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PROBLEM REPORT

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THE CONTROL OF THE HF CONCENTRATION OF
ELECTROLYTE BY ELECTRICAL CONDUCTANCE MEASUREMENTS

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ABSTRACT

In this report the control of the HF concentration of electrolyte in C-216 production units is compared with other methods of HF control.

Absolute values for the specific conductance of electrolyte are given, and their dependence upon the HF content and the temperature are discussed.

The design of conductance cells for controlling the HF content of electrolyte is discussed from theoretical and constructional viewpoints.

The effects of errors that occur in the conductance method are described, and methods for reduction of these to negligible quantities are prescribed. Among these may be mentioned the errors resulting from the contact resistance of electrodes, frequency effects, errors due to dissolved iron or water, etc.

The results of control runs using this method of measurement are described for conductance cells of various design.

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THE CONTROL OF THE HF CONCENTRATION OF
ELECTROLYTE BY ELECTRICAL CONDUCTANCE MEASUREMENTS

Object of the Investigation:

A-2553

To determine whether or not conductance measurements are suitable for the routine control of the HF concentration of cell electrolyte.

Period Covered by this Report:

February 23, 1944 to November 27, 1944.

Historical Background:

In the production of C-216 by electrolysis of molten electrolyte in "medium temperature" cells the HF concentration plays a very important role, for upon it depend such factors as

- (1) Purity of the C-216 produced.
- (2) Ease of electrolysis, i.e. - resistance developed, polarization, power efficiency. etc.
- (3) Corrosion effects upon the integral parts of the cell, such as the electrodes, screens, diaphragms, skirt, body. etc.

It is therefore apparent that the proper control of the HF concentration is one of the most important features upon which successful cell operation is dependent.

Several methods for proper control of the HF concentration have been studied. These include:

- (1) Chemical analysis of the electrolyte.
- (2) Electrical conductance measurements.
- (3) Specific gravity of the electrolyte.
- (4) Level control of the electrolyte by
 - (a) The "nitrogen bubbler" method.
 - (b) Electrical probes.
 - (c) Hand probes.

- 1 -
- (5) Consumption of HF as a function of the ampere-hours of operation of various cells.

On the basis of time and hazards involved it would be advantageous to use a control method that would not involve a shut-down or the opening of a cell producing C-216. Of the methods above, numbers 2, 4a. and 4b are the most promising in this regard.

Conclusion:

(1) Conductance measurements have been shown to provide accurate control of the HF concentration of cell electrolyte in isolated runs in the Semi-Works and East Area plant. Uniform success in HF control by conductance methods has not been possible to the present time for the following reasons:

- (a) Plugging of the conductance cells by sludge developed in the C-216 production units.
- (b) Inadequate temperature control due to the geometrical relationship of instruments in the production units, and failure of temperature recording units in service.
- (c) Breakdown of wire insulation of the conductance cells upon prolonged exposure to cell electrolyte.

However, we believe that conductance cells can now be made that will furnish proper HF control of electrolyte, provided that the C-216 production units are correctly operated so as to keep sludge formation to a minimum.

Summary:

(1) The specific conductivity of cell electrolyte containing 37-43% HF has been determined for the temperature range 85-110°C. (see graph 1). Conductance is a linear function of the temperature with a coefficient of 1.9% per degree Centigrade. In this range a change of 1% in the HF concentration corresponds to approximately a 10% change in conductance.

(2) A number of conductance cells of novel design have been operated in the laboratory, Semi-Works and East Area plant to determine:

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- (a) The amount of circulation of electrolyte through different designs of the conductance cell.
- (b) The life of the various parts of the cell.
- (c) Errors that must be eliminated to yield satisfactory results.

In these trials it was shown that:

- (a) Adequate circulation of electrolyte could be obtained with a cell made of 1/4" hard rubber pipe, provided, however, that sludge formation was kept to a minimum.
- (b) The following materials proved satisfactory for the use indicated:

electrodes - platinum
 cell body - hard rubber pipe
 cell casing - nickel or iron
 wire insulation - "Gencoseal", a vinyl chloride polymer made by the General Cable Co.

- (c) Errors were found to result from the contact resistance of the electrolyte to the electrodes, and from low a.c. frequency across the conductance bridge. The contact resistances found were:

<u>HF Conc. of Electrolyte</u>	<u>Electrodes</u>	<u>Contact Resistance</u>
39.4% by wt.	Platinum	62 ohms/cm ²
" " "	Nickel	130 " "
42.2% " "	Platinum	31 " "
" " "	Nickel	172 " "

It was shown that with platinum electrodes 1.25 cm² in area a 10% absolute error would result from the contact resistance at a cell constant of 5, 2% at a cell constant of 20 and substantially zero at a cell constant of 40 or above.

Variation of the frequency at which the conductance was measured showed that for a cell with platinum electrode surface of 7.7 sq. cm. and a constant of 21 at 1000 cycles, the following relative errors were present at different frequencies:

<u>Frequency</u>	<u>Relative Error</u>
200	10%
1000	2.5%
2000	2.0%
3000	1.3%
4000	0.6%
8000	nil

The frequency error is more pronounced with nickel electrodes than with platinum, for a higher frequency is required before the conductance becomes independent of this variable.

Base platinum electrodes apparently yield essentially identical results as platinized platinum. The base platinum can be quickly cleaned of grease, dirt, etc. by imposing a low a.c. current on the electrodes immersed in cell electrolyte for a short period.

(3) Dissolved iron to a concentration of 2.0% apparently does not appreciably affect the results obtained by conductometric measure.

(4) The conductance does not vary appreciably with the addition of small amounts of water to the electrolyte. The addition of 1% of water to the electrolyte increases the conductance by the amount equivalent to an increase in the HF concentration of 1.4%.

(5) The performance of a large number of conductance cells indicates that with their aid the HF content of cell electrolyte can be controlled to within 0.5%. A comparison of this control method with the "nitrogen bubbler" control of level indicates that the latter method is more exact but upkeep is more difficult. The conductance method is much superior to control by specific gravity or hand probing methods. While not as accurate as chemical analysis, it is a much more rapid method.

Patent Situation:

No search for patentable features has been made. One idea of patentable merit, however, would be to coat parts of the C-216 cell exposed to the corrosive action of cell electrolyte with a protective coating similar to the insulation materials shown in this report to be resistant to electrolyte. This should result in a great decrease in the formation of sludge by corro-

sion, with a consequent prolonged cell life, and savings through reduced upkeep costs, materials cost, power costs, etc.

Plans for Future Work:

Indicated changes leading to improved performance of conductance cells will be made in their design and construction. HF control of electrolyte with the improved cells will be followed.

Experimental Work Notebooks 467, 518

Fredenhagen and co-workers have measured the conductance of dilute solutions of KF in HF (1,2), but their data is not applicable to the control of the HF in electrolyte compositions such as are used in the operation of "medium temperature" cells. Prof. W. C. Schumb of M.I.T. has measured the currents and voltages required to transport the current through the electrolyte between a large carbon blade and a copper probe. He reported (3) that the resistance obtained from the slopes of the voltage-amperage curves was indicated to be approximately $66-91 \times 10^{-4}$ ohms per cm^3 for the composition range KF.1.6HF to KF.2.1 HF over the temperature range of 150-99°C. This corresponds to specific conductivities of 150-110 mhos/cm. However, P. R. Johnson (4) later reported these to be much too high, for with a conductivity cell having nickel electrodes he found a specific resistance of 5.5 ohms per centimeter cube for electrolyte containing 42.4% HF at 100°C., which is equivalent to a specific conductivity of 0.182 mhos/cm. Our later measurements showed this to be more exact.

A. Theoretical:

The specific conductance L of an electrolyte measured in a conductance cell is given by the expression

$$(1) \quad L = \frac{K}{R} = KC, \text{ where}$$

K = the cell constant of the conductance cell

R = resistance in ohms

C = conductance in mhos

Therefore, having once determined the cell constant by measuring the resistance of a solution with a known specific conductance, the specific conductance of any other solution can be determined

by measuring the resistance of the solution in the cell of known constant.

This presupposes, however, that no error is introduced by the contact resistance of the electrodes to the electrolyte. Should this be increased to a measurable factor in transferring the cell from one electrolyte to another of altogether different nature, it is obvious that incorrect conductance values will be obtained. Measurements of the contact resistance of platinum and nickel to cell electrolyte have been made and will be discussed shortly.

The usual conductivity cell is made of glass and is of the closed end or "dip" cell type. Obviously, neither one of these conventional cells would be of use here, for conductance measurements of the electrolyte in the unit producing C-216 were desired, since this would considerably reduce the time, hazards, and trouble attendant with removal of electrolyte and measurements outside the cell. Also, it was necessary to design the cell so that any change in the HF concentration of the electrolyte would be quickly manifest, which meant that good circulation through the conductivity cell must be attained.

To achieve these aims a cell open at both ends was constructed with two platinum electrodes at the ends in parallel and one in the center of the cell. Such an arrangement permitted measurement of the resistance between the center and end electrode while preventing the electrolyte outside the conductivity cell from conducting any of the imposed high frequency a.c. current. A simple cell of this type is shown in sketch 1.

In the usual closed end type of conductivity cell the cell constant is given by the expression

$$K = \frac{l}{A}$$

where $\frac{l}{A}$ = distance between electrodes in centimeters
and $\frac{l}{A}$ = cross-sectional area between electrodes.

For a cell of the type pictured in sketch 1, however, the cell constant will be given by

$$(2) \quad K = \frac{l}{2A}$$

for with the two end electrodes in parallel conduction of current from the center electrode will be equally divided between the end

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LEADS TO CONDUCTIVITY
BRIDGE

A-END ELECTRODES IN
PARALLEL

B-CENTER ELECTRODE

C-CELL BODY OF HARD
RUBBER OR SARAN
TUBING

SKETCH I
OPEN-END CONDUCTIVITY CELL

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APP. *S. G. T.*

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electrodes, making the effective distance between electrodes the same, but doubling the effective cross-sectional area.

Apparatus

Several conductivity cells were constructed to experimentally verify the above postulate and to measure the conductance of electrolyte. These were all of the type indicated in sketch 1. All were twelve inches in length. The materials of construction and other pertinent information are given in Table I. The electrodes were all of sleeve cylindrical form of 5 mils thickness and fitted snugly inside the cell body. One-eighth inch Saran tubing was slipped over the lead wires (22 B & S gauge Monel) to insulate the electrodes and prevent short circuits. The lead wires were spot-welded to the electrodes at several points for good contact.

Table I

=====

Construction of Experimental Cells
(467, 37-40, 56, 68)

Cell No.	Material of Construction	Electrode Metal	<u>Electrode Length</u>		Calc. Cell Constant cm^{-1}
			End in.	Center in.	
1	1/2" Saran tubing	Nickel	1/4"	1/2"	9.5
2	" " "	"	1/2	1	8.7
3	1/2" Saran pipe	Platinum	1/2	1	4.1
4	1/2" Saran tubing	"	1/4	1/2	9.5
5	" " "	"	1/2	1	8.7

=====

For conductance measurements in 1.0 N or 0.1 N KCl the cells were immersed vertically in the KCl solution in a 52 mm. glass tube 18" long closed at the bottom with a rubber stopper. After reaching thermal equilibrium the temperature and resistance were recorded. The conductance values for KCl given in the "Handbook of Chemistry and Physics", 16th edition, 1931, page 1017, were used in the calculations.

For conductance measurements of cell electrolyte the conductivity cells were immersed in 3.5 lbs. of electrolyte in a 20" length of 2" iron pipe closed at the bottom by an iron plate welded in position. This in turn was immersed in an agitated oil

bath which had a capacity of 8.5 gallons. This was heated by two coil heaters (.5 + 2 KVH) controlled by Variacs, one of which was in series with a deKhotinsky control. The temperature of the electrolyte was obtained with Weston thermometers immersed at least three inches. Escape of HF from the electrolyte during the measurements was prevented by closing the iron containers with rubber stoppers, through which the Weston thermometers and the Saran insulation of the lead wires were inserted with a tight fit.

The resistance of the solutions in the conductance cells was measured for the most part with the conductivity bridge Model RC-BC manufactured by Industrial Instruments, Inc., of Jersey City, N. J.

Cell Design - Experimental
467-63

Cell No. 1, which is described in Table I, was used to verify the postulates given above. The resistance of 1.0 N KCl in the cell was determined for various positions of the cell and between different individual electrodes and combinations. In the first four measurements the conductance cell was completely immersed in the KCl solution so that it functioned as the open-end cell for which it was designed, while in the last three measurements the lead wire from the top electrode was completely out of the KCl, although the electrode itself was wetted. In this way the cell functioned as a closed-end conventional type. The results are given in Table II.

Table II

<u>Cell Design - Experimental</u>				
<u>Temperature +26.4°C.</u>				
<u>Trial No.</u>	<u>Position of Cell in 1.0 N KCl</u>	<u>Electrodes used for Conductance Circuit</u>	<u>Resistance Ohms</u>	<u>Cell K cm^{-1}</u>
1	Top lead wire in the KCl	Top and bottom in parallel through KCl to center	91.5	10.5
2		Top to center	96.0	11.0
3		Center to bottom	100.0	11.5
4		Top to bottom	24.2	2.8
5	Top lead wire out of the KCl	Top to bottom	345.0	39.5
6		Top to center	177.0	20.3
7		Top and bottom in parallel to center	90.5	10.3

The cell constants calculated above were obtained by applying the resistance figures and the value for the specific conductance of 1.0 N KCl at 26.4°C., namely, 0.1146 mhos/cm., to equation (1) given above.

In trial No. 1 the cell constant obtained, 10.5, was approximately that of the value, 9.5, calculated from the cells dimensions according to equation (2) above. Trial 5 gave a resistance almost twice that of No. 6, indicating the linear effect of distance between electrodes upon the constant. However, the resistance obtained in trial 7 was only one-half that of No. 6, showing that the effective cross-sectional area had been doubled while the distance between electrodes remained constant, so that the form $K = \frac{l}{2A}$ is correct for this type of cell. It is seen

that the resistance in trials 1 and 7 was the same within experimental error, as it should have been.

The need for "guard" electrodes in the open end conductivity cell is strikingly seen by comparison of trials 1 and 4. Here it is seen that in No. 1 the resistance measured was actually that of the KCl between the electrodes, while in No. 4 most of the current was carried by the KCl outside the cell itself, giving a low resistance. Comparison of trials 4 and 5 also shows this clearly, for in trial 5 no conductance was possible outside of the cell since neither the top electrode nor its lead wire was in contact with the KCl outside of the conductivity cell.

The need for "guard" type electrodes in open-end conductivity cells is thus clearly demonstrated.

Contact Resistance of Electrodes

467-86-92

In any conductance determination it is important that the contact resistance of the electrodes to the electrolyte be small in relation to the resistance of the electrolyte, or a measurable error will result that will vary with the surface of the electrode exposed to the electrolyte. The contact resistance of nickel and platinum electrodes to electrolyte was measured as follows:

Closed-end cells were constructed by sealing off one end of a 16" length of 1/2" Saran tubing. One electrode was set in position at the closed end and its lead wire was insulated with Saran. A movable electrode was inserted at the open end of the tube. With the tube filled with electrolyte at a constant temperature

of 100°C., the movable electrode was moved towards the fixed electrode. Resistance measurements were made for several distances between electrodes. In this way a constant cross-sectional area and a constant electrode surface exposed to electrolyte were maintained. When the electrodes were in contact the resistance of the outside circuit was obtained. After this value had been subtracted from the previously measured resistances, the resistance was plotted as a function of the distance between electrodes. The intercept of the line at zero distance between electrodes gives the absolute error due to contact resistance between the electrodes and the electrolyte.

Total surface area of nickel electrodes = 10.2 sq. cms.
 " " " " platinum " = 7.7 " "

The data thus obtained for the case when the HF concentration of the electrolyte was 42.25% is given in Graph II. It is seen that for bare platinum the contact resistance at zero distance between electrodes was 4 ohms for a 7.7 cm² surface area, or 31 ohms per sq. cm. Similarly, for nickel, the contact resistance was 17 ohms per 10.2 cm² surface area, or 173 ohms per sq. cm.

The data obtained when the HF concentration of electrolyte was 39.4% have been plotted in Graph III. In this case the contact resistance was determined for platinum both before and after platinization by the usual method (5). No difference was measurable, as indicated by the figures:

<u>Electrode Metal</u>	<u>Contact Resistance</u>			
	<u>(39.4% HF)</u>			
Bare platinum	62	ohms	per	sq. cm.
Platinized platinum	62	"	"	"
Nickel	130	"	"	"

This information indicates that unplatinized electrodes will serve without need for platinization provided a sufficiently great frequency in the a.c. circuit is maintained to prevent polarization and shunt capacitance errors.

Frequency Effects 467-90-92

The variation of the measured resistance of electrolyte in cells with base platinum, platinized platinum and nickel electrodes, and with cell constants from 1 to 45, has been measured with frequencies from 200 to 8000 cycles per second (General Radio Oscillator, Type 508 ASI, Ser. No. 114). The data obtained are

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GRAPH 2
 Variation of Resistance with
 $\frac{CK}{}$
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GRAPH 3

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presented in graphs 4 and 5. The cell constants indicated were calculated from the resistances at 1000 cycles and using a figure of 0.137 mhos/cm. for the specific conductance of electrolyte containing 39.4% HF at 100°C. These data were obtained using nickel electrodes with a total surface area of 10.2 sq. cms., and with platinum electrodes with a surface area of 7.7 sq. cm.

In graph 6 the absolute error due to polarization at the electrodes at a frequency of 1000 cycles has been plotted as a function of the cell constant. The magnitude of these errors at different cell constants is as follows:

<u>Cell Constant</u>	<u>Nickel</u>	<u>Absolute Error</u>	
		<u>Platinum</u>	<u>Platinized Pt</u>
10	11%	8%	6%
30	3	2	2
45	2	1	1

From these figures it is concluded that cells with platinum electrodes must have constants greater than 30 in order to reduce the absolute error of measurement of the HF concentration of electrolyte to less than 0.2%.

The Conductance of Electrolyte
at Constant Temperature
467-86-92

The data obtained to determine the contact resistance of electrodes to electrolyte as given above can also be used for the calculation of the conductance of the electrolyte. As has been previously shown for the closed-end type conductivity cell,

$$K = \frac{1}{A} = lR, \text{ or } R = \frac{1}{LA}$$

where the letters have the same significance as previously indicated. If then the resistance R of the cell (corrected for external resistance) is plotted against the distance $\frac{1}{L}$ between electrodes as shown in graphs 2 and 3, the slope of the resultant line will be $M = \frac{1}{LA}$. Since both $\frac{1}{LA}$, the cross-sectional area of

the cell, and $\frac{1}{LA}$, the slope, are determinable, the specific conductance $\frac{1}{L}$ can be calculated.

Cross-sectional area of 1/2" Saran tube = $3.14 \times (.19)^2 \times 6.45$
 = 0.73 sq. cm.

Slope of line at 42.3% HF and 100°C. = 7.3 ohms/cm.
 " " " " 39.4% " " " = 10 " "

Specific conductance at 100°C. and 42.3% =

$$\frac{1}{7.3 \times .73} = 0.187 \text{ mhos/cm.}$$

" " " " " 39.4% =

$$\frac{1}{10 \times .73} = 0.137 \text{ mhos/cm.}$$

By this method of calculation of the specific conductance no error is introduced by any contact resistance, for since this, if present, should be constant throughout one series of determinations at one HF concentration, the slope of the line obtained by plotting R against $\frac{1}{l}$ would be the same as that when there was no contact resistance. This then is not a source of error.

A change in the cross-sectional area along the length of the cell would produce an error, however. Thus, for an average diameter of 0.37 inches rather than 0.38 inches, the conductance value at an HF concentration of 39.4% would be 0.1435 mhos/cm., which would be equivalent to an error of 4.8% in the absolute conductance value.

Temperature Coefficient of Conductance

467-73, 78, 79, 80, 84

The change in conductance of the electrolyte with temperature was obtained at several different HF levels with experimental cell No. 5. In these experiments the temperature of the electrolyte was raised from 90-110°C. slowly over two or more hours, so that good temperature equilibrium was attained. Check results were obtained by lowering the temperature gradually in like manner. The data obtained are plotted in Graph 7. Here it is seen that the slope of all the lines is essentially the same, indicating that within HF concentrations of 39-43% and temperatures of 90-110°C. the specific conductance of electrolyte varies linearly with the temperature, and that the coefficient is 1.9% per degree centigrade. These values are not to be taken as the absolute values for the specific conductance, however, since no correction for contact resistances has been applied either in the determination of the cell constant ($K = 9.58$) of cell No. 5 in 1.0 N KCl, or in the electrolyte.

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GRAPH 4
 Variation of Resistance
 with Frequency

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GRAPH 5
Variation of Resistance
with Frequency
167 90(a)

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Frequency in Kilocycles/sec

± 3 ohms
sensitivity

% HF in Electrolyte = 39.4%

Platinized Pt - K=46.4

Unplatinized Platinum - K=44.0

Nickel - K=43.7

Resistance in ohms

GRAPH 6
Percent Error (Absolute) from
Polarization at 1000 Cycles/sec vs.
the Cell Constant
 467-91, 92

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Absolute Values for the Specific Conductance of Electrolyte

As described above the absolute values for the specific conductance of electrolyte at HF concentrations of 39.4% and 42.3% and 100°C. were 0.137 and 0.187 mhos/cm. Using these values together with the temperature coefficient given above, a family of lines similar to that given in the Summary was constructed. It was later found that these values were apparently slightly in error, for calibration of a large number of conductivity cells in electrolyte gave cell constants slightly less than the apparently true values. Hence the error was corrected and the data were applied to the preparation of the graph in the Summary.

It should be stated that these values can be considered only provisionally correct until such time as they are substantiated elsewhere.

Activation of Platinum Electrodes

467-61, 71

Although it has been shown that the contact resistances of plain and platinized platinum electrodes to electrolyte are essentially equal, it has nevertheless been noticed that the resistance of "dirty" platinum is greater than that of "clean" platinum. "Dirty" platinum may not be easily wetted by electrolyte due to grease, etc., on its surface. Thus cells with new electrodes exhibit a decreasing resistance during the first several hours immersion in cell electrolyte.

We have shown that new electrodes can be quickly cleaned by immersing the conductance cell in electrolyte and passing 60 cycle A.C. through the electrodes at about 200 milli-amperes for ten minutes. The resistance decreased rapidly in the first minute as shown by a current increase at the same voltage, but the current becomes constant after several minutes indicating that grease or other film on the electrode surfaces has been removed, probably through reaction with the C-216 produced.

Effect of Dissolved Iron upon Conductance Measurements

467-101-103

In the generation of C-216 by electrolysis, corrosion of the electrolytic cells causes the introduction of iron into the electrolyte. Some of this iron is present in a slow-settling sludge, while another portion remains dissolved in the electrolyte as K_3FeF_6 , FeF_3 or analogous salts. Since the soluble iron is present in concentrations as high as 5% Fe in some instances, it be-

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came important to determine whether the conductance measurements were affected by the presence of the iron salts.

A sample of electrolyte containing approximately 5% of dissolved iron was allowed to settle for several days to remove the suspended sludge. Then 1100 g. of the clear supernatant electrolyte was mixed with 600 g. of fresh electrolyte with approximately the same HF concentration.

Analysis: %HF = 43.68 (uncorrected for Fe, Ni, Cu)

%Fe = 4.13 ~~4.13~~ 4.46% HF

%Ni = 0.11 ~~0.11~~ 0.07% HF

%Cu = nil

Net HF = 39.2 (corrected for Fe, Ni, Cu)

The conductance of this mixture was measured with Experimental conductivity cell No. 5 between 95-110°C. The electrolyte was then divided in half and an equal amount of fresh electrolyte was added to one portion. Conductance measurements were again taken. The procedure was then twice repeated. The data thus obtained gave the results indicated in Table III.

Table III

=====

Effect of Dissolved Iron
on Conductance Measurements

=====

1	2	3	4	5	6	7	8	9
				HF	HF	HF	Deviation	Deviation
				Uncorrected	Corrected	Conductance	from	from
Run	Iron	Nickel	Copper	for Metals	for Metals	Value	Uncorrected	Corrected
No.	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	HF Value	HF Value
1	4.13	0.11	nil	43.7	39.2	40.9	-2.8%	+1.7
2	2.12	0.09	"	43.2	40.3	43.2	0.0	+2.9
3	1.02	-	-	41.4	40.3	42.1	-0.9	+1.8
4	0.49	-	-	40.3	39.8	40.5	+0.2	+0.7

=====

-15-

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By comparison of the HF concentration values obtained by conductance (column 7) with the uncorrected and corrected values obtained by chemical analysis (5 and 6), it is seen that the net effect of the dissolved iron in amounts as high as 2% is to conduct an equivalent current to that which would have been conducted by the equivalent amount of HF. Above 2%, however, the same conclusion can not be drawn.

It is thus seen that neither chemical analysis (uncorrected for metals) nor conductance measurements will give the true HF concentration when substantial amounts of dissolved metals are present.

Effect of Water upon Conductance Measurements

467-147

If it could be shown that the conductance of electrolyte varied markedly with the addition of small amounts of water, it would be possible to:

- (1) Determine low concentrations of water by conductance measurements.
- (2) Use the method to indicate the presence of water leaks in the jackets of C-216 electrolytic cells.

It has been found, however, that addition of water to electrolyte causes a change in the specific conductance that is equivalent to the change that would result by addition (up to 4% water) of 1.4 times as much HF. Therefore, in low concentrations, 0.67% water is roughly equivalent to 1% HF.

Materials of Construction

(a) Electrodes

- (1) Contact Resistance:

It has already been mentioned that platinum electrodes are superior to nickel electrodes due to a lower contact resistance to electrolyte.

- (2) Film Formation on Electrodes:

Exposure of electrodes to electrolyte has been reported elsewhere as the cause of the formation of an insulating metallic fluoride film that increases the contact resistance. However, we found

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(467-95) that apparently no film formation of this type occurs, at least in normal exposure periods to electrolyte. For over a period of five weeks the resistances of two cells, one made with platinum electrodes and the other with nickel, showed no increase. Each cell, both of which had a constant of 46.9 cm^{-1} , constantly gave a resistance reading of 330 ohms at 100°C . when immersed continually in electrolyte with 39.3% HF concentration. After this period the resistances gradually increased during the next two months to values of 435 ± 20 ohms, but this increase was probably the result of a heavy iron sludge in the electrolyte that was formed from corrosion of the iron container.

(b) The Cell Body

Hard rubber pipe proved superior to Saran pipe or tubing as a material for the body of the cell. As shown below, when immersed in electrolyte it showed a lower "corrosion" rate, a smaller change in hardness, and less embrittlement. The hardness tests were carried out with the Shore scleroscope.

The test (467-53) summarized in Table IV consisted of immersion of the materials in electrolyte (HF conc. = approx. 41%) for 384 hours at $90-100^\circ\text{C}$.

Table IV

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Stability of Insulation Materials to Electrolyte

<u>Material</u>	<u>Corrosion Rate</u> Inches <u>Penetration/Month</u>	<u>Hardness</u>		<u>Change in</u> <u>Hardness</u> <u>Units</u>
		<u>Initial</u> <u>Shore</u>	<u>Final</u> <u>Scleroscope</u>	
1/4" Saran Sheet	5×10^{-4}	42	48	+6
1/2" Saran Tube	5×10^{-4}	42	51	+9
1/2" Saran Pipe	1×10^{-3}	37	44	+7
1" Hard Rubber Pipe	5×10^{-4}	60	61	+1

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In another test (467-94) the pieces of Saran and hard rubber pipe were mounted on a rod in the cathode compartment of a DuPont converted carbon unit, and were exposed to electrolyte at 90-110°C. for 23 days during the operation of the cell. The Saran pipe and tube were then found to be very brittle, while the hard rubber pipe was only slightly embrittled.

<u>Material</u>	"Corrosion Rate"
	<u>Inches Penetration per Month</u>
1/2" Hard rubber pipe	5.6×10^{-5}
1/2" Saran tube	1.9×10^{-3}
1/2" Saran pipe	2.5×10^{-2}

(c) The Cell Casing

The performance of plant cells made of various metallic casings around the insulating hard rubber pipe has been studied. Nickel casings have been shown to be quite satisfactory. However, regular wrought iron pipe, which is more easily available than nickel, has proved satisfactory over prolonged periods providing it has sufficient thickness. Thus, some Hooker conductivity cells failed in service because the one inch iron tubing corroded enough to cause loss of the guard platinum electrodes that were welded to the iron. For this reason schedule 40 and schedule 80 iron pipe have been adopted for use.

(d) Wire Insulation

467-81, 130-133, 144

Although Saran embrittles in electrolyte, it was shown that it could be used as insulation for the lead wires over prolonged periods providing that no shock was applied to the cell. Fracture of the insulation resulted in "shorts" that made further reliable conductometric measurements impossible.

Various types of wire insulation were tested for stability in electrolyte over prolonged periods as follows: Twenty-six inch lengths of the insulated wire (14 B & S gage copper wire) were bent in the center and doubled back upon themselves. These were immersed in electrolyte in an iron container heated at 100°C. in an oil bath. The ends of the insulated wire were above the electrolyte level, so that 22 inches of insulation in each case was exposed to the electrolyte. After prolonged intervals the insulation was tested for leaks by measuring the resistance of the circuit connected as follows: Iron container to conductivity bridge to unexposed end of insulated wire through electrolyte to iron container.

After 35 days of immersion in electrolyte at 100°C., the following insulation materials gave the records indicated:

<u>Material</u>	<u>Record</u>
Performance grade rubber	No insulation breakdown
Code rubber	" " "
Neoprene synthetic rubber (Litharge filler)	" " "
Gencoseal (vinyl chloride polymer)	" " "
Hazakrome (vinyl chloride- acetate polymer)	Partial insulation breakdown
Neoprene (high litharge filler)	" " "
Heat resistant rubber	" " "
Water resistant rubber	" " "
Nylon extruded insulation	Complete insulation breakdown

On the basis of the above tests the choice of Gencoseal insulated wire for the conductivity cells for use in the plant was made. This material, a product of General Cable Co., could be obtained with a wall thickness (0.03 inches) less than that of the others. A wire with the least amount of insulation consistent with good performance was desired, since it would least hinder circulation of the electrolyte through the conductivity cells.

B. Control of the HF Concentration of Electrolyte
by Conductometric Measurements:

467-70, 82, 100, 106-109, 123-126, 136,
146, 150-151; 518-19, 32-64.

Semi-Works Cells

Prior to construction of cells for use in East Area, and at the same time laboratory work was in progress to obtain exact values for the specific conductance of electrolyte, it was deemed advisable to construct and operate in Semi-Works C-216 units several conductance cells for the control of HF. These cells all had platinum electrodes connected to 22 B & S gage monel wire by spot welds; all the lead wires were insulated at the time with Saran. The guard electrodes (each 1/2" sleeves) were connected to the metallic casing by platinum wire spot-welded in position. The "hot" center electrode (a 1" sleeve) and the metallic sheath (upon the upper part of which was a binding post) were connected to the conductivity bridge when taking measurements. A descrip-

tion of the other essential details of these cells is given in Table V. The overall length of the cells was 30-32 inches; the effective length between the two "guard" electrodes was 15 to 16 inches, or 6.5 to 7.5 inches between the guard electrodes and the center electrode.

Table V

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Experimental Control				
<u>Conductance Cells</u>				
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Cell No.	Cell Body made of	Metallic Casing of	Cell Constant	
			Calc.	Found in Electrolyte
1	1/2" Saran Tubing	3/8" Nickel Pipe	11.3	11.9
2	1/4" Hard Rubber Pipe	" " "	24.1	25.2
3 & 4	" " "	3/8" Wrought Iron Pipe	24.1	26.7
=====				

The following information was obtained by the operation of these units in the Semi-Works:

(1) Temperature Control - 467-82 - Cell 1

Reproducible conductance results could not be obtained when the electrolyte temperature was varied rapidly, or when an appreciable distance separated the conductance cell from the thermocouples which gave the temperature. This pointed to the need for thermal equilibrium in the cell while obtaining conductance measurements.

(2) Results from the data obtained in following the HF concentration of electrolyte by conductance measurements and by the "nitrogen bubbler" method are given in Table VI.

Table VI

Control of HF Concentration by
Conductance and "Bubbler"

S.W. Run	S.W. Spot	Type C-216 Unit	Method for Control of HF Concentration	Length of Opera- tion days	Average Deviation of Conductance Value from Chem. Analysis	% of Deviations in the Range			
						0.0-0.3%	0.4-0.6%	0.7-1.0%	>1.0%
-21- 39	2	] DuPont	Conductance - Cell 1	23	0.8	20	15	30	35
"	"		Converted " - Cell 2	"	0.43	43	33	24	0
"	"		Carbon Nitrogen bubbler	"	0.35	65	26	5	4
42	6	816 Nickel	Conductance - Cell 4	9	0.22	77	23	-	-

It is seen that in Semi-Works run 39 the "nitrogen bubbler" method gave better control of the HF concentration in electrolyte than that given by the use of either conductance cell no. 1 or 2. Control with conductance cell 2, which had a constant of 25.2, gave much better control than that by cell no. 1 (constant = 11.9).

Cell no. 4 gave very good control of the HF concentration, but the duration of the run was only 9 days, however.

Hooker Conductance Cells

Shortly after the start-up of the Hooker loop in East Area a set of conductivity cells was installed that was designed and built by the Hooker Company. The design of these instruments is given in Hooker Drawing No. 25728-C. The cell itself consisted of a 15" length of 1/4" hard rubber pipe split in the center by a hard rubber coupling in which the center platinum electrode was inserted. A lead wire from this electrode emerged through the wall of the coupling into a circular bed of Durez plastic which completely filled the space between the hard rubber pipe and a 30" length of 1" iron tubing which served as the casing. Platinum "guard" electrodes were inserted at each end of the hard rubber pipe, and were connected by iron wire to the iron casing, on the top of which a lead wire was soldered in position. The lead wire from the center electrode arose through the Durez insulation in the upper part of the casing.

The conductances obtained in these instruments were measured with a conductivity bridge, the Solu-Bridge Model RD-12CS, which was manufactured by the Industrial Instruments Company of Jersey City. Measurements were corrected to indicate the conductance at 100°C. by means of a variable rheostat with pointer directed to a temperature scale. A check of several of these instruments against known resistances of 100, 200 and 300 ohms indicated that the required degree of accuracy and precision could be obtained with them. The variable rheostats also furnished the proper temperature corrections when used with a cell whose constant was 32, for which the Solu-Bridge was designed. The a.c. frequency of this bridge was 3000 cycles/sec.

Although the constants of the Hooker conductivity cells varied between 21.5-33.2 when determined in 0.1N KCl, with 53% having a constant of less than 28, the instruments were nevertheless used in order to determine whether or not they would suffice as a measure of the HF concentration of electrolyte.

The performance of these cells was closely followed over a period of approximately two weeks. Unfortunately it was not possible to obtain a good idea of the possibilities of HF control by conductance with these cells, which failed so rapidly in service that no prolonged observation was possible. The main reasons for failure were:

- (1) Rapid corrosion of the iron casing of the cell.
- (2) Loss of platinum electrodes and electrode contacts. This occurred as a result of the extreme corrosion rate in some cases, and in others because the externally-grounded electrodes were shorn from the cells during removal from the C-216 cells to permit sampling for chemical analysis.
- (3) Failure of the Durez insulation. It was found that electrolyte penetrated between the Durez and the iron casing, and thence penetrated into the Durez, causing a short between the shell and the inner electrode lead wire.

The following performance was obtained with these Hooker cells:

<u>Period of Operation</u>	<u>Cells Studied</u>	<u>Total Readings</u>	Average Deviation of HF by Conductance from HF by Chem. Analysis	<u>% of Deviation in the Range</u>				
				<u>0.5%</u>	<u>0.5-1.0%</u>	<u>1.0-1.5%</u>	<u>1.5-2.0%</u>	<u>>2.0%</u>
8/26-8/31	35	125	0.74%	45	33	17	4	1
8/31-9/9	24	137	0.87%	42	25	16	10	7

The above figures indicate an increased spread in deviation with prolonged exposure to electrolyte. Cells which had definitely failed in service are not included in the above figures. Some of the higher deviations are definitely due to inaccurate chemical analyses rather than faulty conductivity control.

Improved Conductivity Cells
467-146, 150, 151; 518-19, 32-65

From our experience with the above cells it was seen that a sturdily constructed unit would be required in which the insulating medium was resistant to electrolyte over prolonged exposure periods. After some experimentation the cell described in detail in the attached sketch C-184-1 was made. This unit was modeled for the most part upon our cells used in our Semi-Works runs which had given fairly satisfactory results over moderate lengths of time.

At the same time new cells were made by the Hooker Company which were quite similar to that illustrated in the sketch with 4 exceptions, which were:

- (1) $3/8$ " schedule 40 iron pipe was used instead of $1/2$ " schedule 80.
- (2) The platinum guard electrodes were eliminated and the iron casing itself was used as one electrode.
- (3) A "Durez" seal at the top of the cell to prevent loss of HF was used rather than the compression fitting illustrated.
- (4) A lead wire with an insulation wall of $1/64$ " of vinyl chloride polymer was used in the Hooker cells, while it was $1/32$ " in the DuPont cell.

Six of these Hooker cells and one duPont cell were inserted in new Hooker C-216 cells at their start-up. These new conductance units were followed over a period of a month's time. At the same time the control of HF in electrolyte by chemical analysis and by hand probing was studied. The results of these studies over the first two weeks are given in Table VII.

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Table VII

Control of HF Conc. of Electrolyte by Chemical
Analysis, Conductance and Hand Probing - 10/27 - 11/10

Method of Control	Average Deviation %	% of Deviations in the Range						No. Detns.
		0.0-0.5%	0.6-1.0%	1.1-1.5%	1.6-2.0%	2.1-3.0%	3.0%	
Chemical Analysis	0.47	75	12	8	1	4	-	106
Conductance	0.73	46	27	19	5	3	-	90
Hand Probing	1.17	36	17	17	13	12	5	88

The figures given in the above table were obtained as follows: The conductance cells were immersed in the electrolyte for two days to come to equilibrium. Over the next three days the constant for each individual cell was obtained by taking the average value of the constants calculated from the conductance reading corrected to 100°C. and the specific conductivity of the electrolyte based upon the HF concentration shown by duplicate chemical analyses. Over the indicated period the conductance measurements, hand probe values and duplicate samples for chemical analysis were all obtained on the units within a one-half hour time interval.

As indicated in the above table, control of the HF concentration by the chemical analysis was the most accurate and precise method, for 75% of the duplicate analyses agreed with a deviation between check samples of less than 0.5%. The conductance method proved better than the hand probe method, for the average deviation from the chemical analysis values was 0.73% for the former method, while it was 1.17% for the latter.

However, during the fourth week of immersion in electrolyte the conductance cells commenced to fail. In this period three Hooker cells failed because of a partial breakdown of the insulation of the lead wire from the center electrode; the DuPont cell and a Hooker cell failed due to plugging of the cells by sludge formed in the electrolyte. Only two Hooker cells continued to give good service.

It was concluded from these trials that in order to obtain conductance cells that would give long service in C-216 production cells at their present stage of development the following basic changes in design would be required:

(1) A cell with an increased diameter would be necessary in order to prevent plugging with electrolyte sludge. This would result in less precise control, however, for by this change the cell constant would be decreased.

(2) Lead wire insulation with sufficient wall thickness to prevent breakdown in electrolyte in a short time must be used. It is believed that "Geucoseal", a vinyl chloride polymer insulation, will meet this requirement when used with a wall thickness of 1/32 inch.

In addition, conductance cells would be of much greater value to operations if they could be constructed with such close tolerances that the cell constants of the individual units did not vary more than 32 ± 0.25 , for this would enable operations to use the

same settings on all conductance meters to obtain uniform HF control of the electrolyte.

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mfh-1/11/45

CONDUCTIVITY CELL
ASSEMBLY AND DETAILS
PICKSON LAB. CHED. ENG. DIV.
SCALE: FULL SIZE
DATE: SEPT. 13, 1966
DRAWN: C.J. Smith
CHECKED:
C-184-1

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