation of the characteristics of the chloride system and the corresponding CLISE response to concentration changes suggested four methods by which the CLISE could be used either as a direct in situ sensor or as an indirect sensor through which an analysis could be performed on-line with a sample extracted from the process solution

I. INTRODUCTION

The final step in the recovery and purification of plutonium metal is an electrorefining (ER) operation that is carried out in a high-temperature, molten-salt solvent system. The solvent currently in use at Los Alamos is an equimolar sodium chloride/potassium chloride eutectic mixture. After the ER operation the salt still contains enough uncoalesced plutonium metal and/or unreduced plutonium trichloride that it cannot

be discarded. Thus, we had to develop an aqueous recovery operation that would remove the residual plutonium from the salts.

The steps in this operation are as follows: (1) the salt is treated with approximately 6 M hydrochloric acid to dissolve the plutonium; (2) the total chloride concentration is adjusted to 7 M with concentrated HCl; (3) sodium chlorite is added to oxidize Pu(III) to Pu(IV); and (4) the Pu(IV) hexachloroplutinate dianion complex, $PuCl_6^{2-}$, is absorbed on an anion exchange resin. The degree to which the complex adsorbs on the resin is very strongly dependent on the total chloride ion concentration. Therefore, an accurate measurement and adjustment of chloride ion concentration must be made to optimize the amount of recovered plutonium.

The current procedure used for chloride analysis consists of extracting a sample from the process solution and then subjecting it to a traditional argentiometric · titration. Even when an automatic titrator system is used, this method is still very time consuming. It also suffers from an inherent lack of accuracy, estimated at ±5%, and requires the direct handling of solutions, possibly exposing the operator to increased radiation.

A more desirable approach to performing this analysis involves the use of an in situ chemical sensor that continuously monitors the chloride ion concentration in the process solution. Such an approach eliminates the need to extract samples for analysis and significantly reduces the time required to carry out the analysis and adjust the solution concentration levels.

Two types of chloride-ion-specific electrodes (CLISEs) that might be used for this application are commercially available. Both types use silver chloride as the sensing element. One uses a single crystal of the salt, whereas the other uses the salt dispersed in a porous polymer membrane. The stated dynamic operating range for these electrodes is a chloride concentration from $5 \cdot 10^{-5}$ to 1 M and a solution pH range from 0 to 14. The solutions used for the aqueous plutonium recovery process lie outside both of these limits, having chloride concentrations from approximately 4 to 10 M and acidities from 1 to 10 M, which translates to a nominal pH range of 0 to -1. If the stated dynamic ranges for the CLISEs are accurate, the sample solutions would have to be diluted with a buffer before being analyzed to bring them within the operating ranges of the sensors.

This report summarizes the results of the evaluation of the commercially available CLISEs as chemical sensors for determining chloride concentrations in both a direct in situ measurement mode and an indirect measurement mode after sample pretreatment.

II. EXPERIMENTAL METHODS

Several different chloride salts and hydrochloric acid solutions were used to make calibration curves for the CLISEs. The salt standard solutions were prepared by dissolving accurately weighed quantities of reagent-grade salts into a fixed volume of water, then diluting this stock solution until standard solutions of

lower concentrations were obtained. The range of concentrations extended from near the salt solubility limit at the high end to approximately 10^{-4} M at the low end. Standard solutions of hydrochloric acid were prepared by dilution of reagent-grade concentrated hydrochloric acid. An accurate analysis of the acid concentration of each of these solutions was then carried out via acid-base titration using standardized sodium hydroxide solution.

In order to simulate process solutions, an equimolar mixture of sodium chloride and potassium chloride was weighed into a 1-liter bottle; then water was added until about 50% to 60% of the salts had dissolved, yielding a saturated solution. Aliquots of this solution were then removed and various amounts of concentrated hydrochloric acid were added, which resulted in precipitation of some of the salts from the solution. These solutions were filtered and analyzed for total acidity and total chloride content via acid/base and argentiometric titration, respectively.

A 1.0 M sodium bicarbonate buffer was used to dilute some of the samples prior to analysis. This solution was prepared by dissolving the appropriate amount of reagent grade salt in deionized water.

Chloride measurements were made either with an Orion solid-state combination-chloride electrode, model 96-17B, or with an Orion membrane-type electrode, model 93!700, with a separate saturated calomel reference electrode. Potential measurements were made with an Orion pH meter, model 811. Final potential readings were obtained by connecting a Houston Instruments 100 time base recorder to the pH meter and monitoring the changes in electrode response to changes in solution concentrations. The electrodes typically required 2 to 3 minutes to reach their final equilibrium potentials.

III. THEORY

The response of a CLISE to chloride ion activity is given by the Nernst equation:

$$E_{meas} = k - \frac{RT}{nF} \ln|a_{Cl}|. \tag{1}$$

where E_{meas} = measured potential; k = cell constant, which includes the standard redox potential and the reference electrode potential; R = ideal gas constant; T = absolute temperature; n = number of electrons; F = Faraday value; and a_{Cl} = the Cl⁻ ion activity.

The activity of the ion to be measured is the product of the activity coefficient multiplied by the ion concentration. If the ion to be measured is in relatively low concentration, its activity coefficient can be held constant by adjusting the ionic strength of the solution with the addition of a much higher concentration of an inert electrolyte salt. This procedure results in a modified version of the Nernst equation:

$$E_{meas} = k' + \frac{RT}{nF} \ln[Cl^-]. \tag{2}$$

where k' is the same as k in Eq. (1) but now also takes into account the fixed activity coefficient; and $[Cl^-]$ = the chloride ion concentration.

If values are substituted for the constants and converted to base-10 logarithms, this equation has the following form when the mixtures are held at $25°C$:

$$E_{meas} = k' - 0.059 \log_{10}[Cl^-] \qquad (3)$$

Typically the solution is analyzed as follows: the potential of several standard solutions is measured over the concentration range of interest, then E_{meas} is plotted against the log of the chloride ion concentration. This technique yields a straight line calibration curve whose slope is equal to -0.059 volts per log chloride ion concentration. The potentials of the unknown solutions are then measured and converted into concentrations from this calibration curve.

The solutions generated in the dissolution of the ER salts have a very high chloride concentration, ranging from approximately 4 to 10 M. Under these conditions the ionic strength cannot be adjusted accurately to some constant value, and the activity of the chloride ion can vary dramatically, depending on the nature of the counter cation. Thus, the CLISE response might be expected to differ from one salt system to another and to deviate from the standard Nernstian response for any of the salt/acid systems. When we conducted this investigation, we hoped that the CLISE response, whatever its nature, would be reproducible so that the chloride concentration in the test solutions could be quantified.

IV. RESULTS AND DISCUSSION

Figure 1 shows E_{meas} versus log chloride ion concentration plots for a series of standard hydrochloric acid and sodium chloride solutions using both the membrane and the solid-state-type CLISEs. Both electrodes gave a fairly linear response to sodium chloride over a three to four order of magnitude concentration range up to the salt solubility limit of approximately 5 M. For the membrane electrode the slope was -0.044 volts per decade, whereas for the solid-state electrode the slope was -0.053, somewhat closer to the expected Nernstian response of -0.059.

The response of both electrodes to hydrochloric acid solutions was markedly different than that seen in sodium chloride. There were two distinct regions. From low concentrations up to approximately 1 M, the electrodes gave linear responses with slopes of -0.050 and -0.062, respectively. At concentrations greater than 1 M, a dramatic increase was seen in the response of the electrodes to concentration changes. For the membrane electrode, the increased sensitivity was not a smooth function, with the electrode increasing in sensitivity with increasing concentration. For the solid-state electrode, there was a second linear portion of the plot from 1 to 10 M with a slope of -0.179 volts per decade, approximately three times the theoretical Nernstian response. Because the responses of the solid-state CLISE matched more closely the theoretical

responses predicted by the Nernst equation [Eq. (1)] than did the responses of the membrane-type CLISE, we limited all further study to the solid-state CLISE.

Calibration curves for solutions containing only lithium chloride or calcium chloride were also prepared. Results obtained for each of the calibration plots are summarized in Table 1. Similar responses were obtained for all of the salt solutions independent of counter cation. Slopes very near the theoretical Nernstian response of 0.059 volts per log chloride ion concentration were observed over the entire range studied, including the high concentration region. Only the hydrochloric acid solutions exhibited a deviant response.

Table I. Slope/Intercept Data from Chloride Calibration Plots Obtained from the Solid-State CLISE

Compound	Concentration Range	Slope	Intercept
NaCl	$10^{-4} - 5$ M	-0.058	-0.092
CaCl$_2$	$10^{-4} - 10$ M	-0.054	-0.090
LiCl	$10^{-4} - 10$ M	-0.048	-0.095
HCl	$10^{-4} - 1$ M	-0.063	-0.124
HCl	$1 - 10$ M	-0.176	-0.125

Solutions containing both hydrochloric acid and a chloride salt might be expected to produce a CLISE response representing some combination of the responses of the individual components. Because the dissolved ER salts are a mixture of sodium chloride, potassium chloride, and hydrochloric acid solutions, we felt that a closer look at the characteristics of this system would give us a better understanding of the CLISE response.

Solubilities of individual chloride salts of alkali metals in hydrochloric acid solutions have been studied by Noble et al.[1] The composition of a solution prepared by dissolving a 1:1 sodium chloride/potassium chloride mixture in hydrochloric acid can be estimated by taking into account the common ion effect on the solubility of the individual salts. The results of these calculations are shown in Fig. 2. In a solution saturated only with the salts, the total chloride concentration was estimated to be 6.6 M, with approximately two-thirds sodium and one-third potassium salt. As hydrochloric acid is added to the solution, it replaces the salts on essentially a one-to-one basis such that the total chloride concentration stays between 6 and 7 M until the hydrochloric acid content exceeds 6 M. Beyond this point the salt concentrations become vanishingly small and the total chloride concentration is only slightly greater than

the hydrochloric acid concentration. We verified predicted behavior experimentally by saturating different strength hydrochloric acid solutions with a 1:1 sodium chloride/potassium chloride salt mixture and then measuring the total solution chloride concentration. The experimental results are also shown in Fig. 2 and demonstrate quite close agreement with the calculations, including the surprisingly slight decrease in total chloride concentration at the intermediate hydrochloric acid levels.
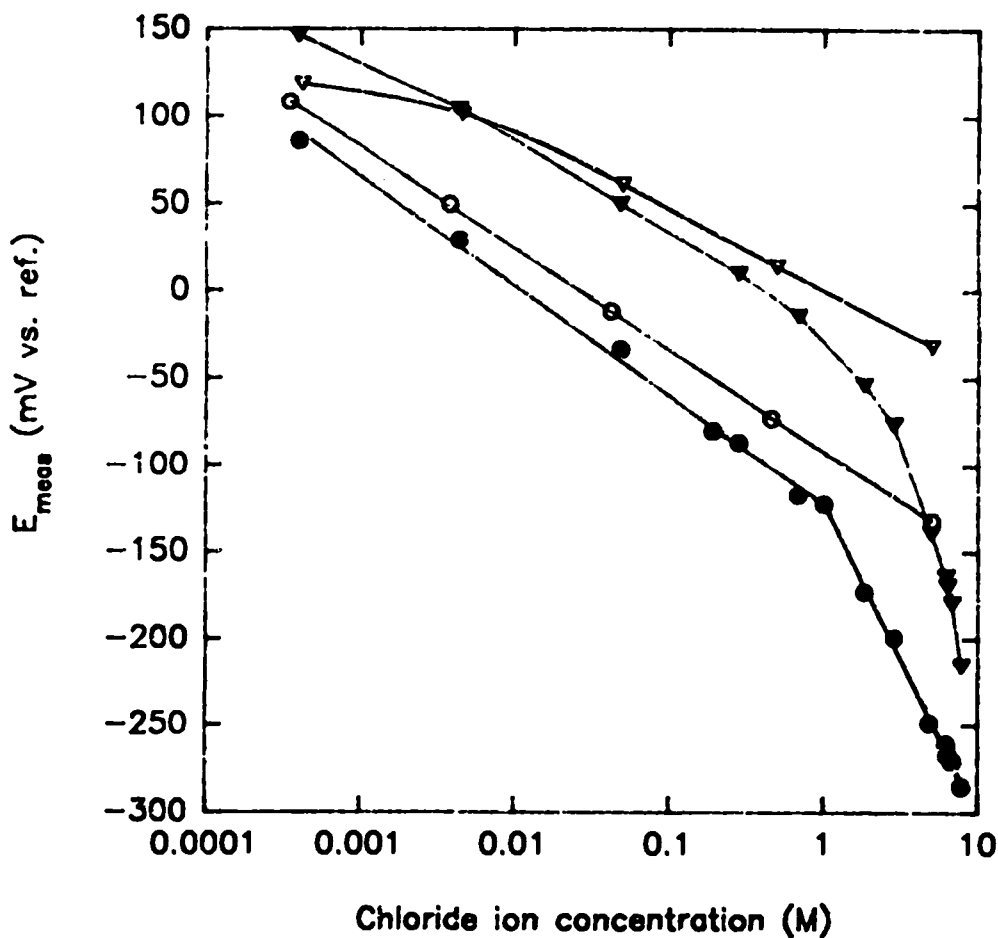

Fig. 2. Calibration curves for sodium chloride and hydrochloric acid with the solid-state and membrane-type CLISEs. Solid-state CLISE: (O) sodium chloride, (●) hydrochloric acid. Membrane CLISE: (▽) sodium chloride, (▼) hydrochloric acid.
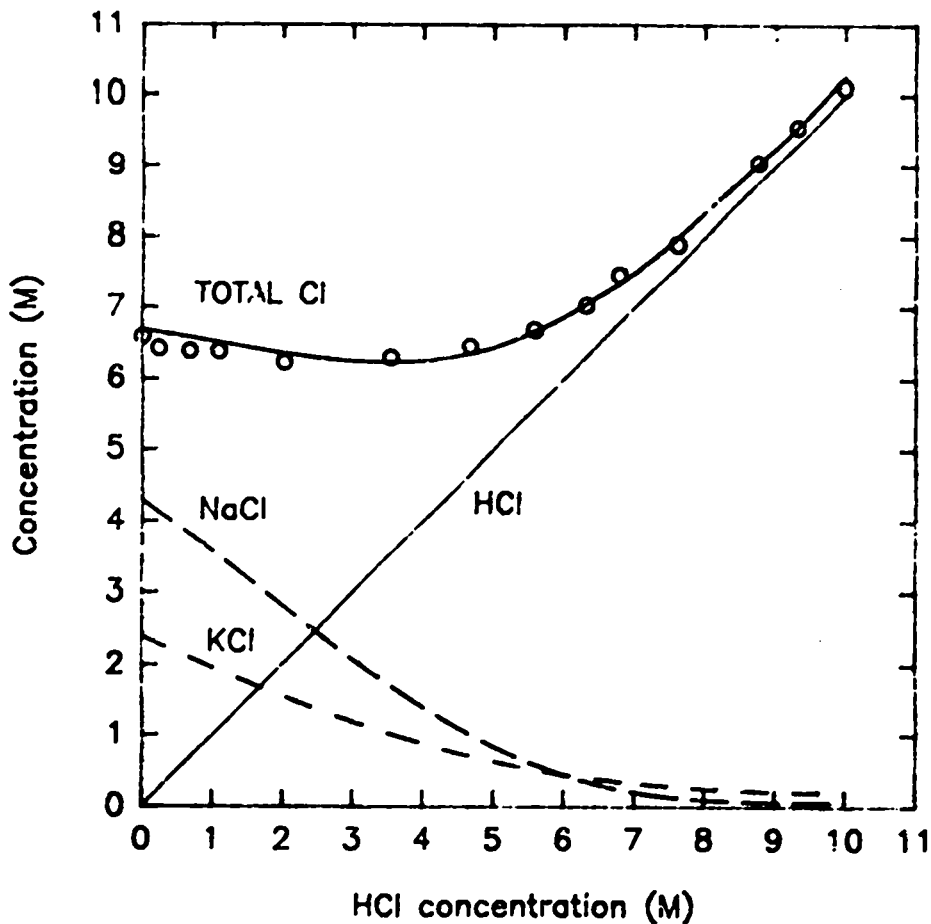
Fig. 2. Sodium chloride and potassium chloride solubility as a function of hydrochloric acid concentration. Solid lines calculated from data found in Noble et al., 1991; (O) data collected in this study.

We calibrated the mixed salt/acid system by adding various measured quantities of hydrochloric acid to a saturated sodium chloride/potassium chloride solution, then measuring the ion activity with the CLISE. These results are shown in Fig. 3. Initially the solution contained only salt chlorides and the measured response was that which would be expected from the sodium chloride and/or potassium chloride calibration curve. Because the CLISE responds differently to acid chloride than to salt chloride, the measured potential becomes more negative as the acid chloride increases at the expense of the salt chloride, even though the total chloride remains essentially constant. This response is represented by the vertical portion of the curve. At approximately 8 M acid, the salts have been largely precipitated from the solution and any further addition of acid merely increases the acid concentration. At this point the CLISE response follows the acid chloride response calibration curve and is represented by the sloping portion of the graph.
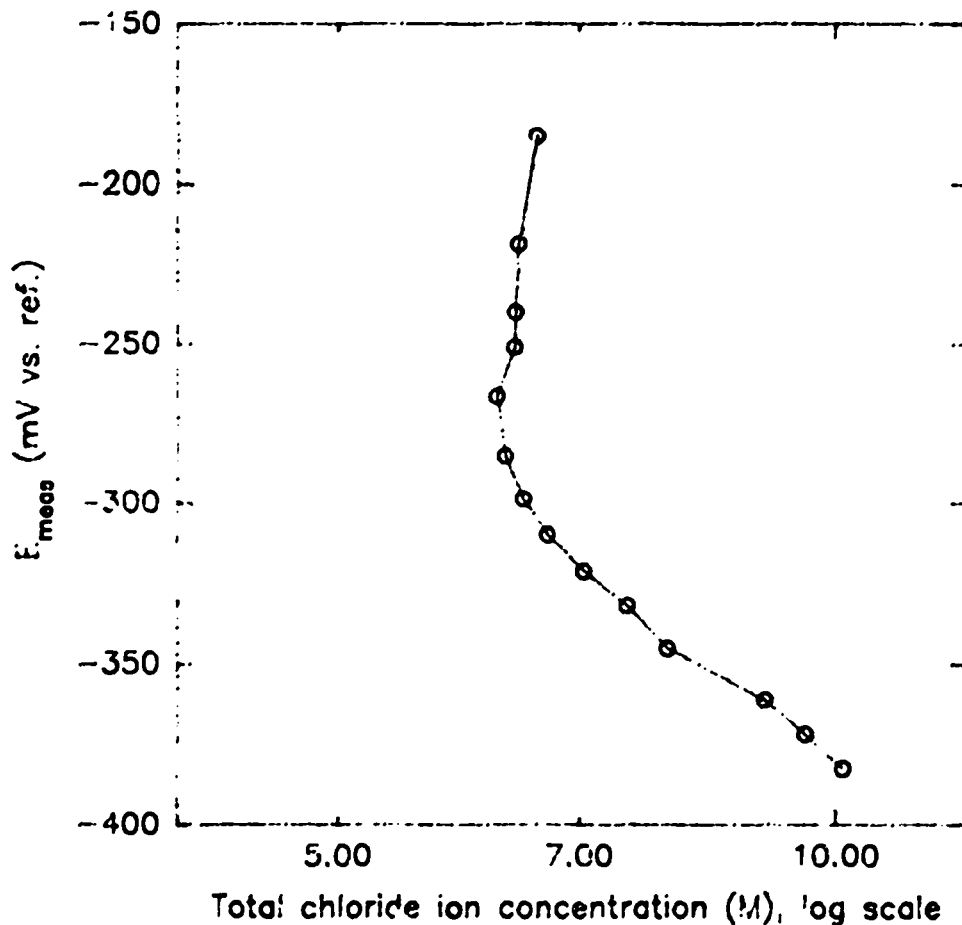
Fig. 3. Solid-state CLISE response to saturated sodium chloride/potassium chloride solution after addition of concentrated hydrochloric acid.

The measured response of the mixed system suggests that the CLISE not only distinguishes between salt chloride and acid chloride, but that the responses are additive: that is: $E_{meas} = E_{salt} + E_{acid}$, or, if we substitute in values for the slope and intercept from the calibration curves, we find that

$$E_{meas} = -0.0956 - 0.053 \cdot \log[salt] - 0.1229 - 0.179 \cdot \log[acid]. \tag{4}$$

It is interesting at this point to review the plutonium absorption behavior on an anion exchange resin as a function of solution chloride composition. This behavior is dependent on the chloride ion activity of the solution, both with regard to formation of the hexachloroplutonate complex and to the exchange of this complex for chloride ion absorbed on the resin. When we prepared a log distribution coefficient versus hydrochloric acid plot for this system we obtained a parabolic response with a maximum K_d at approximately 7 M hydrochloric acid. If the CLISE is truly measuring chloride ion activity, then the optimum absorption efficiency can be obtained only in hydrochloric acid solutions. For example, a solution saturated in sodium and potassium chlorides is approximately 6.8 M in total chloride concentration. The

chloride ion activity of this solution as measured with the CLISE would be the same as that exhibited by a solution only 1.2 M in hydrochloric acid. Even for lithium and calcium chlorides, whose higher solubilities can generate chloride concentrations greater than 10 M, the chloride ion activity of these solutions is still less than that of a 7 M hydrochloric acid solution. It is also interesting to note that at 7 M hydrochloric acid, where maximum absorption of the complex occurs, the total salt concentration approaches a minimal value.

Total Chloride Measurement Alternatives Using the Solid-State CLISE

Due to the unique nature of the system under investigation and the response characteristics of the CLISE, there are four ways in which the CLISE can be used to measure chloride ion concentration.

Method 1 — Sample Extraction And Preconditioning. Since the CLISE responds differently to acid versus salt chloride, the total chloride must be converted into another form, to be determined by the normal calibration curve procedure. This conversion can easily be accomplished by extracting a sample from the process solution and diluting it with a sodium bicarbonate buffer solution. The reaction between the bicarbonate and acid chloride is
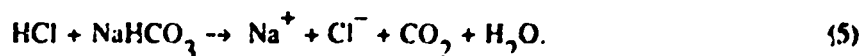
$$HCl + NaHCO_3 \rightarrow Na^+ + Cl^- + CO_2 + H_2O. \qquad (5)$$

TABLE II. Results of CLISE Analyses of Sodium Chloride – Hydrochloric Acid Mixtures

Sample	[HCl]	[NaCl]	[Cl⁻] Total	CLISE Analysis	Error
1	0.97	4.00	4.97	5.02	+0.05
2	1.92	3.00	4.92	4.89	−0.03
3	2.94	2.00	4.94	4.85	−0.09
4	3.92	1.00	4.92	4.87	−0.05
5	4.93	0.00	4.93	5.06	+0.13

Note: Samples were diluted 20 : 1 with 1 M sodium bicarbonate, and the sodium chloride calibration curve was used. The average relative error is 1.4%.

The acid chloride is converted to salt chloride. The total chloride can then be determined from a previously prepared calibration curve for sodium chloride. Results of this analysis for some mixed acid/salt chloride samples are given in Table II.

The shortcoming of this method lies in the necessity for extracting a sample from the process stream. However this extraction could easily be automated via a flow injection type procedure and would not require direct operator handling. Also, the finished process sample with the buffer added could be placed back into the process solution tank so that no additional waste solution is generated.

Method 2 — Direct Measurement with Calculation of Acid Chloride and Salt Chloride. In the special case presented here, where the solution is always saturated with salt and the salt concentration is a function of acid concentration, both the acid and salt concentrations can theoretically be determined from a single measurement. A curve fit of the data used to generate Fig. 2 requires a minimum fourth-order equation to express the relationship between total salt and acid concentrations with a reasonable degree of accuracy. This renders the concentration calculations somewhat tedious, but they could easily be handled by a preprogrammed microprocessor attached to the system.

This procedure does not require removal of a sample from the process stream but does require precalibration and possibly periodic recalibration of the CLISE.

Method 3 — Direct Measurement with No Concentration Calculation. A simpler and less costly alternative to method 2 is that of simply placing the precalibrated CLISE into the process solution and adding concentrated hydrochloric acid to the solution until a predetermined set point, corresponding to a given acid concentration, is reached. This procedure requires no data analysis and is very amenable to automation. It also is characterized by a simpler calibration procedure. The only standard solution necessary is one having the desired final composition of the process solution. Adjustments can then be made to the process solution until its measured potential is the same as that of the standard solution.

Method 4 — Determination of Solution Acidity. Once again examining the behavior of the ER salt/hydrochloric acid system (Fig. 2), we achieved the final solution condition of 7 M chloride when most of the salt chloride had been displaced by acid chloride and the solution was essentially all acid chloride. Thus, if the acid chloride in the process solution is measured, the amount that must be added to arrive at the final concentration can easily be calculated.

Shown in Fig. 4 is a plot of the CLISE's measured response versus hydrochloric acid concentration for the ER salt system; the plot is presented on a linear rather than log scale. It is surprisingly linear for acid concentrations greater than 1 M. The serendipitous result is a combination of the complex correlation between salt solubility and acid concentration and the different response of the CLISE to acid versus salt chloride. This result would be expected to be quite different for other salt systems since the salt

concentration behavior for other chloride salts in hydrochloric acid is quite different. However, this technique does provide a very convenient and simple way to measure the total solution acidity for the ER salt system.
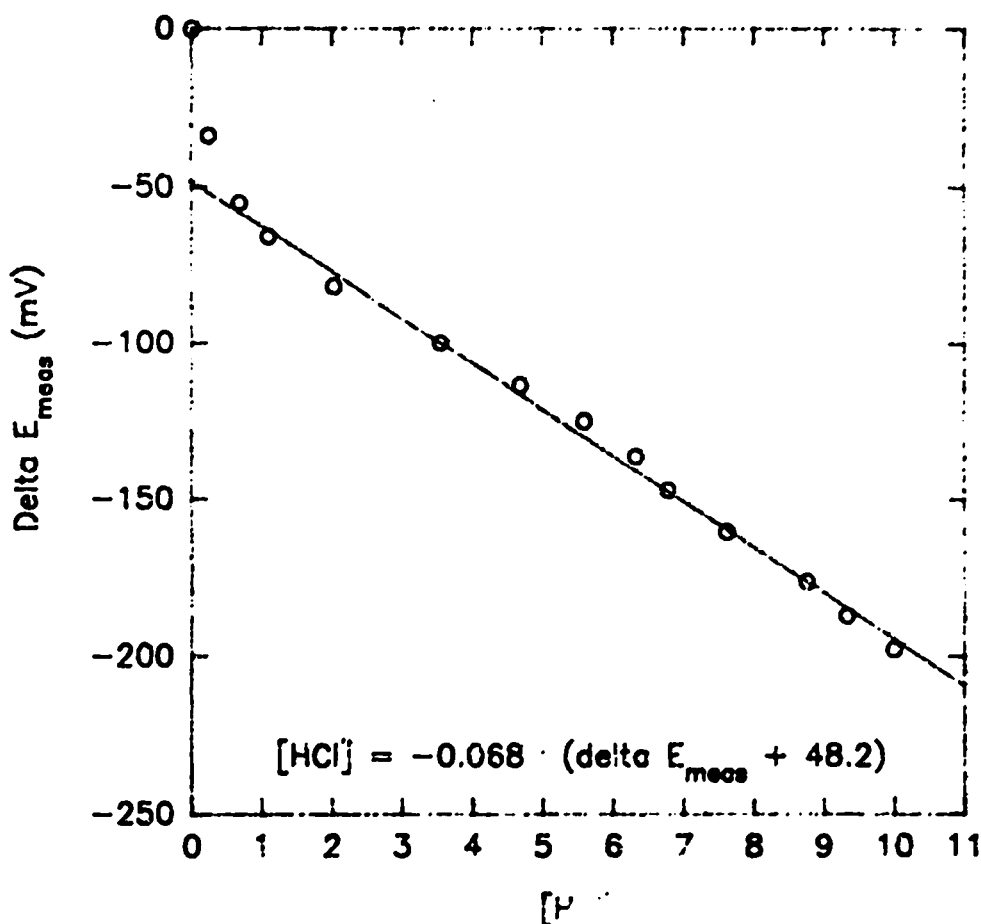

Fig. 4. Measured potential versus linear acid concentration plot for a sodium chloride/potassium chloride/hydrochloric acid system.

V. SUMMARY

Of the two commercially available CLISEs, the solid-state electrode exhibited better behaved response to chloride ion concentration changes than did the corresponding membrane-type electrode. The solid-state device also exhibited a linear log chloride concentration versus measured potential response in the high (>1 M) concentration region, which allowed us to make direct in situ measurements in ER salt process olutions. Also, a study of the dynamics of the sodium chloride/potassium chloride/hydrochloric acid tem indicates that a single measurement can be used to determine not only total chloride concentration 'so the distribution between acid versus salt chloride.

REFERENCE

E. G. Noble, D. E. Shanks, and D. J. Bauer, "Solubilities of Chloride Salts of Alkali and Alkaline-Earth Metals When Sparged with Hydrogen Chloride," US Bureau of Mines, 1991.